

Supporting Information

Synthesis, Characterization and Electro-conducting Study of Isomeric Polythiophene

Devendra Kumar, Rudramani Tiwari, Dipendra Kumar Verma, Shashikant Yadav, Pubali Adhikary, S. Krishnamoorthi*

Department of Chemistry, Center of Advanced Study, Institute of Science, Banaras Hindu University, Varanasi-221005, India

* Corresponding Author- Dr. S. Krishnamoorthi, (Email: dr.skmoorthi@gmail.com), Tel: +91 9450200221

Optimization of Reaction condition: (S1)

Table No. 1

Solvent optimization^a:

S. No.	Solvents	Isolated yield (%)
1	N,N-Dimethylformamide	-
2	Dimethyl sulfoxide	-
3	Tetrahydrofuron	-
4	Acetic acid	-
5	Propanoic acid	-
6	N,N-Dimethylacetamide	-
7	Nitrobenzene	-
8	1,4-Dioxane	-
9	Acetonitrile	-
10	Water	-
11	Ethanol	-
12	Methanol	-
13	N-methylpyrrolidone	-
14	Benzene	25
15	Toluene	15
16	Dichloromethane	73
17	Dichlorobenzene	78
18	Chloroform	80
19	Chlorobenzene	78
20	1,2-Dichloroethane	90

^aThiophene monomer- 50µL or 0.6 mmole, DDQ- 1 Eq., Reaction time- 10 min., H₂SO₄ (acid)- 62µL or 2 Eq., Reaction Temp-40°C Solvent volume 10 mL.

Table No. 2**Acid optimization^b:**

S.No.	Acids	Acid amount ($\mu\text{L}/\text{mg}$)	Isolated yield (mg)
1	Hydrochloric acid	74.	-
2	Nitric acid	70	-
3	Trifluoroacetic acid	92	-
4	Perchloric acid	73	-
5	Monochloroacetic acid	190	-
6	Trichloroacetic acid	328	-
7	Benzoic acid	244	-
8	Picric acid	458	-
9	p-Toluenesulphonic acid	344	-
10	Hydrobromic acid	162	-
11	Sulfuric acid	62	90

^bThiophene monomer- 50 μL or 0.6 mmole, Reaction time- 10 min., Reaction Temp- 40°C, DDQ- 1 Eq., Dichloroethane (solvent) - 10 mL

Table No.3**Optimization of reaction condition^c:**

S.No.	Time (min)	Temp. ($^{\circ}\text{C}$)	Acid (μL)	DDQ (mg)	Isolated yield (%)
1	5	40	62	136	88
2	10	40	62	136	91
3	15	40	62	136	88
4	30	40	62	136	91
5	60	40	62	136	90.
6	120	40	62	136	88
7	240	40	62	136	91
8	5	50	62	136	91
9	10	50	62	136	91
10	15	50	62	136	91
11	30	50	62	136	88
12	60	50	62	136	91
13	120	50	62	136	90
14	5	75	62	136	90
15	10	75	62	136	90
16	15	75	62	136	91
17	30	75	62	136	91
18	60	75	62	136	91
19	120	75	62	136	90
20	10	40	31	136	39

21	10	40	124	136	91
22	10	40	16	136	25
23	10	40	62	68	32
24	10	40	62	272	47
25	30	0.0	62	136	91

^cThiophene monomer- 50 μ L or 0.6 mmole, Dichloroethane (solvent)- 10 mL.

Solvent effect on polymerization: (S1)

Since solvent play very important role for controlling the rate of reaction by solvating the reactants. So a large number of commonly used solvent has been screened varying from neutral (Water, table no. 1 Sr. no. 10) to weakly acidic one (Acetic acid, table no. 1 Sr. no. 4) It is quite clear from **table 1** that polymerization reaction does not take place in solvent containing nitrogen and oxygen atom as their elemental constituent (Sr. no. 1 to Sr. no. 13). The main reason for this observation lies in the fact that the solvent molecules get protonated more preferably by the concentrated sulfuric acid than the reactant molecule. Protonation of reactants molecule by the concentrated sulfuric acid is a necessary step for the polymerization of monomer. Not only the amount of solvent is much more as compared to reactant but also the solvents are more nucleophilic than reactant so reactant molecule does not find good chance for getting protonated over solvent molecules hence polymerization reaction does not take place in these solvents. In aromatic hydrocarbon based solvents (Sr. no. 14 & 15) although polymerization reaction does take place but yield of product is low (below 30%), most probably it may be due to the poor solubility of either of reactants in these solvents which responsible for the low reaction rate and hence low yield of the product with in constant reaction time. Chlorinated solvents (Sr. no. 16 to 20) have been found to be better one for the polymerization reaction. As chlorinated solvents dissolve all the reactants molecule perfectly and also does not inhibits polymerization reaction by mean of self protonation by concentrated sulfuric acid. Among various chlorinated solvents 1,2-dichloroethane solvent produce product in appreciable yield (> 90%).

Acid effect on polymerization: (S1)

Since protonation of the thiophene molecule with acid is a crucial step for the polymerization reaction, so several type of acids having varying degree of ionization efficiency or acidic strength have been tested in polymerization reaction. It becomes quite clear from **table 2** that only concentrated sulfuric acid allows the polymerization reaction to take place under given set of reaction condition. While all other acids which are either weaker or stronger than concentrated sulfuric acid does not facilitate the polymerization reaction under similar reaction condition. Acids which are weaker than sulfuric acid are not able to protonate the thiophene ring sufficiently and hence do not allow the polymerization reaction. On the other hand acids which are stronger than sulfuric acids may inhibit polymerization in two different possible ways. First one involve the protonation of all available thiophene molecules at once so no neutral thiophene molecule present in the medium to carry out the reaction. Second most possible way involves the

protonation of thiophene molecule and DDQ reagent both. The process of protonation of reactant and reagent and their effect on polymerization can be represented schematically as follows **figure 1**.

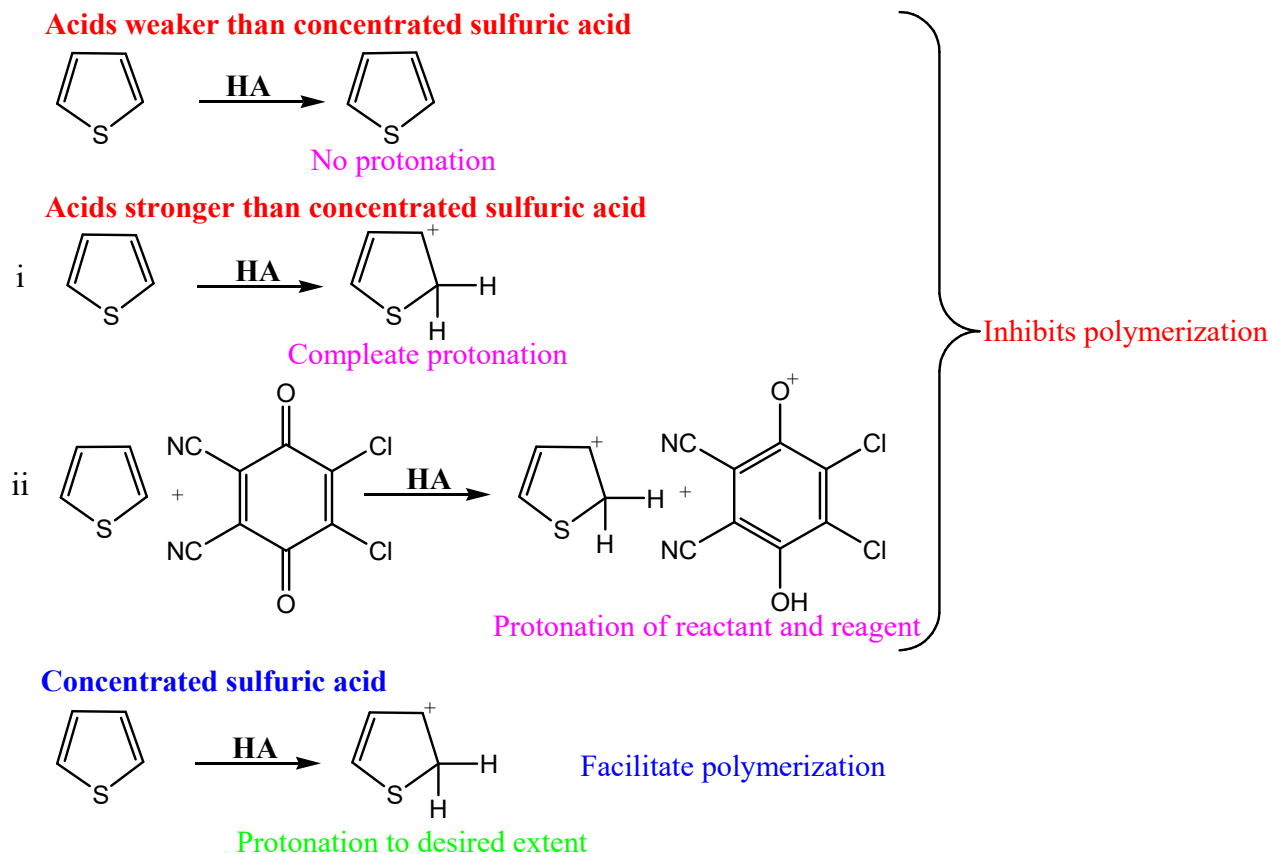


Figure 1: Schematic representation of acids effect on polymerization of thiophene

