

Supporting Information

Isomeric Polythiophene: Promising Material for Low Voltage Electronic Devices

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Synthesis of IPTh from Thiophene: (S1)

In a 25 ml test tube 10 ml of dichloroethane (DCE) solvent was taken then 136 mg (0.6 mmole) of DDQ was dissolved in it. Now 50 μ L (0.6 mmole) thiophene was added, reaction mixture was stirred at 40 °C, within few second after addition of thiophene solution turned into red color due to the formation of charge transfer complex between DDQ and thiophene. Now 62 μ L (1.2 mmole) of concentrated sulphuric acid was added into above reaction mixture. Within one minute of conc. sulfuric acid addition polymerization started, evidenced by the appearance of formation of black colour precipitate. Initially polymer formed get stuck on the inner wall of the test tube has been scratched. After continuing stirring of reaction mixture for ten minutes the black precipitate of isomeric polythiophene settle down and solution became colorless. The black colour of IPTh precipitate was filtered by using vacuum filtration technique. Filtered black precipitate was washed four times by using 5.0 ml acetone each. Now precipitate was dried in oven at 80°C for 6 hour. (Note: All chemicals and glassware are being used for polymerization reaction should be dry). The yield of the IPTh polymer has been found to be 90-95%.

Result and Discussion: (S2)

Electrical conductivity:

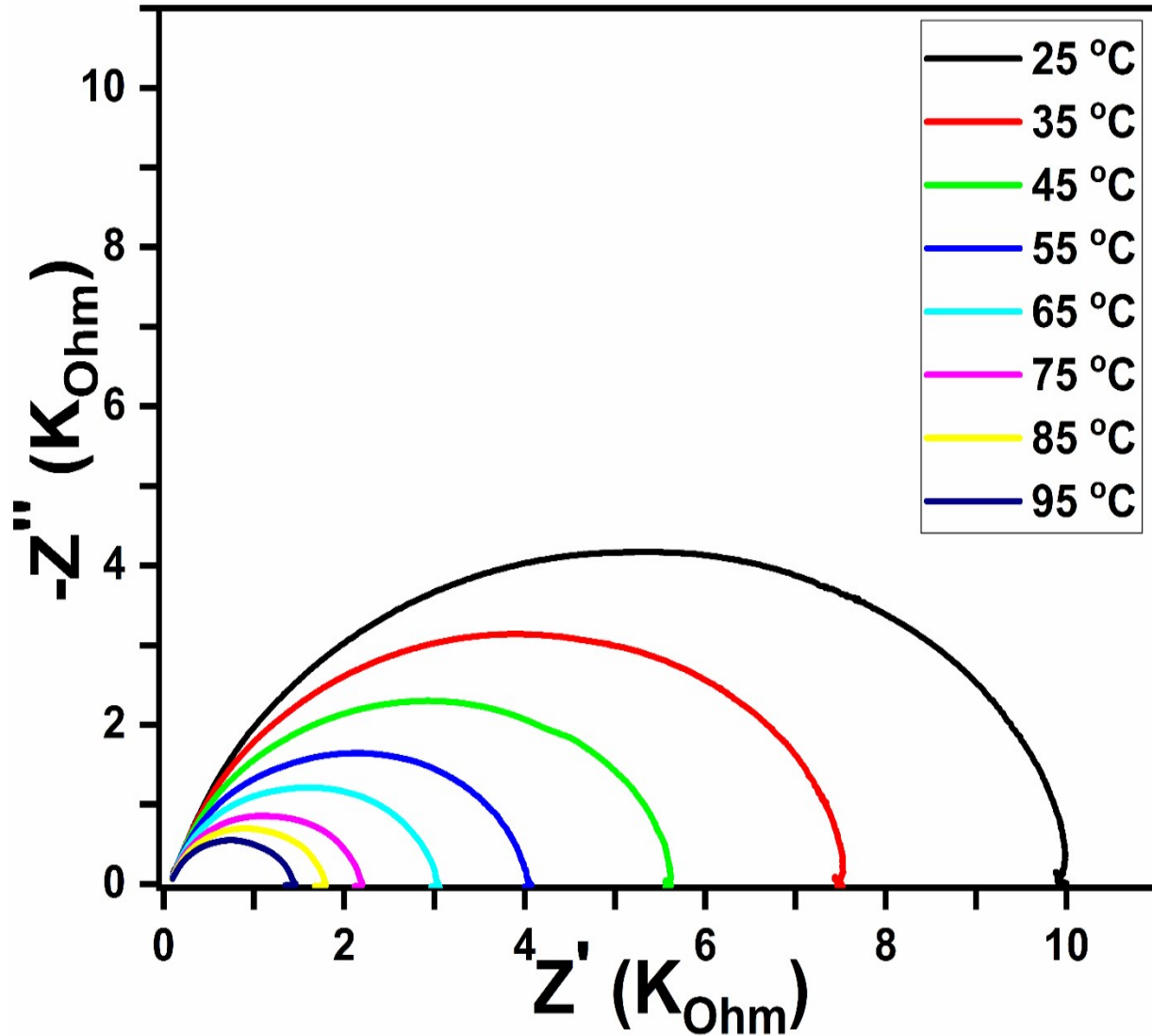


Figure 1 Nyquist's plots for IPTTh

Electrical conductivity property of IPTTh sample was studied by precision impedance analyser and results are exhibited in term of Nyquist plot given in figure 1. The semi-circular arcs obtained from Nyquist plot were used to calculate dc conductivity of the polymeric materials by using following empirical relationship.

$$\sigma_{dc} = 1/R_b \cdot l/A$$

By using above empirical equation dc conductivity of the sample at different temperature has been calculated. It has been found that dc conductivity increases with increasing temperature from 0.25 μ S/cm at 25 $^{\circ}$ C to 1.8 μ S/cm at 95 $^{\circ}$ C. In undoped polymeric system the electrical conductivity

increases with increasing temperature due to increase in thermally induced charge carrier concentration. In contrast to dc conductivity AC conductivity shows exponential dependence over the applied field frequency. AC conductivity of undoped sample has been plotted and given in figure 2. It has been found that AC conductivity values have little dependence over the temperature but has significant dependence over frequency. AC conductivity plots usually consist of three regions namely first dispersion region, observed in low frequency region due to the accumulation of charge carrier species near the electrode-electrolyte interface, middle frequency region which is frequency independent correspond to the bulk dc conductivity, higher frequency dispersion regions in which conductivity exhibits exponential enhancement with increasing frequency owing to increase charge carrier mobility between localized states. For better understanding of electrical conductivity and transport behaviour of charge carriers in medium, AC conductivity behaviour analysis of polymeric material is a very important parameter. AC conductivity behaviour of polymeric sample follow Jonscher's Power Law (JPL) which can be expressed with the help of following relationship.

$$\sigma_{ac} = \sigma_{dc} + Af^n$$

In this equation σ_{dc} is the bulk dc conductivity of the sample, f is the applied angular frequency, A is a pre exponential dispersion factor which is temperature dependent and n is fractional power exponent which usually acquire value of $0 < n < 1$. Temperature dependent AC conductivity data were fitted as function of non linear curve fitting by using the above simple equation. It has been found that temperature dependent ac data follow JPL behaviour and value of n varies in between 0.8-1.05, The observed value of n exhibits correlated hopping conduction mechanism. From AC conductivity plot the dc conductivity can be obtained by extrapolation of mid frequency plateau region on to the y-axis, dc conductivity calculated from Nyquist plots and obtained by extrapolation from AC graph shows good agreement. The value of σ_{dc} , A , n and R^2 are given in table 1 for undoped polymeric sample IPTH at various temperature.

Table No. 1 Temperature dependence of electrical parameter σ_{ac} , σ_{dc} , n and R^2

Temp(°C)	σ_{ac} ($\mu\text{S/cm}$)	σ_{dc} ($\mu\text{S/cm}$) [#]	σ_{dc} ($\mu\text{S/cm}$) [*]	n	R^2
25	0.148	0.264	0.251	0.7960	0.9968
35	0.207	0.336	0.335	0.7963	0.9967
45	0.314	0.455	0.448	0.8224	0.9965
55	0.485	0.622	0.621	0.8551	0.9964
65	0.698	0.814	0.832	0.8924	0.9964
75	1.03	1.15	1.15	0.9431	0.9967
85	1.31	1.40	1.41	0.9777	0.9971
95	1.65	1.65	1.76	1.0472	0.9983

