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p-type doping of tetrafluorotetracynoquinodimethane (F_4TCNQ) in poly (para phenylene vinylene) (PPV) derivative "Super Yellow" (SY)

Manisha Bajpai[1,3], Ritu Srivastava[2], Ravindra Dhar[1], R .S. Tiwari[3], Suresh Chand[2]

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In this paper, we have reported a case of hole transport in tetrafluorotetracynoquinodimethane doped poly (para phenylene vinylene) derivative "Super Yellow". The hole mobility of pristine and doped polymer thin films has been determined by using impedance spectroscopy. The increases in hole mobility upon doping is also verified by current density –voltage measurements. It has been found to be increased by two orders of magnitude. The increase in hole mobility upon p-type doping has been explained on the basis of Extended Gaussian Disorder Model by measuring current density–voltage characteristics in the same devices. Initially at low bias, J-V characteristics exhibit clear space charge limited conduction in pristine case whereas Ohmic behaviour on doping. Further, at higher voltages the current density increases nonlinearly due to the field dependent mobility and carrier concentration by means of filling of tail states of highest occupied molecular orbital of the host material. The room temperature J-V characteristics have been well described with the single value of free hole density at low fields. At higher fields it becomes field dependent followed by a field enhancement factor γ.

Introduction:

Organic semiconductors based devices have advantages as compared to inorganic semiconductors because of their high absorption coefficient since most of organic dyes emits in visible range which makes them suitable for very thin organic photo detector (OPD) [1-3] and photovoltaic (OPV) [5] applications. Other than this, some of the fluorescent dyes show strong red shift during emission as compared to the absorption and this property makes them perfect for organic light emitting diodes (OLEDs) [6, 7] with no absorption losses.

Organic semiconductor can be doped either by removing an electron from highest occupied molecular orbital (HOMO) or by adding an electron to the Lowest unoccupied molecular orbital (LUMO) to increase its conductivity [8-10]. Doping in organic semiconductor creates high charge carriers which move in an electric field. This movement of charge is responsible for electrical conductivity in organic semiconductor.

Doping of a polymer is different than that of inorganic semiconductor in which elements with excess or shortage of electrons are introduced. In polymer, both doping process involves an oxidation and reduction process [11-13]. The first method involves exposing a polymer to an oxidant such as iodine or bromine or reductant such as alkali metals. The second is electrochemical doping in which a polymer-coated electrode is suspended in an electrolyte solution. The polymer is insoluble in the solution that contains separate counter and reference electrodes. By applying an electric potential difference between the electrodes, counter ion from the electrolyte are diffused into the polymer in the form of electron addition (n doping) or removal (p doping). One of the problem with organic semiconductors is that p-type material is more prevalent than n-type because electron rich n-type is unstable in the presence of oxygen. Organic semiconductor can only be useful for devices if both p-type and n-type are incorporated.

p- type doping was realized in terms of enhanced hole injection into matrix followed by the modification of the interfaces by Blom et al [15]. They gave a new approach to understand the effect of doping in organic semiconductors. Since conductivity of any material is the product of carrier mobility and number of charge carriers therefore if we dope the materials, conductivity rise would result from simultaneous increase of carrier concentration and carrier mobility. Generally, the carrier transport in semiconducting materials takes place via hopping between the Gaussian density of states (GDOS). Consequently, if we ignore carrier density dependence, it will lead to an underestimation of the hopping distance and the width of the density of states in these polymers. Therefore a density dependent mobility model in combination with electric field and temperature has been proposed [16-18].

In this paper, we demonstrate the effect of p- type doping on the hole transport of Super Yellow (SY) in terms of carrier mobility and carrier density.