Doping mechanism: (S2)

50 mg of powdered IPTH has been exposed to the vapour of iodine for 24 hours of period lead to the doping. IPTH upon exposure to vapour of iodine lead to the formation of charged polymer which involve radical cation species having a spin of $\frac{1}{2}$ and dication species having no net spin. During the course of doping of polymer by the iodine vapour, the molecules of iodine undergo disproportionation reaction in which they form iodonium ion and triiodide anion. Under low doping level triiodide anion remain as such and act as counterion for doped polymeric sytem but in high doping level triiodide anion react with neutral iodine molecule and form symmetrical pentaiodide anion. Iodonium ion owing to electron deficient act as oxidizing agent for the polymer molecule and accept electron from the polymer backbone and lead to the formation of resonance stabilized radical cation also termed as polaron. Polaron furthure gets oxidized by available iodonium ion and form resonance stabilized dication species also termed as bipolaron

figure 2. The positive charge of both polaron and bipolaron are delocalized over several thiophene rings. Positive charge of both polaron and bipolaron are electrostatically stabilized by symmetrical pentafluoride anions which are non-nucleophilic in nature.

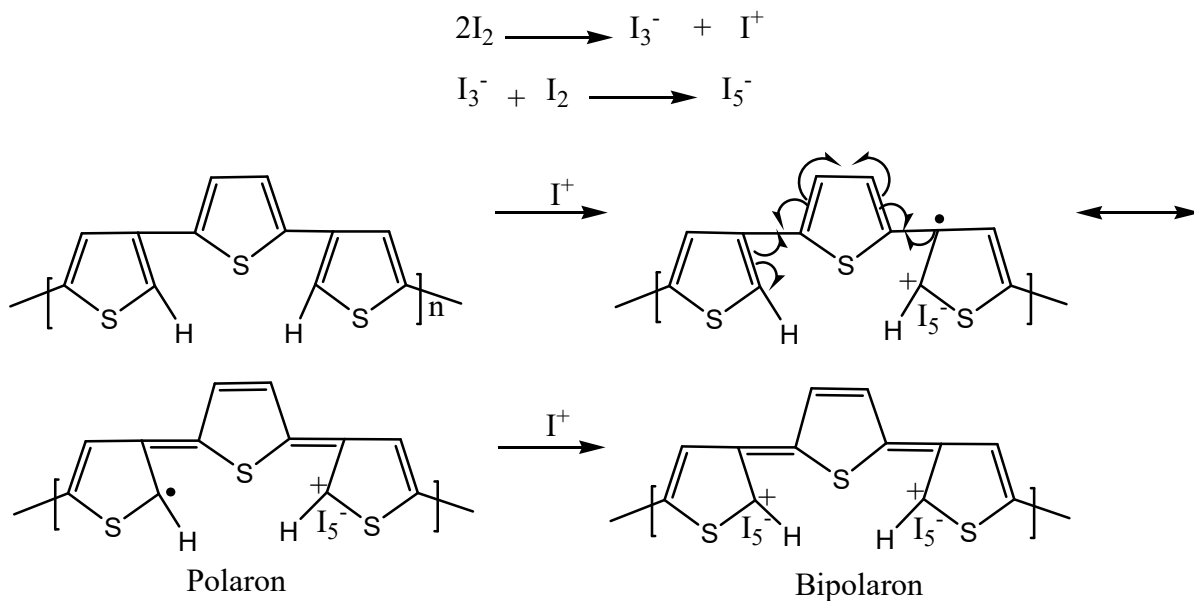


Figure 2 Illustration of doping mechanism of IPTTh by iodine molecule.

Result and Discussion:

NMR spectrum:

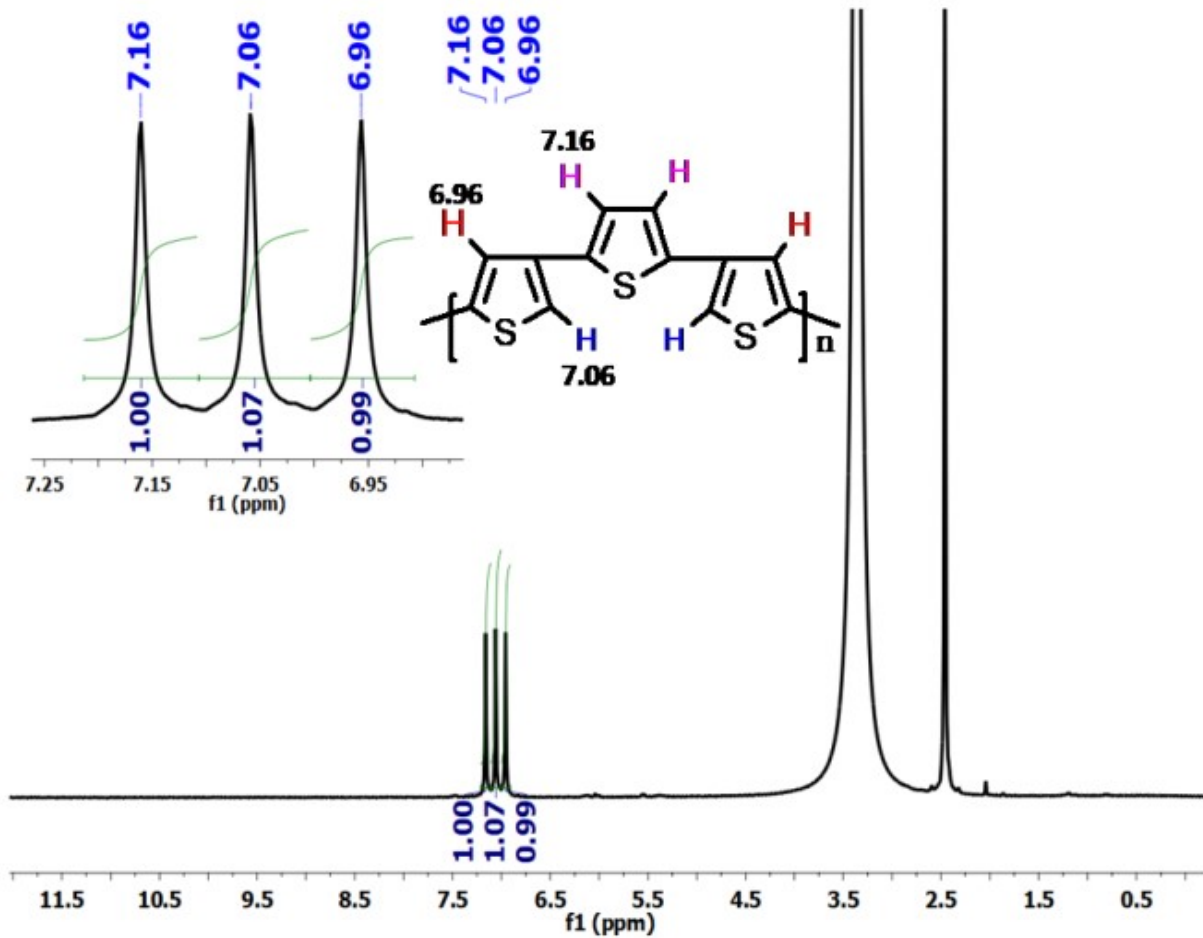


Figure 3: NMR spectrum of IPTTh

FTIR:

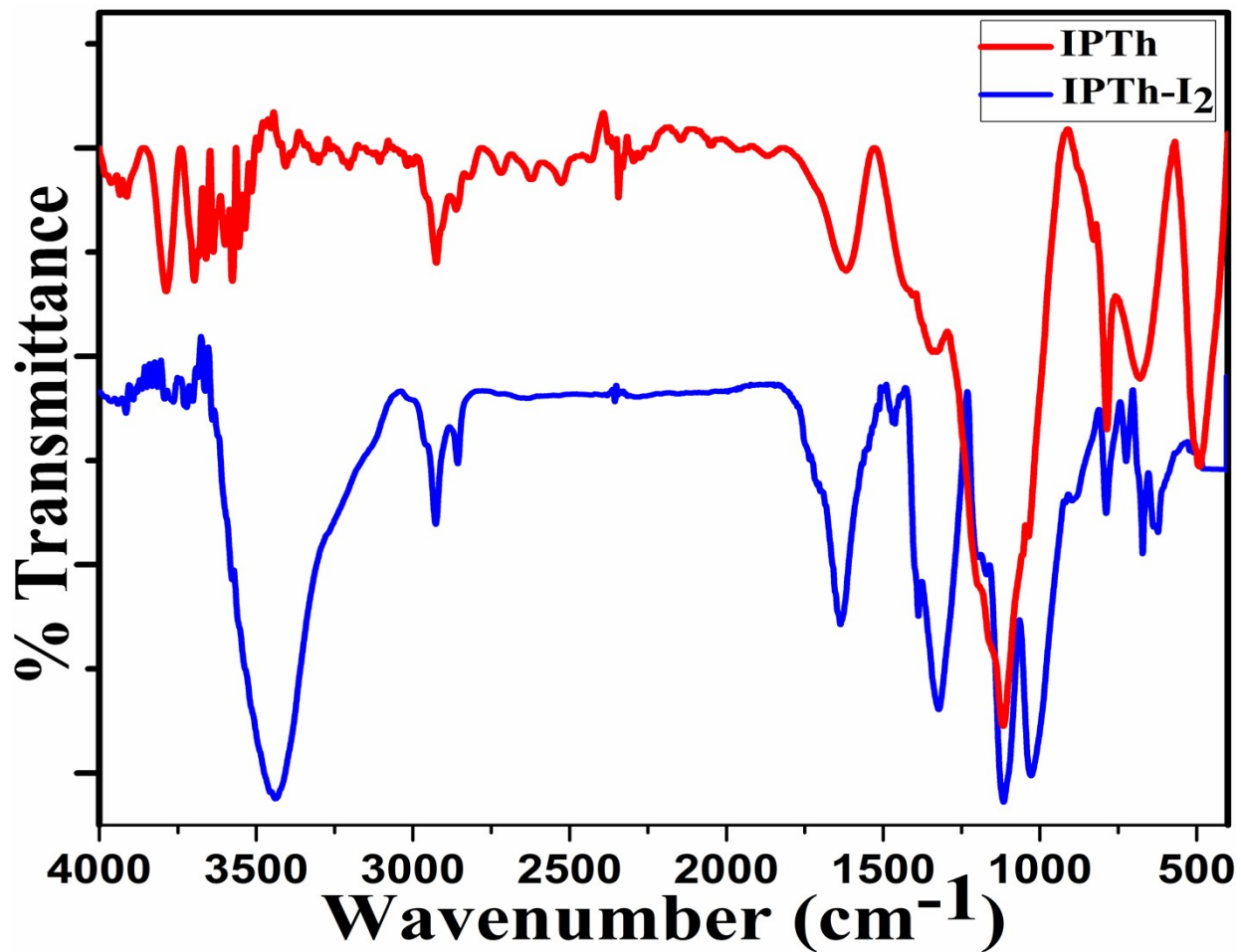


Figure 4: FTIR Spectra of IPTh & IPTh-I₂

Raman:

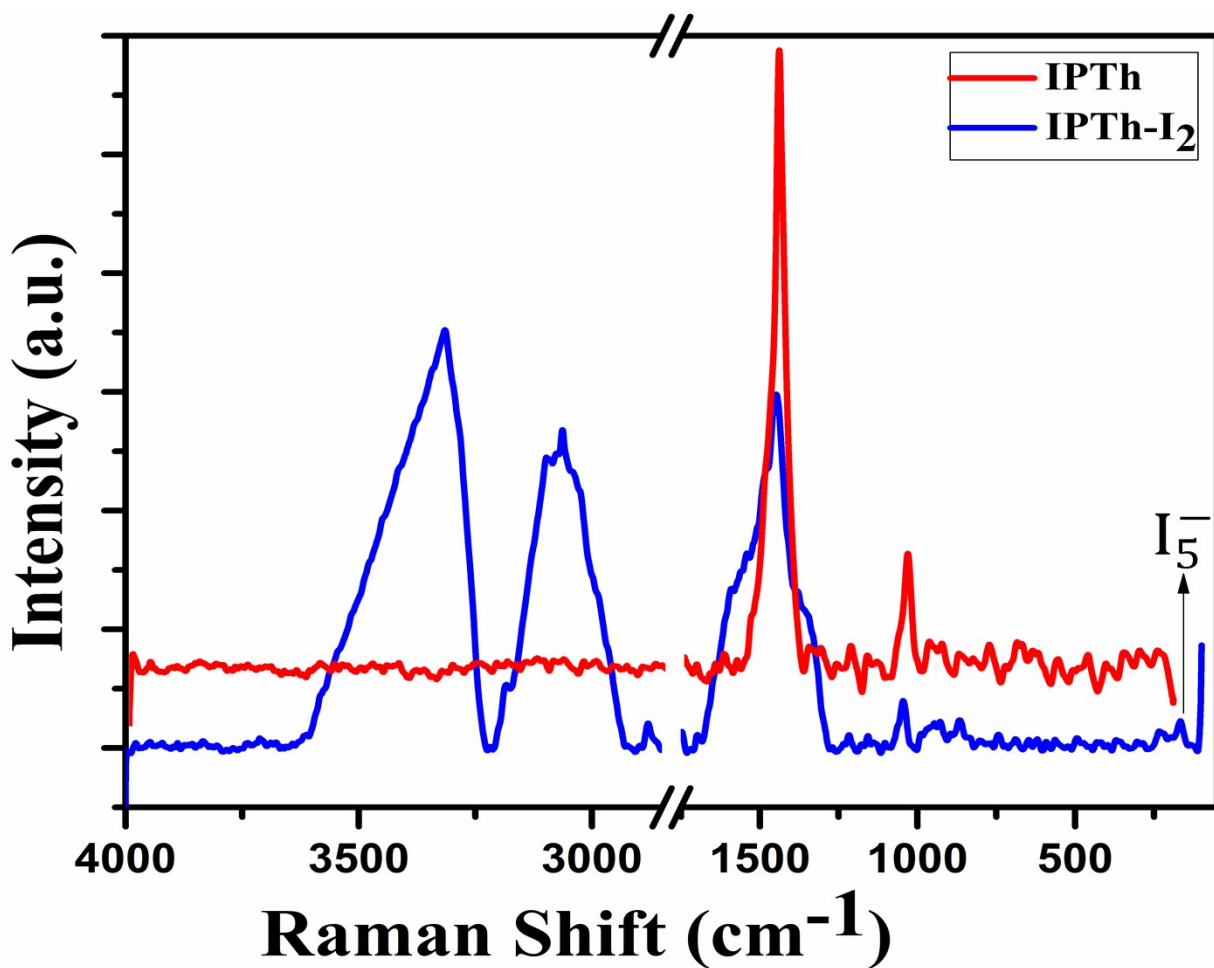
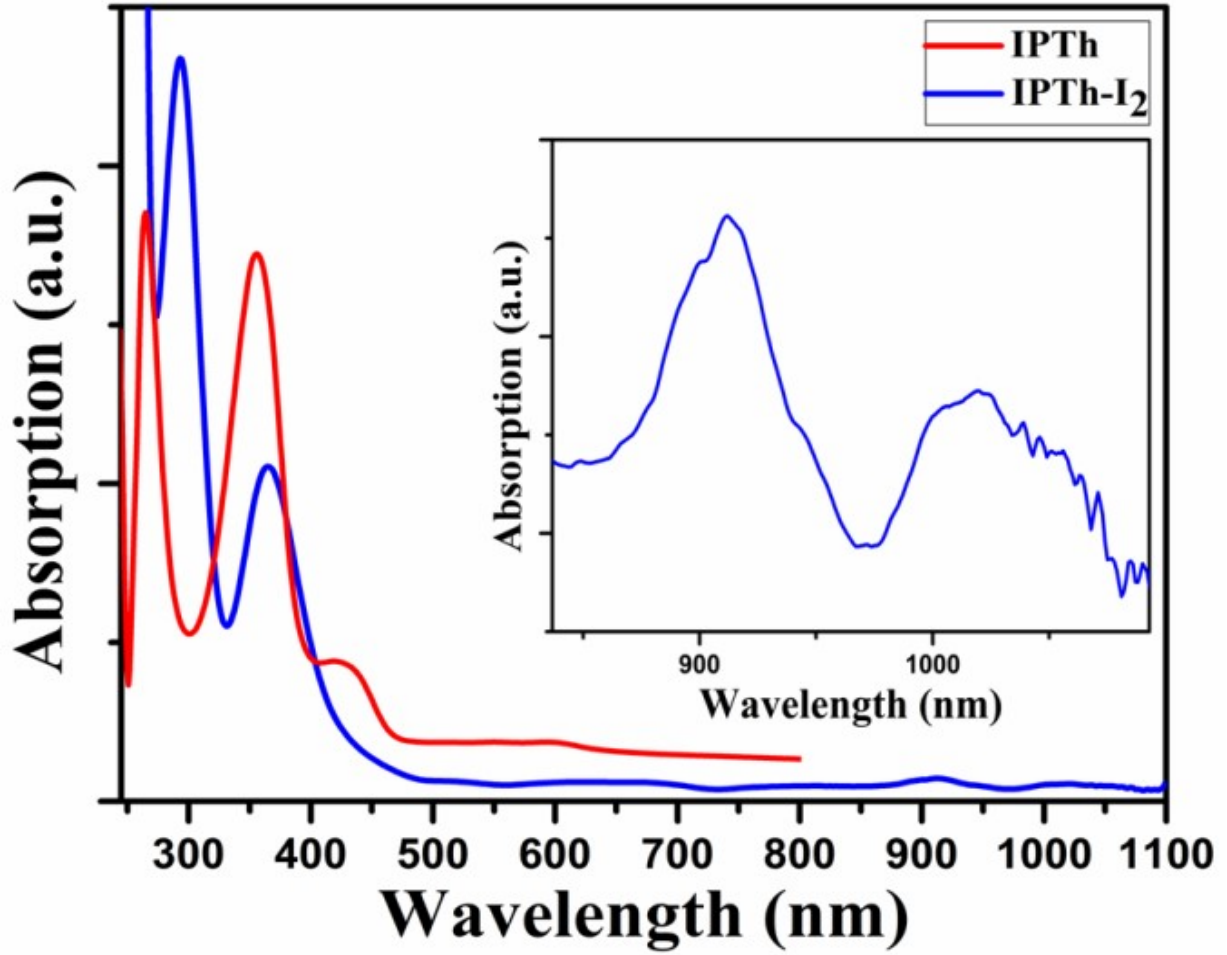
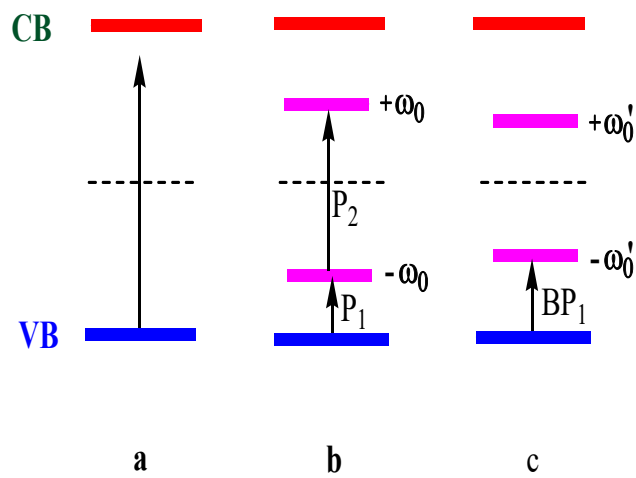