dc conductivity obtained from ac plot by extrapolation

* dc conductivity calculated from Nyquist's plot

Nearly 1000 time of increase in electrical conductivity has been observed in the doped sample. Doping with oxidizing agent (molecular iodine), resulted into the oxidation of the polymeric backbone, which led to the formation of polaron and bipolaron and reduced form of iodine molecule namely iodide, triiodide and pentaiodide ions. In this way doping not only responsible for facilitating the formation of polaronic energy band in between valance band and conduction band, which is responsible for better electronic properties but also enhances the charge carrier's concentration, which ultimately result in higher electrical conductivity. AC conductivity behavior of iodine doped sample has been analyzed and like IPTh, temperature dependent ac conductivity data of IPTh-I₂ also follow JPL law. DC conductivity value for iodine doped sample has been obtained from the extrapolation of mid frequency region of AC conductivity plots on to the y-axis, has been found to be in the range of 10⁻⁴ S/cm range and decreases with increasing temperature, owing to the loss of molecular iodine due to sublimation at higher temperature. Various electrical conductivity parameters are given in table 2 for doped polymeric sample IPTh-I₂ at various temperature. The value of power exponent 'n' obtained by the JPL fitting of AC data of IPTh-I₂ exhibits cage type hoping conduction mechanism. Hence we have observed change in conduction mechanism from correlated hoping mechanism in IPTh to cage type hoping in IPTh-I₂ due to change happens in the polymeric matrix after incorporation of dopant molecule in between polymeric chain.

Tabel No. 2 Temperature dependence of electrical parameter σ_{ac} , σ_{dc} , n and R²

Temp(°C)	σ_{ac} ($\mu\text{S/cm}$)	σ_{dc} ($\mu\text{S/cm}$) [#]	n	R ²
25	126.2	122.4	1.261	0.9852
35	119.6	115.1	1.166	0.9246
45	100.5	96.7	1.142	0.9939
55	88.7	85.5	1.111	0.9970

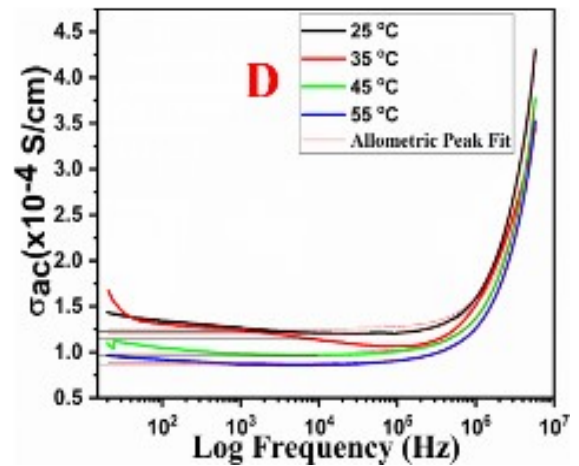
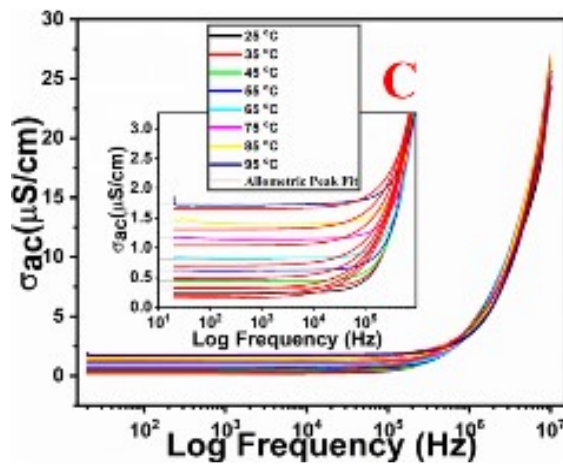
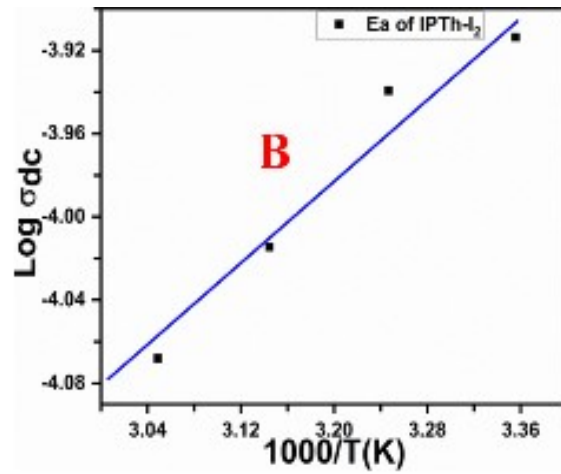
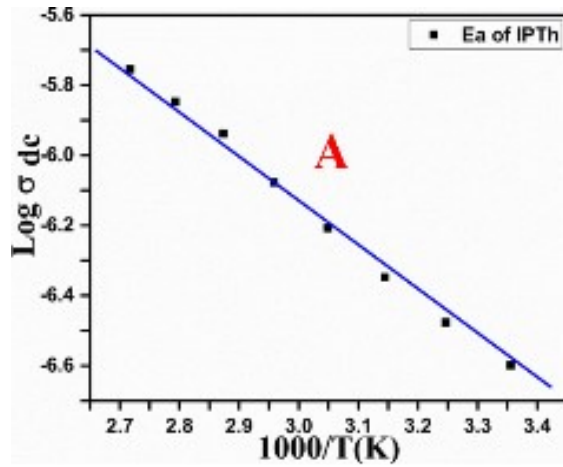