Experimental

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[1] *Soft Materials Research Laboratory, Centre of Material Sciences, Institute of Interdisciplinary Studies, University of Allahabad, Allahabad, 211002 India*
[2] *Physics for energy harvesting division, National Physical Laboratory (Council of Scientific and Industrial Research), Dr. K. S. Krishnan Road, New Delhi 110012, India*
[3] *Department of Physics, Banaras Hindu University, Varanasi-221005, India*

For the hole transport study of SY polymer as a function of p-type doping, hole-only devices of SY polymer with different doping concentration of F$_4$TCNQ were fabricated. SY and F$_4$TCNQ were dissolved in toluene under the concentrations of 6 mg/ml and 0.1mg/ml respectively. The solutions were stirred on a hot plate at 70 °C for 12 h and then filtered separately. Then SY and F$_4$TCNQ solutions were blended in different doping concentrations by using a volumetric pipette in nitrogen atmosphere. We have added 25 µL dimethyl sulfoxide (DMSO) into the solutions to prevent aggregation. Further, we have fabricated the hole only devices in configuration ITO/SY: F$_4$TCNQ/Au. The devices were prepared onto the ITO coated glass substrates (purchased from Vin Karola, USA (sheet resistance ~18 Ω/m^2). Prior to any use, the ITO coated glass substrates were cleaned by using deionized water, acetone, trichloroethylene and isopropyl alcohol for 20 min and finally dried in vacuum. Thereafter, the active layer was spin coated onto these cleaned glass substrates from solution with a spin speed of 1200 rpm resulting in a typical film thickness of 200 nm. These films were then annealed at 150°C in vacuum for 2 h. On top of these films, Au electrodes of 500 nm thickness were deposited by vacuum thermal evaporation at 5×10^{-6} Torr. The devices so obtained were sealed using UV irradiated epoxy resin to inhibit atmospheric oxidation of electrodes. J–V characteristics of the pristine and doped samples in different temperature range were measured using a low temperature setup coupled with a Keithley 2400 Source Meter unit interfaced with a PC. A Solartron SI 1260 Impedance/Gain-Phase analyzer was used to measure the capacitance –frequency (C-*f*) spectra of the samples.

Results and Discussion:

In this work we have studied the effect of doping on the hole transport of super yellow (SY). The hole mobility of pristine and doped SY thin films has been independently determined from impedance spectroscopy (IS) method [19-22] by measuring frequency dependent capacitance spectra by varying the applied bias.