Figure 5: Raman spectra of IPTTh & IPTTh-I₂

UV-Visible:



A



B

Figure 6: (A) UV-Vis spectra of IPTh & IPTh-I₂ (B) Schematic energy level diagram of polymer (a) Neutral (b) Positive polaron (c) Positive bipolaron

GPC Analysis:

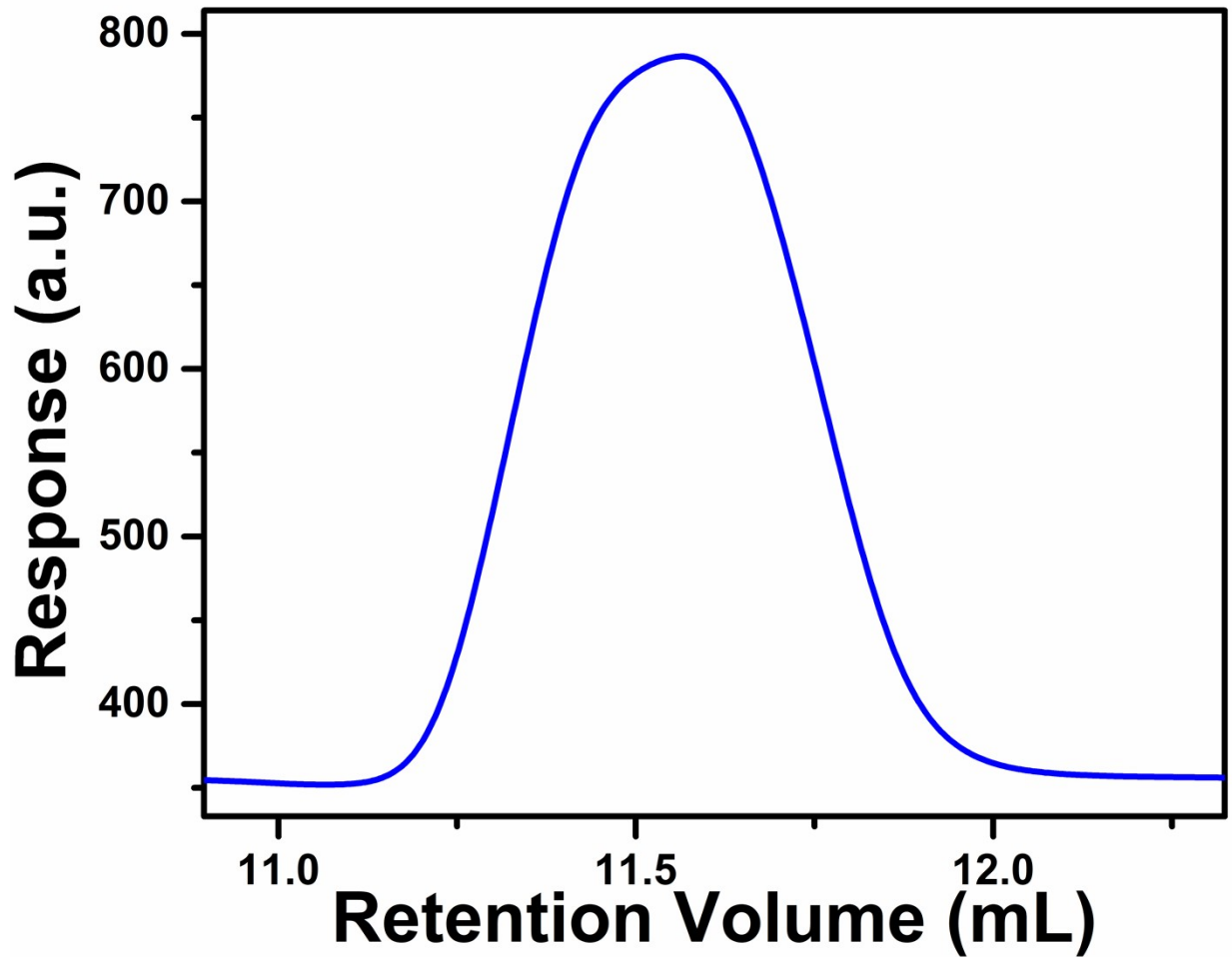


Figure 7: GPC Chromatogram of IPTh

TGA:

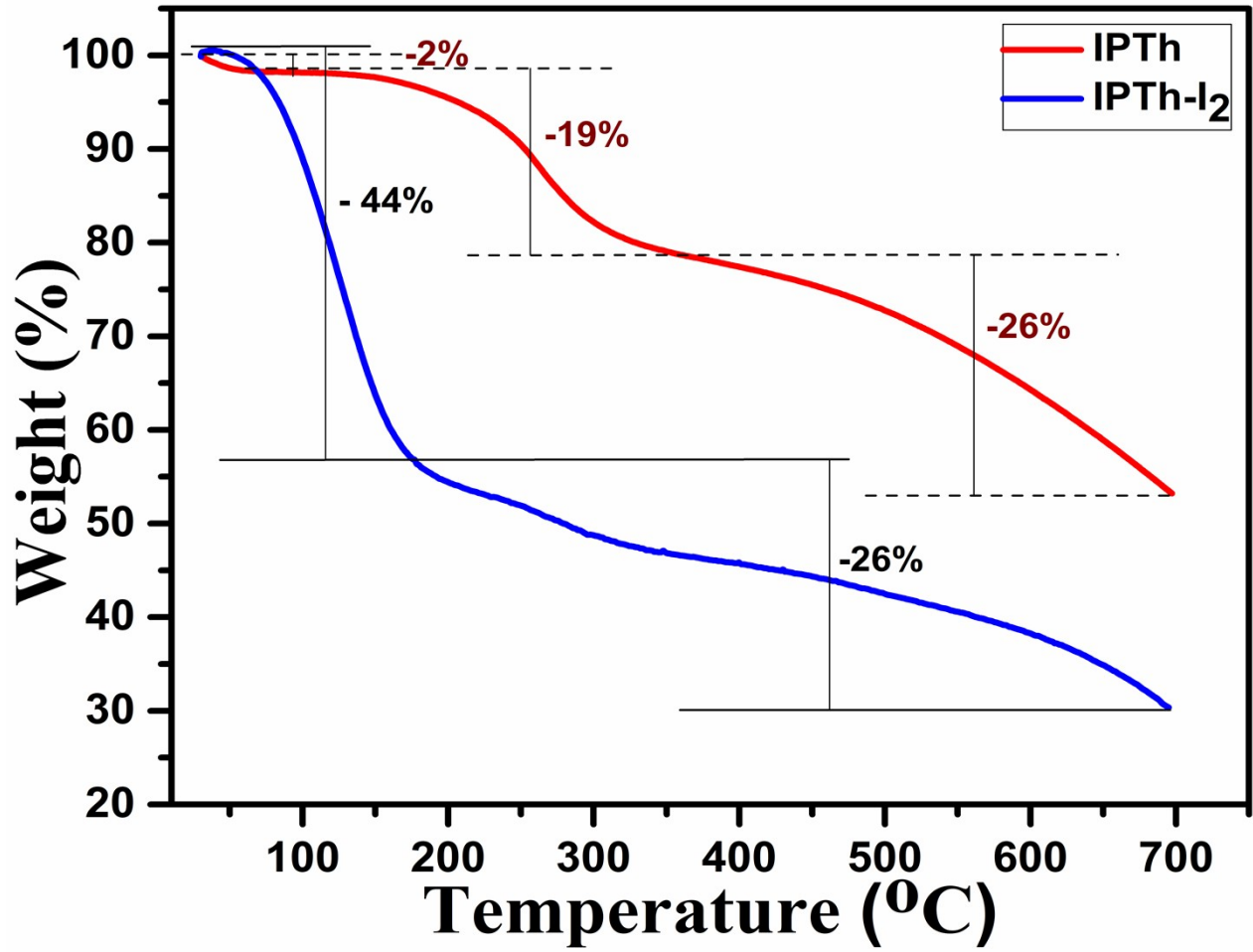


Figure 8: Thermograms of IPTTh & IPTTh-I₂

Powder XRD:

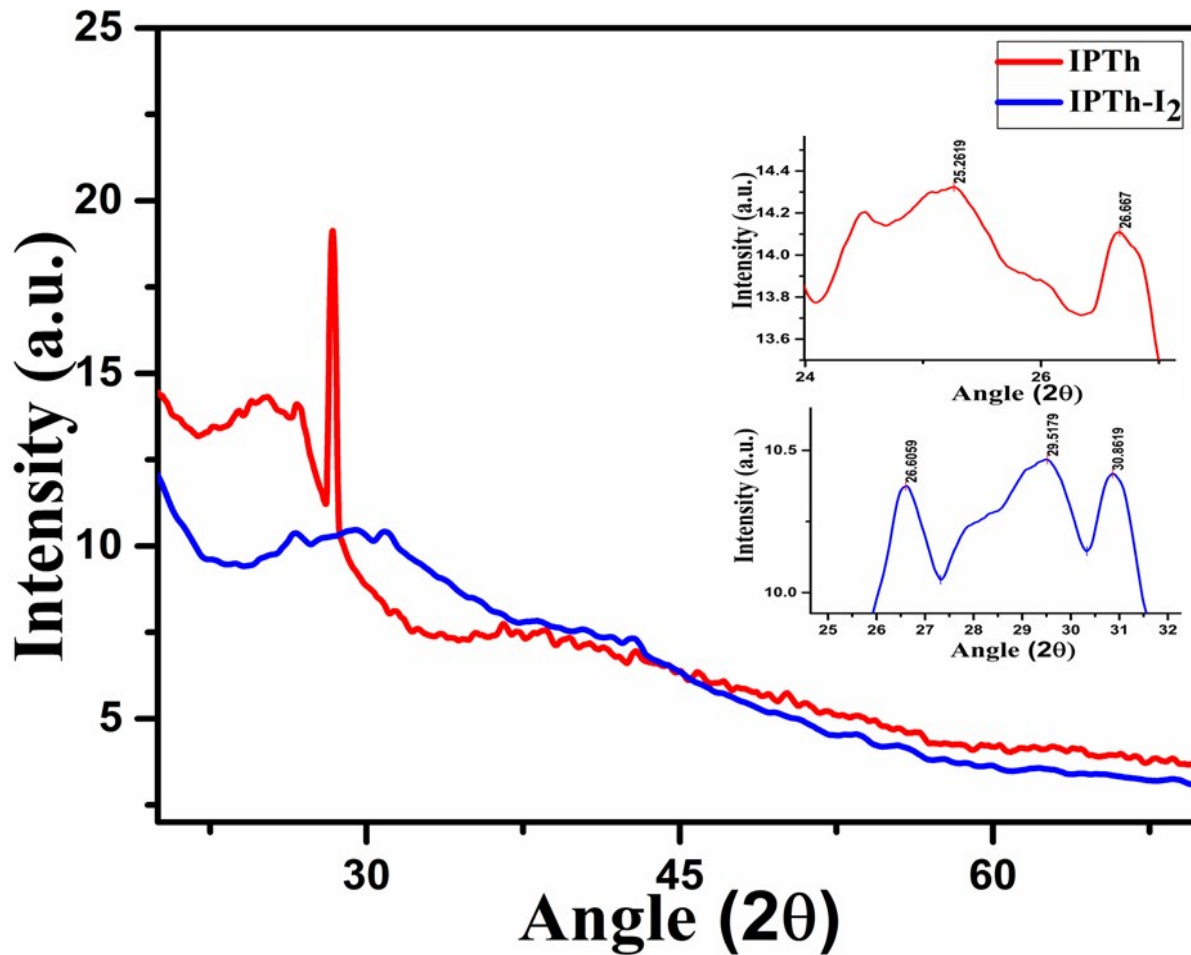
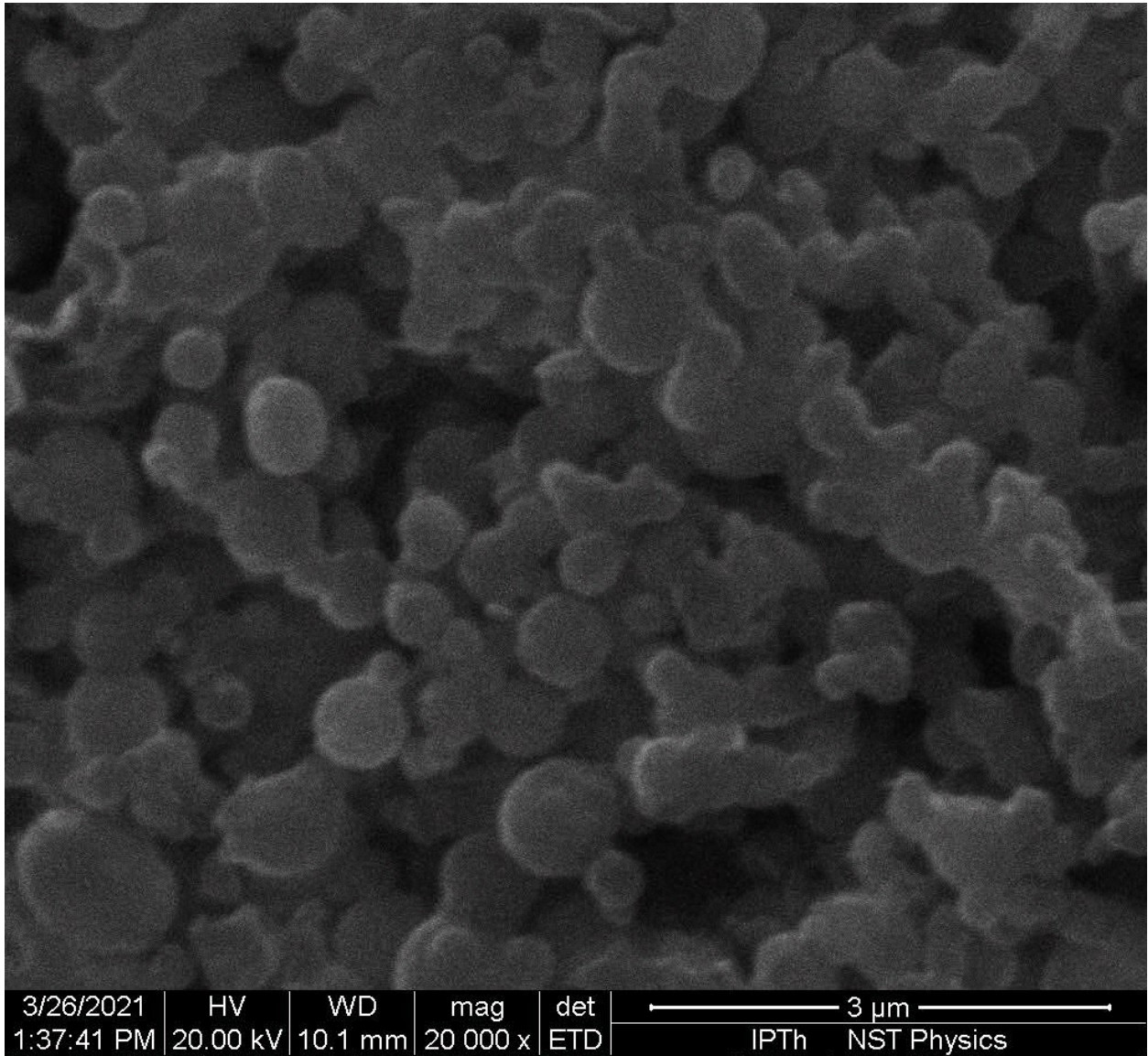
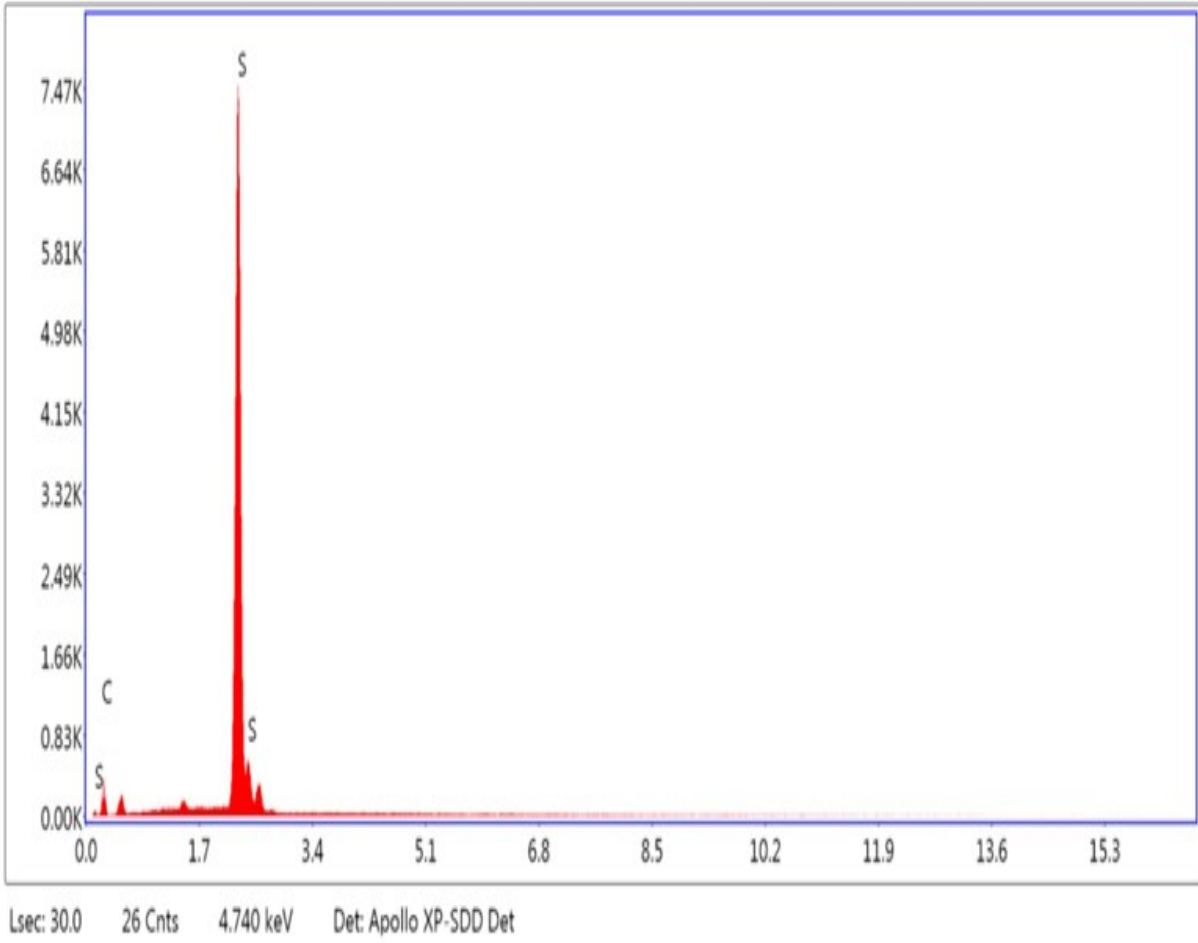