Figure 2 Depicting Arrhenius plots and AC conductivity plots for Polymeric material (A) Arrhenius plot for IPTTh (B) Arrhenius plot for IPTTh-I₂ (C) AC conductivity plots for IPTTh (D) AC conductivity plots for IPTTh-I₂

Thermal dependence of electrical conductivity follows Arrhenius type of behaviour which was given by following relation:

$$\sigma_t = \sigma_0 \exp - Ea/KT$$

Where Ea is the activation energy which is the minimum amount of energy required for the charge carrier to move within the polymeric matrix, σ_0 is the pre exponential factor, K and T are Boltzmann constant and temperature respectively. Ea value calculated from the plot of $\log \sigma_{dc}$ vs $1000/T$, has been found to be 0.2495eV. Since electrical conductivity of IPTTh enhances with increasing temperature hence Ea has positive value for undoped sample but due to decrease in electrical conductivity with increasing temperature Ea has negative value ($Ea = -0.1037\text{eV}$) for iodine doped sample. AC conductivity plots and Arrhenius graphs for IPTTh and IPTTh-I₂ has been given in figure 2.

Dielectric characteristic:

In order to understand the response of material to an applied electric field dielectric behaviour of material has been studied by impedance spectroscopy. Complex dielectric constant or complex permittivity is a complex quantity which comprises both real and imaginary part which are termed as dielectric constant and dielectric loss respectively. Dielectric permittivity is a measure of ability of material to polarise under the influence of an applied electric field and it denotes the amount of energy stored under the influence of applied electric field. It is defined as the ratio of permittivity of dielectric to the permittivity of free space. However imaginary part of complex dielectric constant is a measure of ability of material to dissipate the electrical energy as heat in response of applied electric field. Dielectric loss is related to the conductivity and depend on the resistance offered by material to the flow of electric current. Complex dielectric permittivity is a complex phenomenon which can be expressed as following.

$$\epsilon^* = \epsilon' - j\epsilon''$$

where ϵ' and ϵ'' are real and imaginary part of dielectric permittivity. Dielectric constant and dielectric loss can be calculated using following relation.

$$\epsilon' = Cd / \epsilon_0 A$$

$$\epsilon'' = \epsilon' \tan \delta$$

Where C, d and A are capacitance of the polymeric material, thickness of the polymeric film and Area of the electrode respectively. Dielectric permittivity plots of both doped and undoped sample are given in figure 3 & 4. Dielectric constant as name imply is not a constant but it is a variable which shows its dependency over both temperature and frequency. ϵ' observed for undoped, IPTh sample has been found to be positive and having higher value in lower frequency region at any temperature and decreases with increasing frequency owing to unavailability of sufficient time for the orientation of the molecular dipole in response to the fast periodic switching of the applied electric field. ϵ' value increases with increasing temperature due to the higher polarization of molecular dipole arising due to the increased segmental motion of polymeric backbone at higher temperature. Likewise, ϵ'' value observed for IPTh exhibits higher positive value at lower frequency region and increases with increasing temperature but decreases with increasing frequency. In contrast to IPTh, iodine doped sample- IPTh-I₂ exhibits negative capacitance in lower frequency region that's magnitudes decrease with increasing frequency and temperature. Hence the dielectric constant ϵ' found to be have large negative value in short frequency region and at room temperature and ϵ' value become lesser negative with increasing both frequency and temperature similar behaviour was observed for ϵ'' , Since ϵ'' value observed for IPTh-I₂ is more negative at any frequency and temperature than ϵ' . Due to the presence of more polarizable dopant species (I₂, I⁻, I₃⁻ and I₅⁻) and electrically charged polymeric chain in doped polymeric sample the magnitude of ϵ' & ϵ'' for IPTh-I₂ has been found to be much larger than corresponding value for IPTh under identical condition of temperature and frequency.