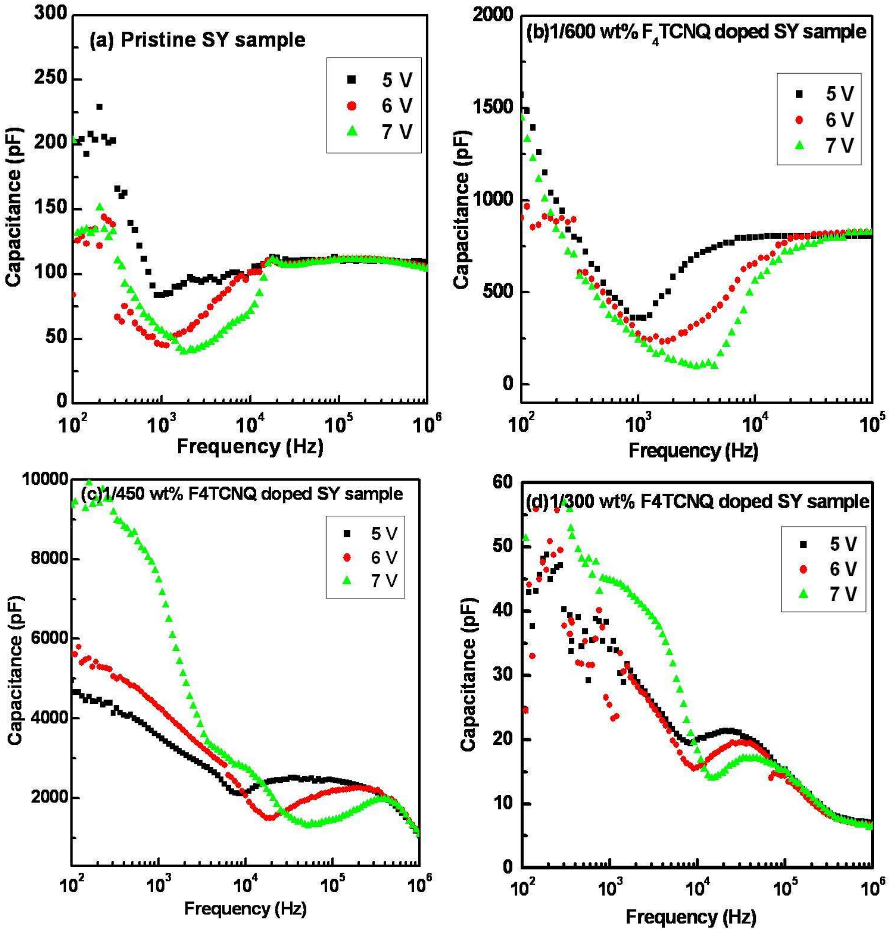

FIG. 1: Capacitances of (a) pristine (b) 1/600 wt % F$_4$TCNQ doped (c) 1/450 wt % F$_4$TCNQ doped (d) 1/300 wt % F$_4$TCNQ doped hole only devices at room temperature.