Figure 9: XRD patterns of IPTTh & IPTTh-I₂

SEM-EDAX:



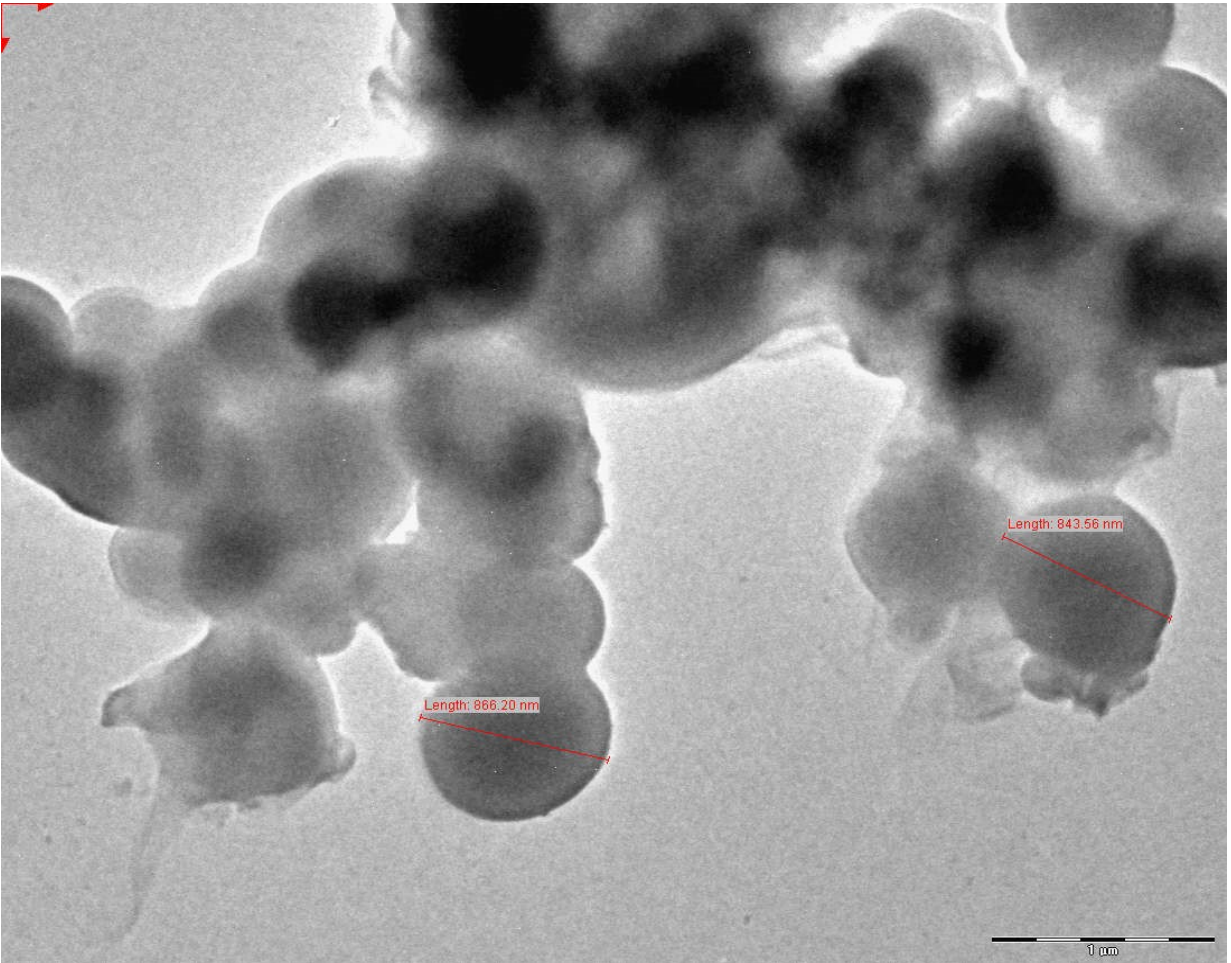
A



B

Figure 10 (A) SEM image and (B) EDAX spectrum of IPTb

TEM:



A



B

Figure 11: (A) TEM micrograph (B) SAED pattern of IPTb

Mechanism of charge transport in polymer: (S3)

Like most common polymer PTh, IPTh is also fully conjugated polymer having alternated single and double bond. However unlike PTh in case of IPTh one cannot delocalize the π electron of the ring over several thiophene rings. Generally in case of semiconducting polymer fastest transport of the charge carrier takes place in conjugation direction (Interchain transport). Second fastest transport of charge carriers in conjugated polymer takes place along π - π stacked direction (interchain transport) by overlapping of π orbital. As in case of IPTh delocalization of π electron along the polymeric backbone is limited to fewer thiophene units so transport of charge carrier in conjugation direction would be slower than PTh. As the actual structure of the IPTh molecule is the hybrid of all resonating structure that one could write by delocalization of π electron so transport of charge carrier along conjugation direction could not be zero. As IPTh molecules has rigid polymeric backbone and having ability to gets crystallize which results into the packing of polymeric chain. When the polymeric chains packed, supermolecular ordering happens in such a manner that the π orbitals which are belonging to different polymeric chain stacked cofacially. This partial overlapping of the π orbital is solely responsible for the transport of charge carrier in between two different polymeric chains **figure 12**.