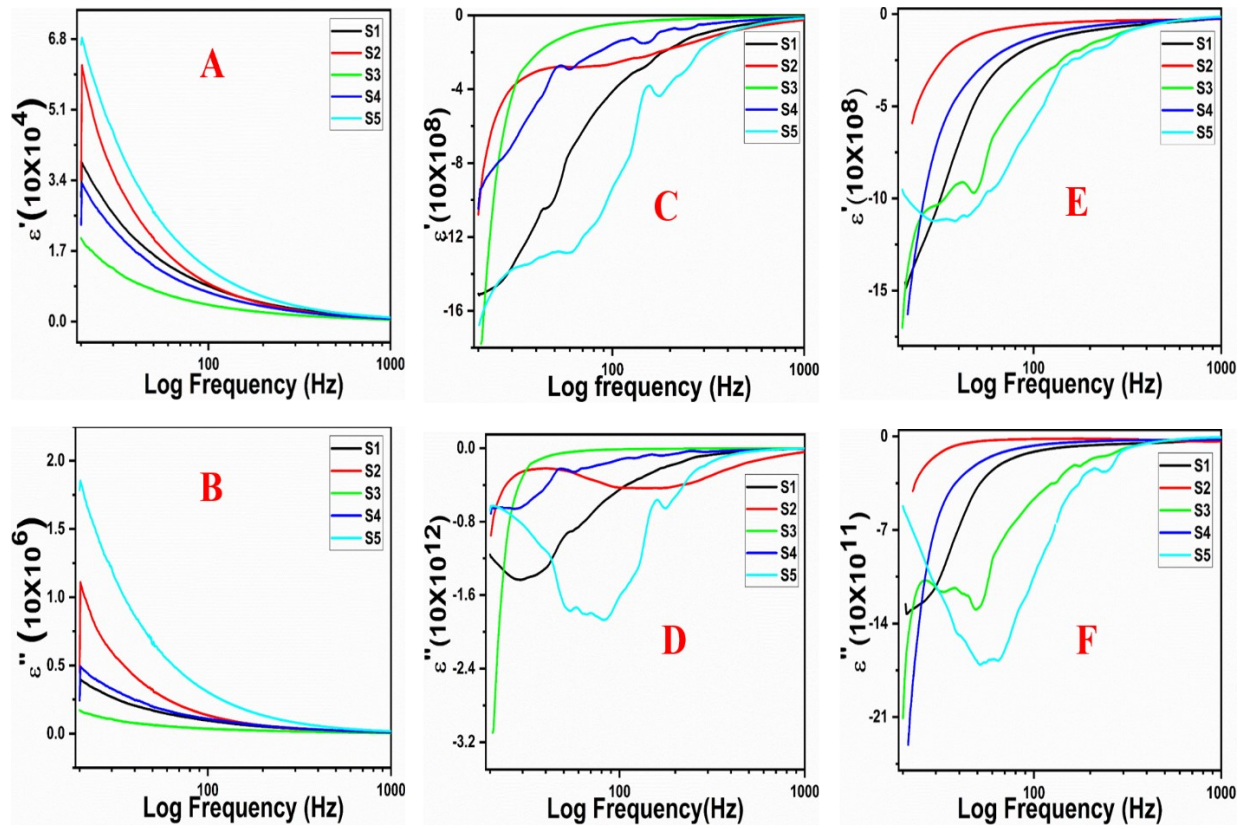


Figure 3 Illustrating dielectric constant and dielectric loss. **A,C,E** –dielectric constant of undoped, doped and redoped samples respectively. **B,D,F**–dielectric loss of undoped, doped and redoped samples respectively.

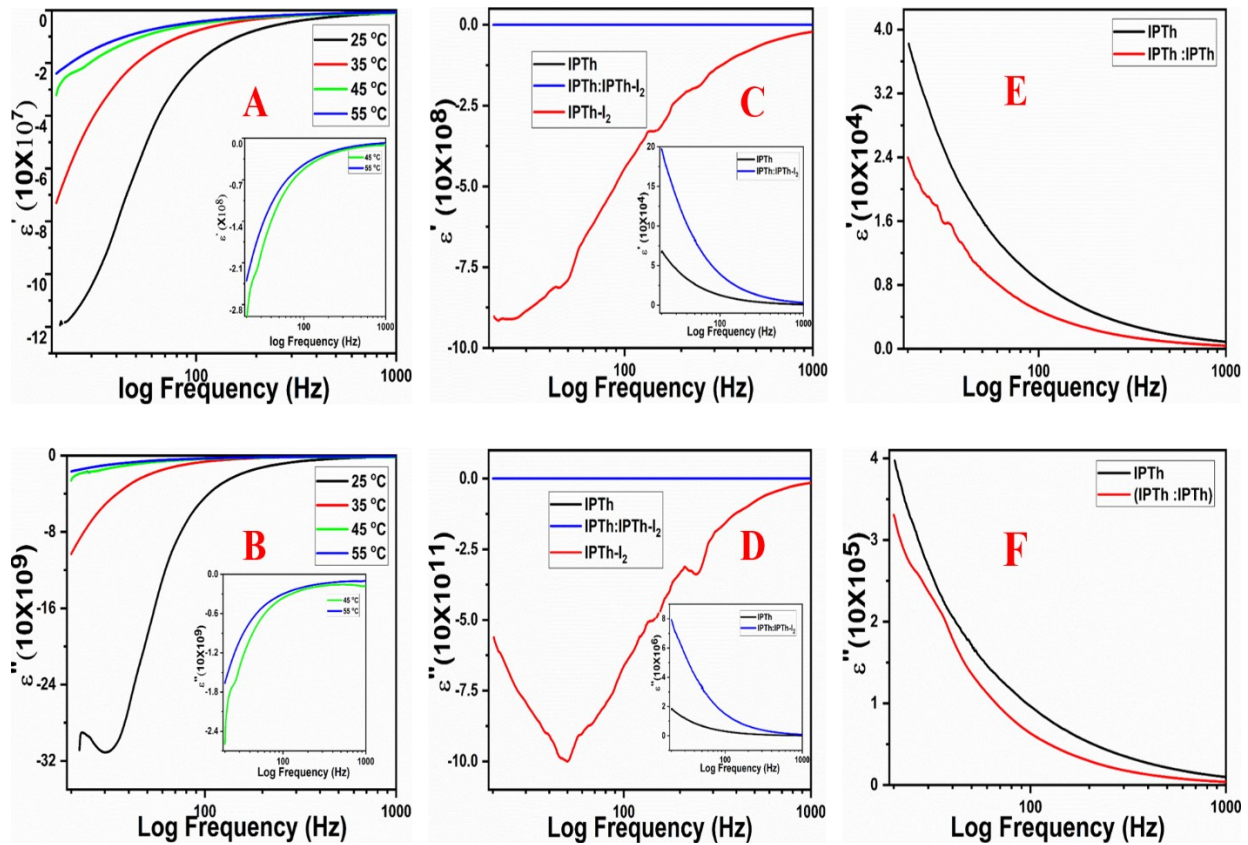


Figure 4 Representing dielectric constant and dielectric loss. **A,B-** thermal dependence of dielectric constant and dielectric loss of doped sample. **C,D-** Enhancement of total dielectric constant and dielectric loss respectively for bi-layer system comprising series connection of IPTh-I₂ and IPTh. **E,F** Variation of dielectric constant and dielectric loss respectively for bi-layer system comprising series arrangement of IPTh:IPTh.

Note: Herein we have reported capacitance and dielectric (both negative and positive value for doped and undoped respectively) for five different samples namely S1-S5. Herein our aim was to show the reproducibility of results and we have observed very good reproducibility of results. From the capacitance and dielectric graphs although values observed are similar but not identical for all five sample considered, there are two main reason for this observation the first one involve extent of doping which is a variable quantity, varying in the range of 85-97% and second involve nature of electrode-electrolyte interface which formed after placing thin film of polymer (electrolyte) in between electrode. The nature of electrode-electrolyte interface formed can never be identical on microscale (molecular level). These two variation ie. available dopant concentration and nature of electrode-electrolyte interface formed collectively results into the variation of observed value of dielectric property and capacitance for polymeric sample. The variation observed in the plot of complex dielectric constant in figure 2 B&C for samples S2&S3, and for S3&S5 respectively is related with the improper contact between electrode and electrolyte.

and same factor is responsible for abnormalities observed in dielectric loss (ϵ'') and dielectric constant (ϵ') results.

Note For information regarding structural and molecular characterization of polymeric sample kindly visit our previous publication (DOI <https://doi.org/10.1039/D1SM01217G>).

Configuration of single sided p-n junction diode: (S3)

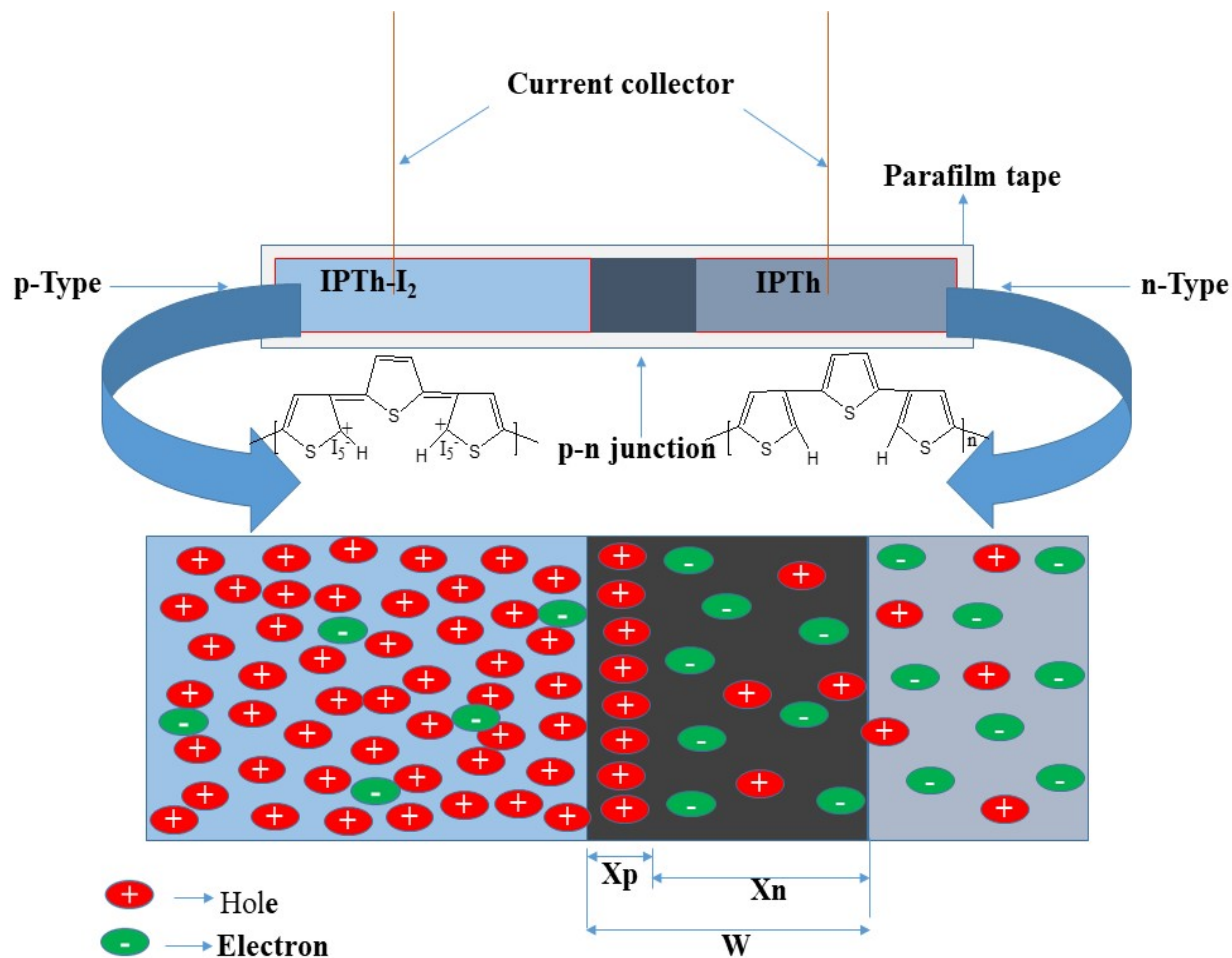


Figure 5: Diagrammatic representation of single sided p-n junction diode