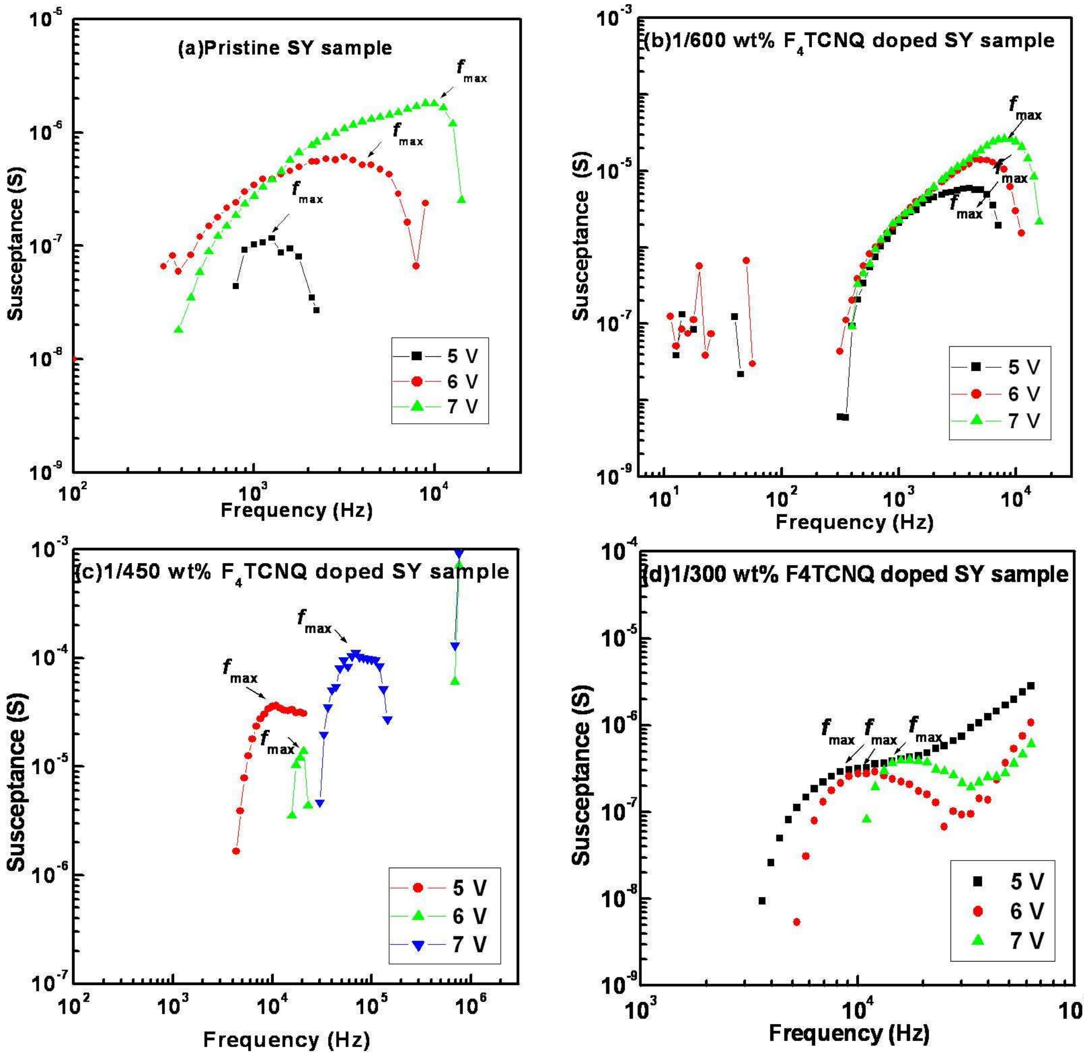

FIG. 2: Differential susceptance (ΔB) spectra at different bias voltages of (a) pristine (b) 1/600 wt % F_4TCNQ doped (c) 1/450 wt % F_4TCNQ doped (d) 1/300 wt % F_4TCNQ doped hole only devices at room temperature.

We have employed the frequency dependent capacitance spectra for different applied dc bias (V_{dc}=5, 6 and 7 volt) with measuring a.c. signal of 100 mV over the frequency range 10 Hz-10 MHz.

Fig 1 shows the capacitance spectra of pristine and doped devices as a function of a.c. frequency (*f*) from 100 Hz to 1 MHz for the d.c. bias voltage 5, 6 and 7 V. Bias voltage is essentially required to drift/hop charge carriers (holes) which otherwise not possible under the small ac test voltage of 100 mV. At higher frequencies, the sharp cutoff appears in C-*f* spectra which approaches to the vanishing of the capacitance signal (see Fig 1c). It is due to the reactive cutoff frequency of the structure. With the increase of the capacitance value, reactive cutoff frequency goes down [23]. Since the capacitance value is highest in Fig 1c hence the reactive cut off frequency is lowest in it. With the increase of the bias voltage, the capacitance-frequency spectra have drastically changed at transit frequency (f_t). This may be due to the fact that the injected current lags behind the signal voltage due to the finite transit time (τ_{tr}). Therefore Injection of additional space charge increases with applied voltage and further these injected charge carriers will moves into the device to relax to achieve the new equilibrium space-charge distribution. Due to the finite τ_{tr} the corresponding current lags behind the ac voltage, and this gives an inductive contribution to the capacitance. The amplitude of extremum point enhances and its position shifts towards the higher frequencies with increase of the bias voltage. This effect is more pronounced in doped samples as compared to pristine sample. At frequencies above the transit frequency, the period of applied ac field is too short to redistribute the space charge in the device. Hence, we have used C-*f* spectra at the intermediate frequency range to extract the carrier mobility where transit time effect occurs.

We have estimated the hole mobility of pristine and doped hole only device by using susceptance method [24-26]. In this method the peak in susceptance provides a definitive way of determining the transit time of the charge carriers in organic materials corresponding to the frequency ($f_{\max}$) where susceptance shows peak. As the voltage across the sample is changed, the $f_{\max}$ and hence the average transit time shifts enable the determination of mobility as a function of electric field. In this method we extract the carrier transit time from susceptance plot, where negative differential susceptance is calculated as

$$-\Delta B = -\omega\{C(\omega) - C_0\} \tag{1}$$

Where, ω= $2\pi f$ is the angular frequency of the ac oscillations, C (ω) is the observed capacitance at a particular frequency and C_0 is geometrical capacitance of the organic layer ($C_0=\varepsilon_0 A/L$, where ε_0 is the free space permittivity, A is the area of plates and L is the thickness of organic thin film).
The position of maximum of susceptance curves gives the transit time of hole ($\tau_{tr,}$) according to the eq. 2. [27]

$$f_{\max} = \frac{0.72}{\tau_{tr}} \tag{2}$$

In Fig 2, we show the differential susceptance as function of the ac modulation frequency. The position and magnitude of the maximum of the ΔB curve are dependent on the bias voltage V_{dc}. When V_{dc} increases, the peak shifts towards high frequency side and its amplitude grows. Using the peak positions of the ΔB curves at different applied voltages, the hole mobility in pristine and doped SY films has been determined by using [28]