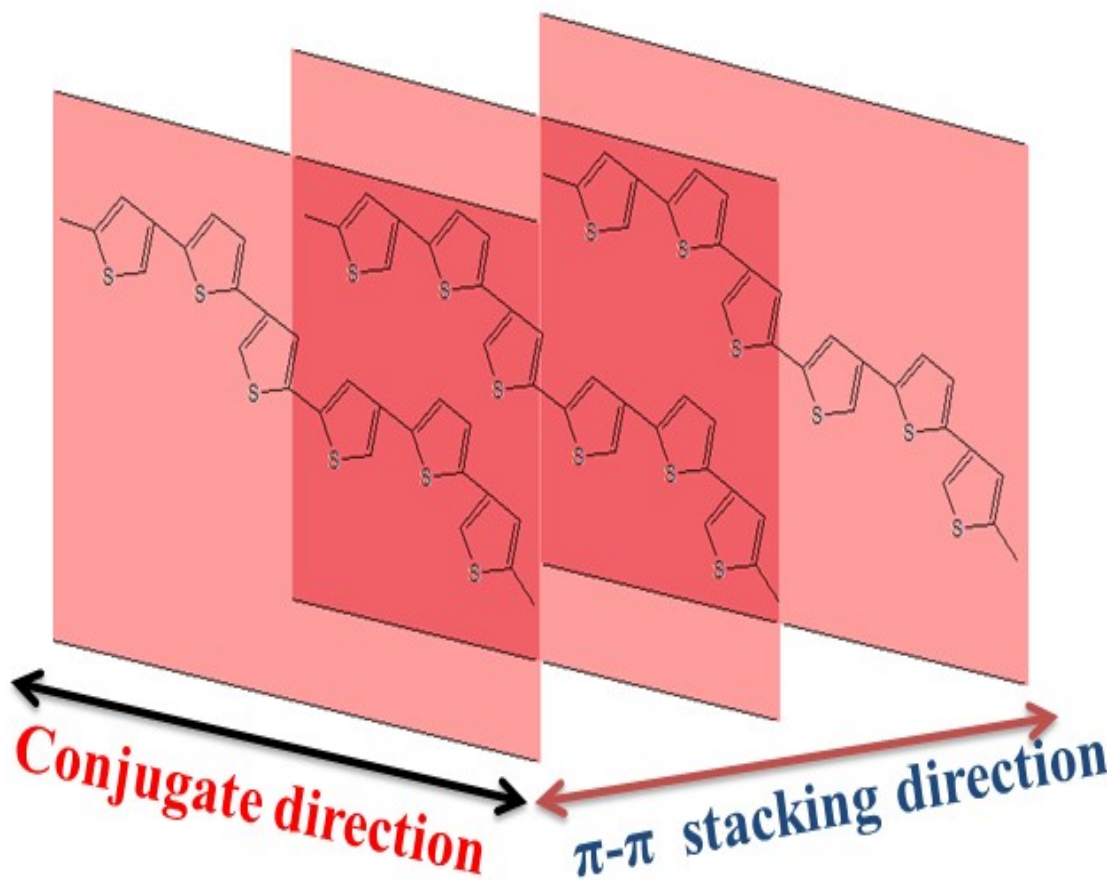
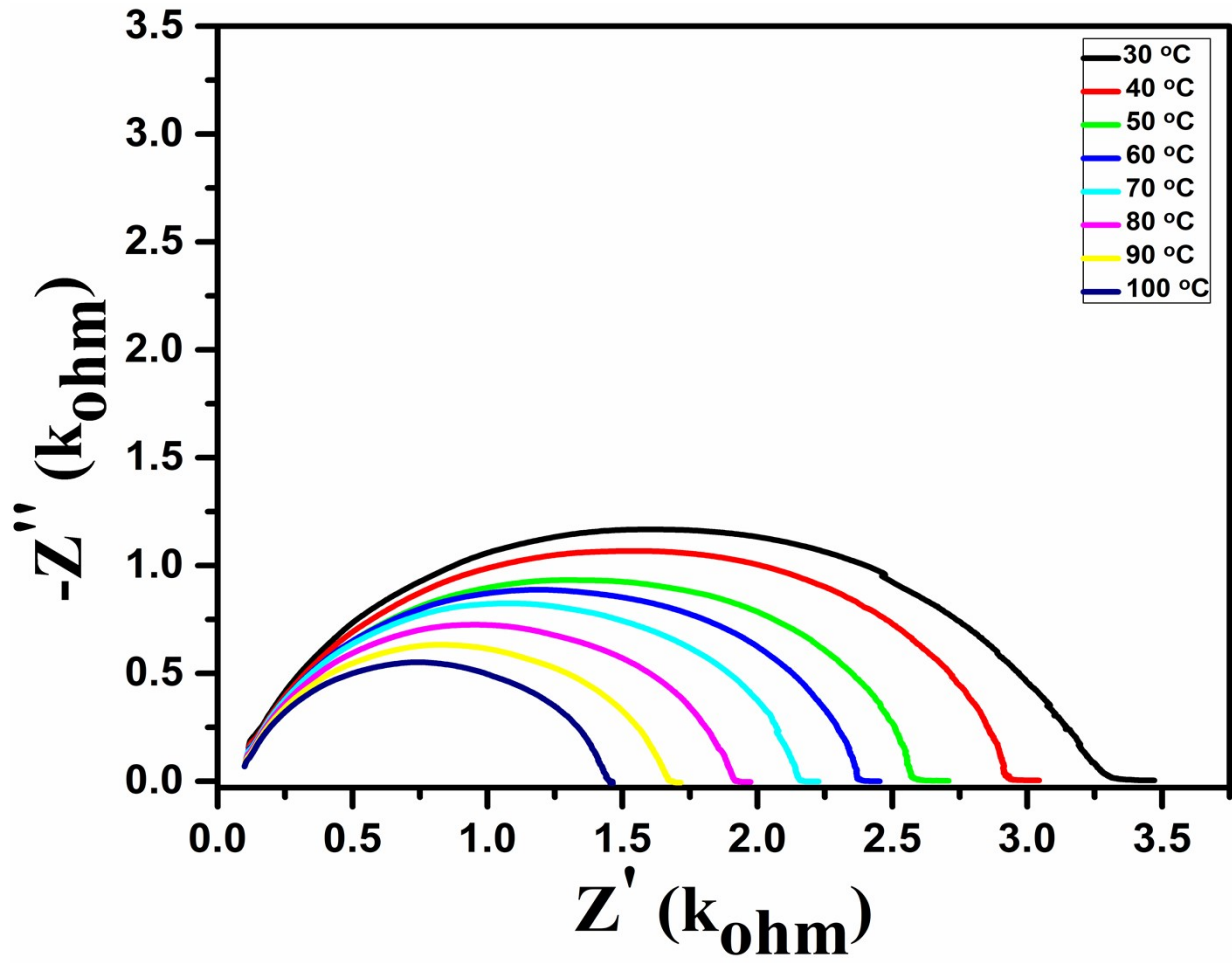
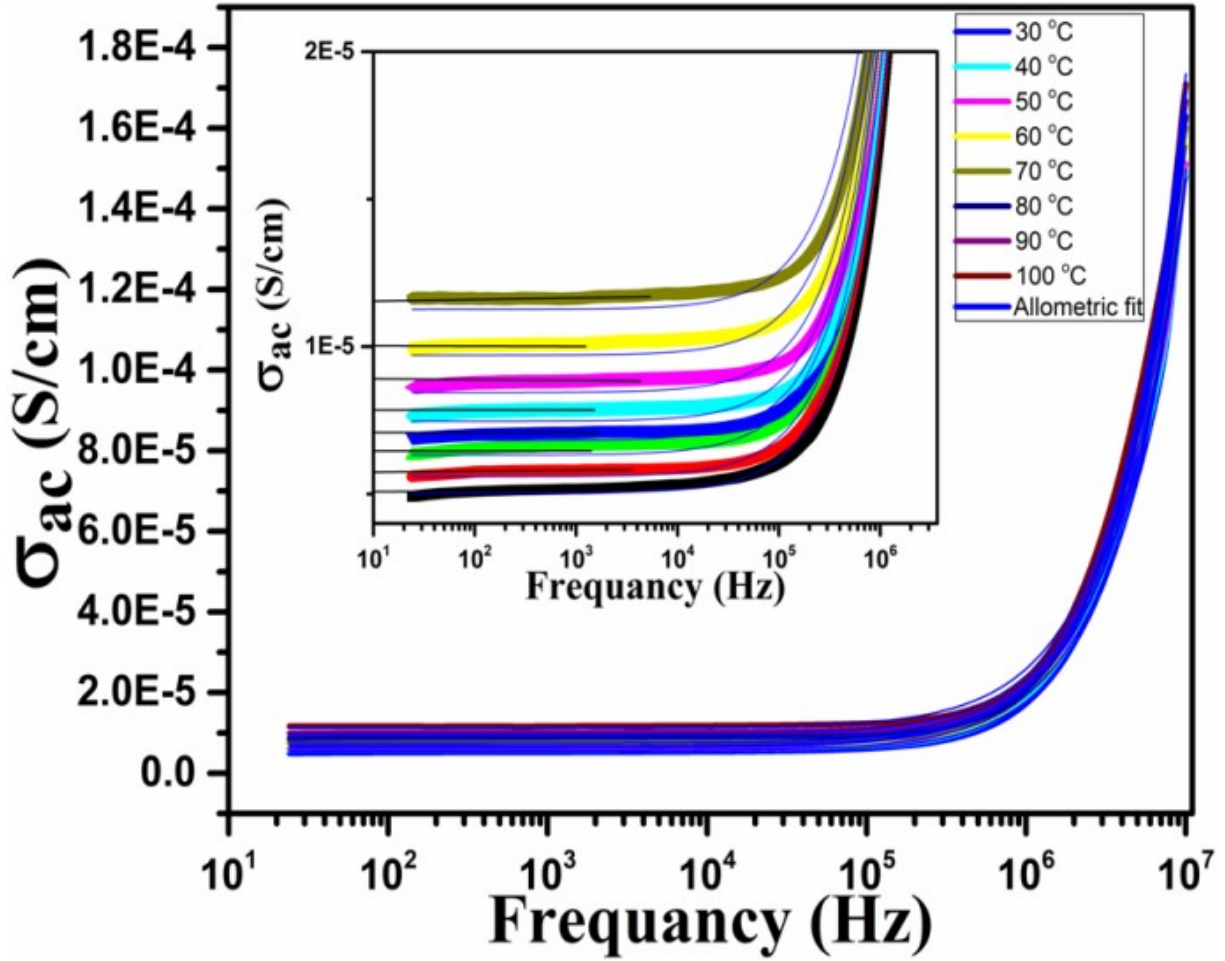