$$\mu_p = \frac{4}{3}\frac{d^2}{V_{dc}}\frac{1}{\tau_{tr}} \tag{3}$$

Where μ is the hole mobility and d is the thickness of the polymer films. The hole mobility has been calculated to be 2.58×10^{-8} cm^2/V-s to 2.40×10^{-7} cm^2/V-s for pristine SY thin films, 5.34×10^{-8} cm^2/V-s to 1.28×10^{-7} cm^2/V-s for 1:600 doped SY thin films, 3.21×10^{-7} cm^2/V-s to 2.71×10^{-6} cm^2/V-s for 1:450 doped SY thin films and 6.80×10^{-7} cm^2/V-s to 1.00×10^{-6} cm^2/V-s for 1:300 doped SY thin films for V_{dc} ranging from 5 to 7 volts. The mobility obtained in pristine sample is comparable to those measured by Bisquert et al. using the impedance spectroscopy technique [29]. These results are further supported by the d.c. measurements on the samples described in the forthcoming paragraphs.

For the d.c. analysis, we have measured J-V characteristics of pristine and doped SY samples at the room temperature as well as at the elevated (230-290 K) temperatures.

Fig 3 shows the current density versus voltage (J-V) characteristics of SY hole only device with and without dopants at room temperature. At low bias voltages, the hole mobility (μ_p) is constant and the J–V characteristics follow Child's law given by [30]

$$J_{SCLC} = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_p\frac{V^2}{d^3} \tag{4}$$

Where J_{SCLC} represent space charge limited current density. ε_r and ε_0 are the relative permittivity, free space permittivity respectively.

J–V characteristics at low voltages have shown a slope of 1 i.e.it shows ohmic conduction. It is requisite condition to achieve space charge limited (SCL) conduction that metal-semiconductor interface must be an ohmic contact. Therefore, to confirm the hole injection property ITO-SY interface the measured (observed) current density (J_{obs}) has been compared with the current density expected (J_{cal}) [31] from trap free space charge limited of negatively charge p-dopants. The injection efficiency (η) is given as:

$$\eta = J_{obs}/J_{cal} \tag{5}$$

The calculated injection efficiency has been found ~ 1 and therefore the formation of an ohmic contact with SY is confirmed. Hence, we can directly calculate hole mobility from J-V curves in case of pristine as well as doped SY samples.

When F_4TCNQ is doped into polymer, free holes are generated into the polymer via p-type doping and these additional free holes are compensated by the negative charge of the corresponding acceptors. Therefore doping induced free charge carriers will not contribute in the space charge. Hence, in our calculations, we have not considered the effect of negatively charged p-dopants. Therefore; an Ohmic-like current will flow at low voltages, given by [32]

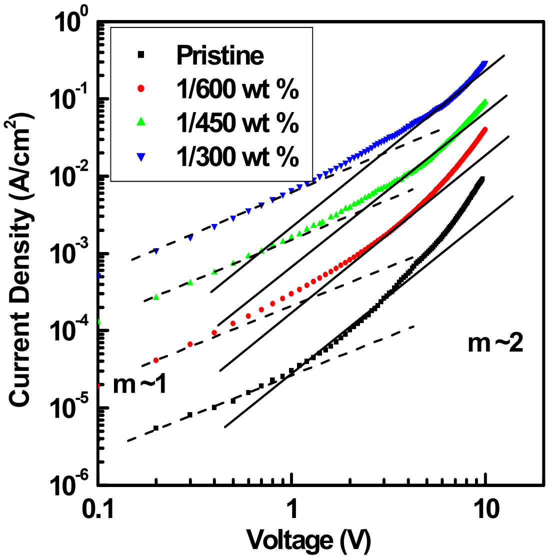

FIG 3: Current density versus voltage characteristics of SY devices for different doping concentrations. The broken lines with slopes of 1 denote the Ohmic current whereas the solid lines with slopes of 2 denote the space-limited current.

$$J_{\Omega} = q p_0 \mu_p \frac{V}{d} \tag{6}$$

Where p_0 is doping induced free hole density. Upon addition of p-type doping free holes are introduced into the organic semiconductor. At low voltages, p_0 will largely outnumber the charges that are injected from the contacts. Since p_0 is temperature-dependent due to a thermally activated ionization process of the dopant, therefore the mobility will not only depend on temperature but also on p_0, hence carrier density and mobility have been included into eq 6, which becomes: [33]

$$J_{\Omega}(V,T) = q p_0(T)\mu_p(T, p_0(T), E)\frac{V}{d} \tag{7}$$

Further, to investigate the conduction mechanism in doped SY samples, the J–V characteristics have been measured at various temperatures for doped SY devices with different doping ratios and are shown in Fig 4(a-d). At low bias voltage the current density increases by 1–3 orders of magnitude with increasing doping concentrations. The solid lines with slope of 1 and 2 denote the Ohmic and the space-limited current, respectively (it is already shown in fig 3 at room temperature , as doping concentration and field increases more and more free charge carriers are generated and then ohmic like current will flow (already discussed in above section)). The J–V characteristics have numerically modelled by using a recently developed transport model [34]. In this model, hole mobility depends on field E and hole density p. The hole mobility is given by: [34]

$$\left.\begin{aligned}
&\mu_p(T,p,E) \approx \mu_p(T,p)\,f(T,E)\\
&\mu_p(T,p) = \mu_0(T)\exp\left[\frac{1}{2}\left(\hat{\sigma}^2-\hat{\sigma}\right)\left(2pa^3\right)^{\delta}\right]\\
&f(T,E) = \exp\left\{0.44\left(\hat{\sigma}^{3/2}-0.22\right)\left[\sqrt{1+0.8\left(\frac{Eea}{\sigma}\right)^2}-1\right]\right\}\\
&\delta = 2\,\frac{\ln\left(\hat{\sigma}^2-\hat{\sigma}\right)-\ln(\ln 4)}{\hat{\sigma}^2}\\
&\mu_0 = \frac{a^2\nu_0 e}{\sigma}
\end{aligned}\right\} \qquad (8)$$

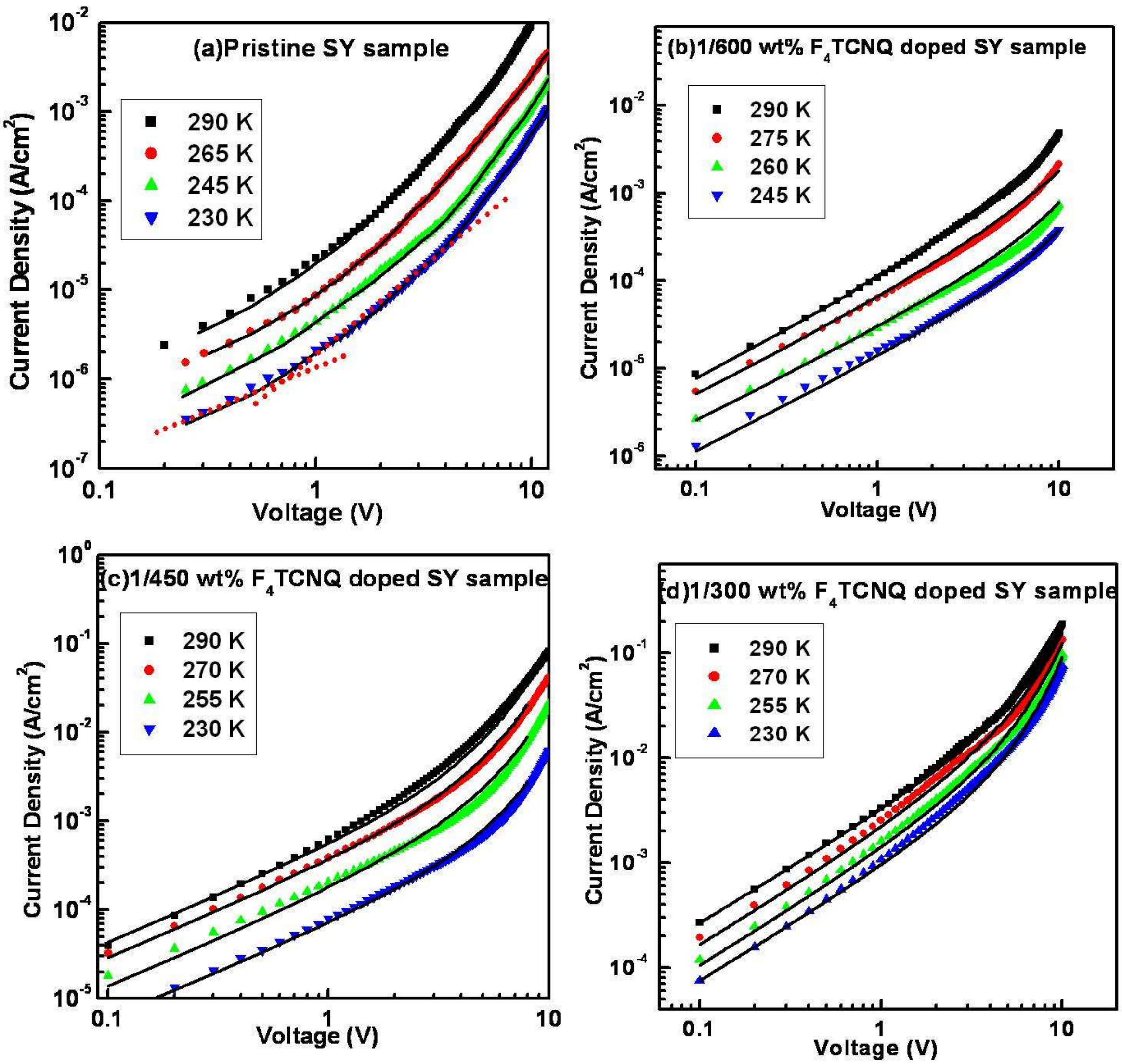

FIG.4: Temperature dependent current density versus voltage plot of (a) pristine (b) 1/600 wt % F$_4$TCNQ doped (c) 1/450 wt % F$_4$TCNQ doped (d) 1/300 wt % F$_4$TCNQ doped hole only devices.

Where $\hat{\sigma} = \sigma / K_B T$ and σ is the width of the Gaussian density of states, a (= $1/N^{1/3}$) is the inter site distance (in our case a=1.29 nm for SY), and N is the density of transport sites. We find the field-dependent mobility for pristine as well as doped SY samples as previously described in disordered materials in reports [34]. The fittings of the experimental J–V curves with eq 8 are shown by the solid lines in Fig. 4 (a-d) and fitting parameters are listed in table 1. In our calculations, we have taken a field-dependent p_0 (E) with a Poole–Frenkel like dependence on the applied electric field [35] The fittings of experimental J–V curves is shown by the solid lines in Fig. 4 (a-d). These parameters fitted to J-V curves for all devices and listed in table 1. In our calculations, we have taken a field-dependent p_0(E) with a Poole–Frenkel like dependence on the applied electric field [35]

$$p_0(E) = p_0(E=0)\exp\left(\gamma\sqrt{E}\right) \qquad (9)$$

Where, γ is the field-enhancement factor, p_0(E=0) is the zero field free hole density.

The field enhancement factor γ is the dependent on electric field and temperature both. Fig 5 shows the electric field dependent hole density as a function of temperature. We have found that hole density dependence on field is strongest in 1:450 wt % SY: F_4TCNQ doped sample as compared to other samples. We have observed the similar effect with IS method as shown in Fig 1. This result is attributed to relatively low value of σ Fig 5 Electric field dependent free hole density (p_0(E)) at 230 K for 1:450 % and 1:300 % doped samples. For high doping concentrations, it is expec2ted that the average distance that holes will have to hop from dopant to host will decrease [36].

The calculated J-V data for all devices has been found to fit in the above model and parameters obtained from simulation are summarized in Table 1. Increase or decrease in the transport parameters upon doping can be qualitatively understood on the basis of a simple model based on disorder.

It is well known fact that in an organic semiconductor, HOMO has a Gaussian distribution. The density of states of pristine SY material is shown in Fig 6. In the disordered semiconducting materials, the carrier transport usually occurs via hopping of charge carriers localized in the deep tail of GDOS. Charge carriers occupy only those states where the average distance between the charge carriers is large enough such that the transport of carrier is not affected by the presence of other carriers. This level is represented by $E_m = -\sigma^2 / KT$.Thus carriers will hop from E_m to next possible states. In the organic materials, the carrier transport is generally governed by SCL currents at low electric fields since there are less number of free carriers. At higher electric fields, background carrier concentration increases. Thus, carrier mobility is found to be electric field and density dependent. Further, in the case of F_4TCNQ doped SY material obviously more carriers will be transferred to the lowest unoccupied molecular orbital (LUMO) of F_4TCNQ and therefore all F_4TCNQ molecules will be ionized. These ionized carriers will contribute to a doping induced free hole density by transferring the electrons from the tail states of GDOS and filled with holes. However, all these ionized carriers will not contribute in resulting enhancement of carrier density. Only localized ionized F_4TCNQ carriers within the tail of HOMO of SY will produce the resulting enhancement.

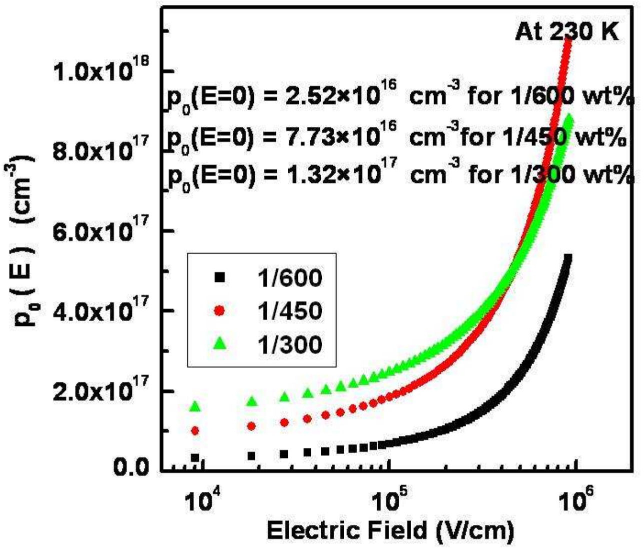

FIG.5 Electric field dependent free hole density (p_0(E)) at 230 K.

Samples	Hole mobility (cm²/V-s)		Disorder (meV)
	J-V (SCLC) method	IS method at DC bias=5V	
Pristine	2.6×10^{-7}	2.58×10^{-8}	0.046
1:600	2.8×10^{-7}	5.34×10^{-8}	0.044
1:450	5.92×10^{-7}	3.21×10^{-7}	0.041
1:300	7.8×10^{-7}	6.80×10^{-7}	0.040

Table 1: Comparison of calculated parameters from J-V (space charge limited current) and susceptance method.

Conclusions

We have demonstrated the hole conduction mechanism in SY thin films as a function of doping. The charge carrier mobilities of SY thin films have been determined using impedance spectroscopy of the pristine and doped SY thin films. F_4 TCNQ has been used as p-type dopant. The hole mobility has been found to be increased by 2 order of magnitude upon doping. It has been observed that both, the mobility and the carrier density have increased with the doping of F_4TCNQ in SY. The dependence of the hole mobility on doping has been explained by combining space-charge limited, field-effect and carrier density dependent measurements. It has been realized that free carriers are generated from acceptor molecules.

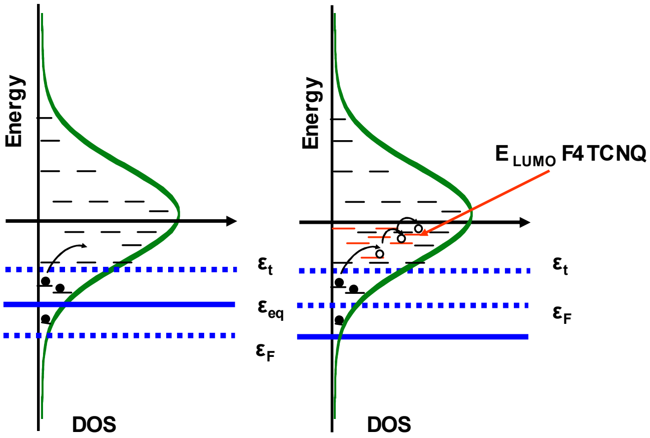

FIG 6 Schematic representations of the density of states and the position of the Fermi level in (a) pristine SY sample and (b) in SY doped with F_4TCNQ. The red dashed line represents the LUMO level of F_4TCNQ.

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