Figure 12: Illustration of Charge transport

Electrical conductivity study:

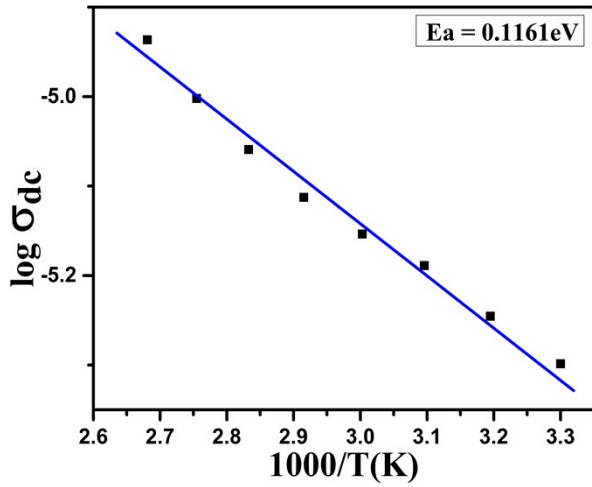


A

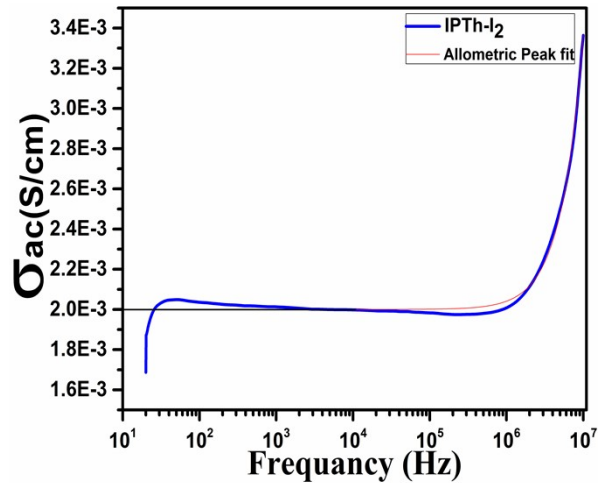


B

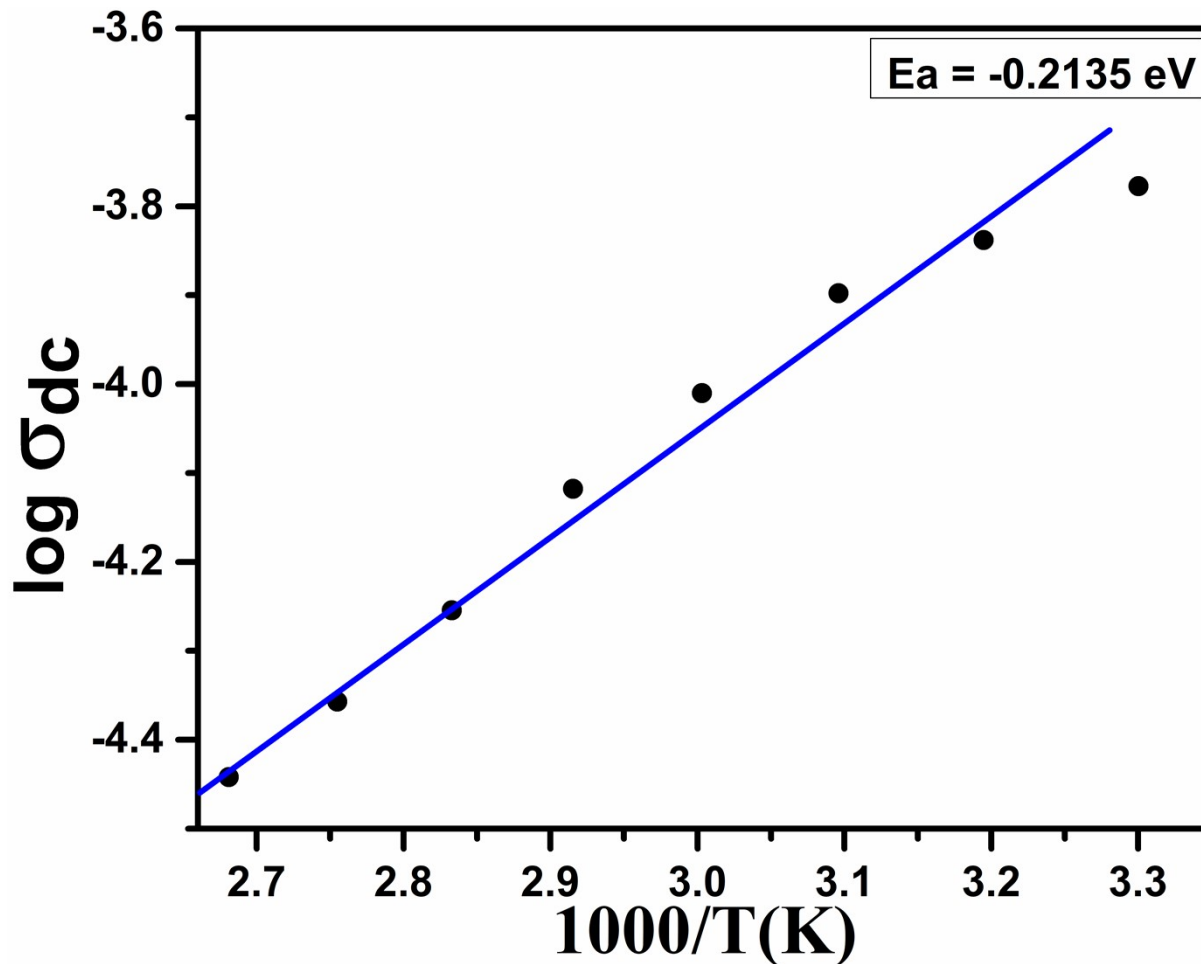
Figure 13: (A) Nyquist plot and (B) AC conductivity plot of IPTTh



A



B



Fi

Figure 14: (A) Arrhenius plot for IPTTh (B) AC conductivity plot of IPTTh-I₂ (C) Arrhenius plot for IPTTh-I₂

The value of electrical conductivity of iodine doped IPTTh directly depends over the concentration of polaron and bipolaron present in the polymer matrix which in turn depends on the concentration of oxidizing agent, (iodine molecule) present in the polymer matrix. At lower temperature (30°C) the concentration of available iodine molecule is highest so electrical conductivity has highest value, but as the temperature increases from 30°C the concentration of iodine molecule decreases, hence concentration of polaron and bipolaron decreases which leads to decrease in electrical conductivity. So the Arrhenius plot plotted between $\log \sigma_{dc}$ and $1000/T(K)$ for doped sample is reverse to Arrhenius plot for pristine IPTTh i.e. with positive

slope. Reverse Arrhenius plot for iodine doped IPTH also give negative value of activation energy for electrical conductivity ($E_a = -0.2135$ eV).

Table of Contents:

