Electronic Supplementary Information

Solvent Free Chemical Oxidative Polymerization as a Universal Method for the Synthesis of Ultra High Molecular Weight Conjugated Polymers Based on 3,4-Propylenedioxythiophenes

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General: Iron (III) tosylate [$Fe(OTs)_3.6H_2O$] was purchased from Aldrich and used as it was. Anhydrous iron(III) chloride ($FeCl_3$) and bromine were purchased from Merck and used without any further purification. Tetrahydrofuran and toluene were distilled over sodium /benzophenone under nitrogen before use. Acetone, methanol and chloroform were used after distillation. All other chemicals were of reagent grade and used without further purification. Nylon Syringe filter with 0.22 μm pore diameter was purchased from Agela Technologies. GPC was done at room temperature on JASCO system equipped with 600×7.5 mm Polymer Laboratories PL gel 5 μm mixed D column and UV

detector (254 nm wavelength was used for Polystyrene and 540 nm was used for the detection of PProDOT-Hex_2) in chloroform using a flow rate of 1 ml/min. 20µL of the samples were injected for GPC analysis and Polystryrene was used as the standard for calculating the molecular weights. ^1H NMR was recorded on a Bruker AVANCE^{III} 400 MHz NMR spectrometer. Ocean optics USB2000+ spectrometer with LS-1 tungsten halogen lamp was used for measuring absorbance in UV-Visible region. GSM glass slides of 25 mm x 75 mm size were cut into three pieces of 25 mm x 25 mm size and used as a substrate for thin films. For electrochemical characterization, potentiostat CHI760D from CH instruments was used. Sheet resistance measurements were carried out using Keithley 2400 source meter with Pro4 probe from Lucas labs. SP4 probe head from SIGNATONE made up of tungsten carbide with 0.01 inches tip radius, 0.040 inches tip spacing and 85 grams pressure was used for all the measurements. Measurements were made at 5 different places on each film and their average was taken as the sheet resistance of that film. Profilometer from Dektak Veeco was used for thickness measurement. Radius of the Stylus was 2.5 µm and 1 mg force was applied. For casting the thin film, a solution of 5.6 mg poly (ProDOT-Hex_2) in 730 µl toluene was prepared and filtered through 0.22 µ Nylon filter. Films were casted by spin coating on glass at 1000 rpm, 500 acceleration for 10 s and dried on hot plate at 40-50 °C temperature for 5-10 min. They were then exposed in I_2 chamber for 30 minutes for doping and excess of I_2 was removed by applying vacuum. Three electrode system was used for electrochemical studies. Thin film of PProDOT-Hex_2 casted on ITO and was taken as working electrode along with Pt foil as counter and silver wire as reference electrode.

Solvent Free Chemical Oxidative Polymerization: Iron(III) p-toluenesulfonatehexahydrate (8.44 g, 12.3 mmol) was crushed to fine powder with help of mortar and pestle. ProDOT-Hex_2 (1g, 3.1 mmol) was added to this yellow Iron(III) p-toluenesulfonatehexahydrate powder in mortar and mixed thoroughly with the help of pestle. Color of mixed solid changed to green within 10 seconds. This green solid was transferred to a sample vial and kept in oven at 100^0C for 8 hours. Dark solid obtained was crushed to fine powder in mortar and pestle and was sonicated in 15 mL of methanol for 10 min to dissolve excess iron(III) p-toluenesulfonatehexahydrate. Yellow color methanol layer was decanted off and remaining black solid was dissolved in 50 mL chloroform, washed with water (4x 100 mL) and then washed two times with hydrazine hydrate/water solution to get reduced bright purple color polymer solution. Chloroform layer was again washed with water (2x 100 mL) and concentrated to get solid. The final purification was done using soxhlet extraction with methanol to remove oligomers and then with chloroform to get final purified polymer in 90% yield.

Direct Synthesis of Thin Films on Glass Substrate: ProDOT-Hex_2 (0.025 g in 100 µl n-Pentanol) and Iron(III) p-toluenesulfonatehexahydrate (0.21g in 330 µl n-pentanol) solutions were mixed together just before casting films by spin coating. Films were prepared on cleaned glass slides at 2000 rpm for 20 s (500 rpm/s acceleration) and baked at 100 °C for 1 h. Films were washed in isopropanol which resulted in partial dedoping. These films were then redoped using bromine vapors or completely dedoped using hydrazine solution (**Figures S5 and S6**).

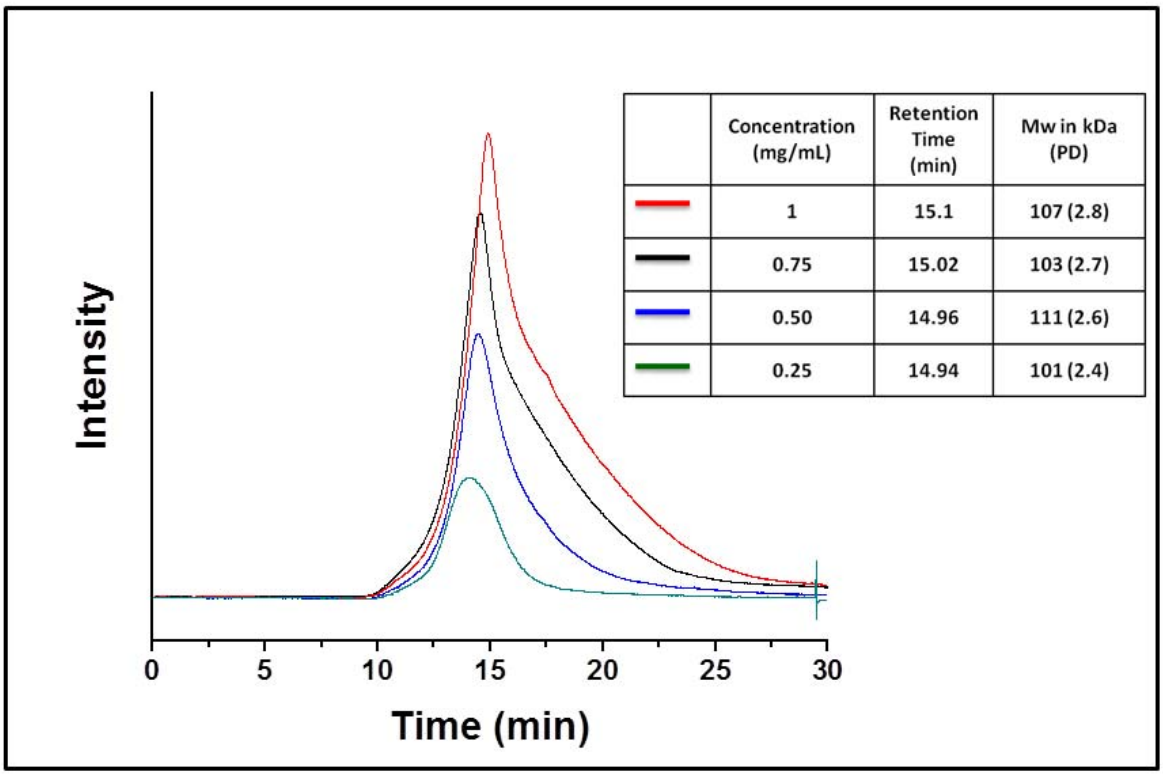

Figure S1. GPC traces of PProDOT-Hex_2 in chloroform as a function of concentration to prove that ultra high molecular weight nature of the polymer is not due to aggregation.

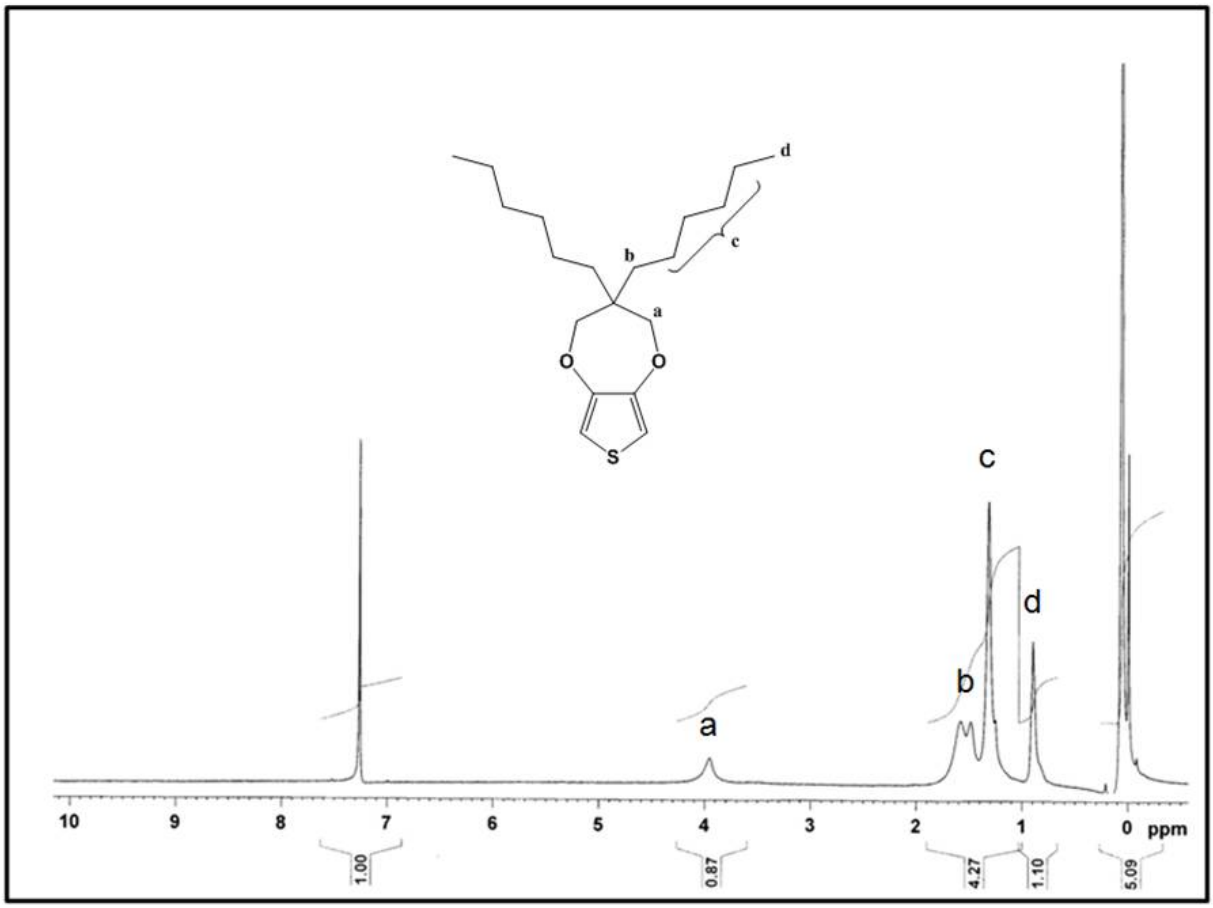

Figure S2. ^{1}H NMR Spectrum of PProDOT-Hex$_2$ in CDCl$_3$.

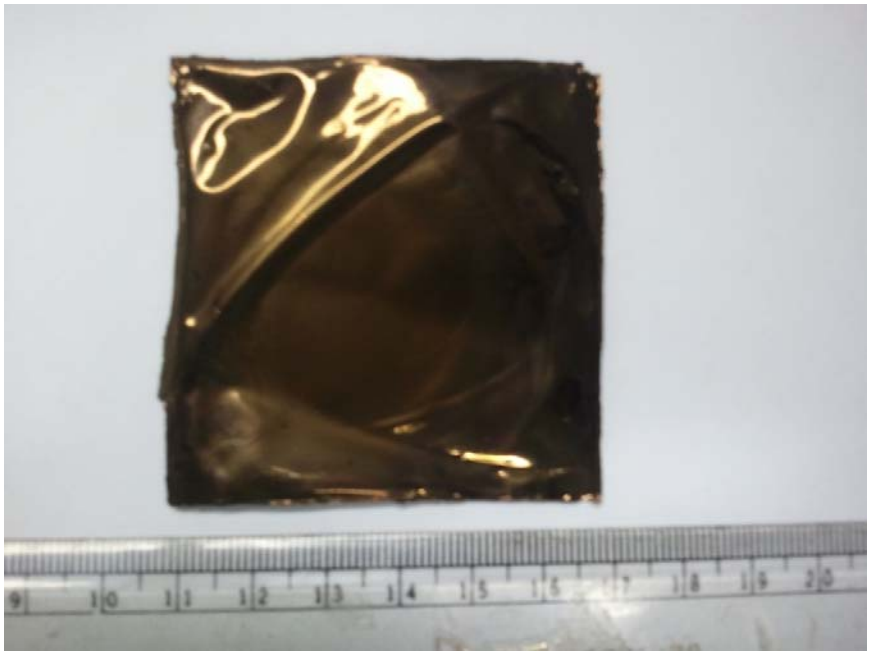

Figure S3. Free standing film (6 x 6 cm) of the PProDOT-Hex$_2$.

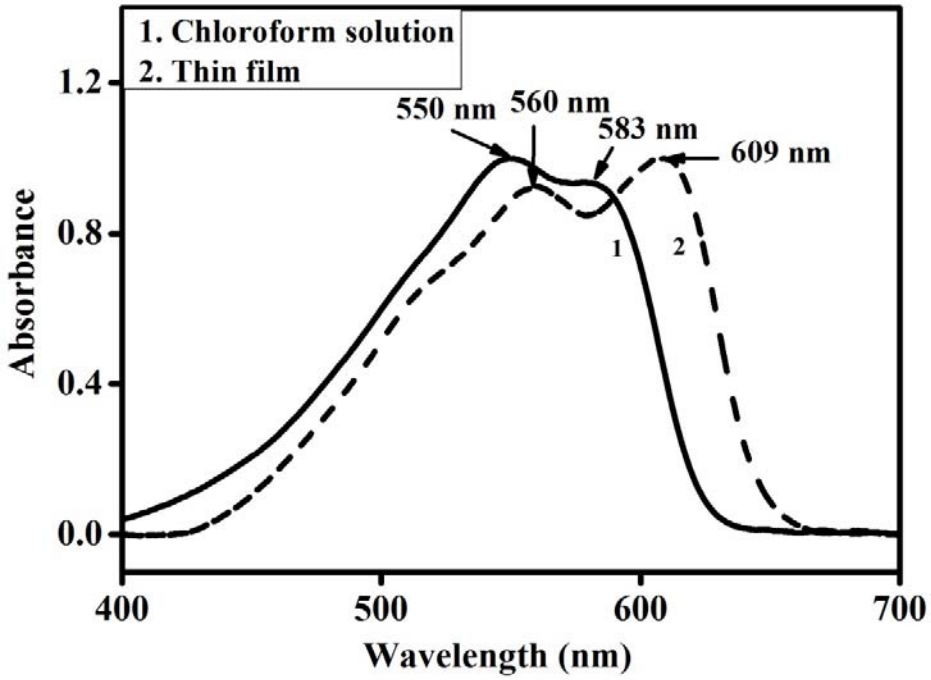

Figure S4. UV-vis spectrum of PProDOT-Hex$_2$ in chloroform solution and in thin film.

a)  b) 

Figure S5. Doped (a) and dedoped (b) PProDOT-Hex$_2$ as prepared by direct synthesis of thin film on glass substrate

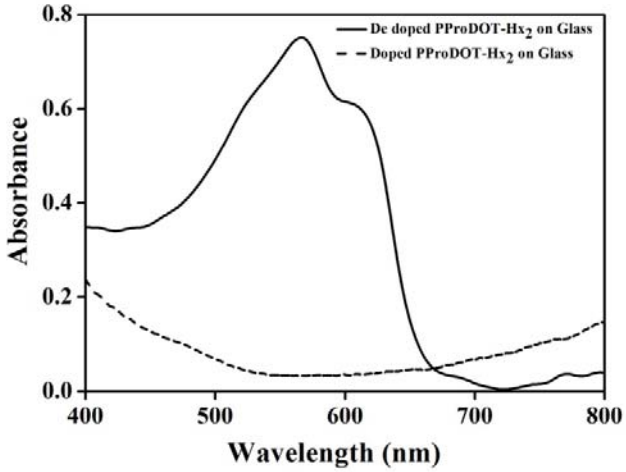

Figure S6. UV-vis spectrum of the doped and dedoped PProDOT-Hex$_2$ as prepared by direct synthesis of thin film on glass substrate.

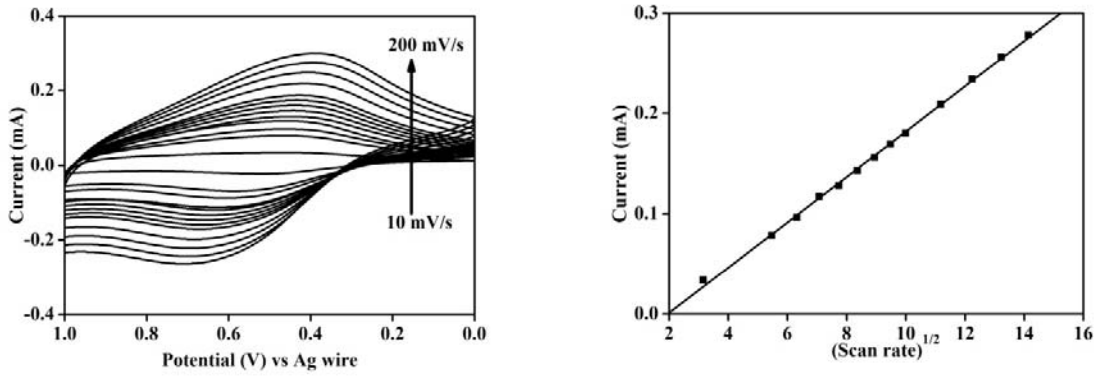

Figure S7. Cyclic Voltammogram as a function of scan rate and current vs square root of scan rate plots for PProDOT-Hex$_2$.

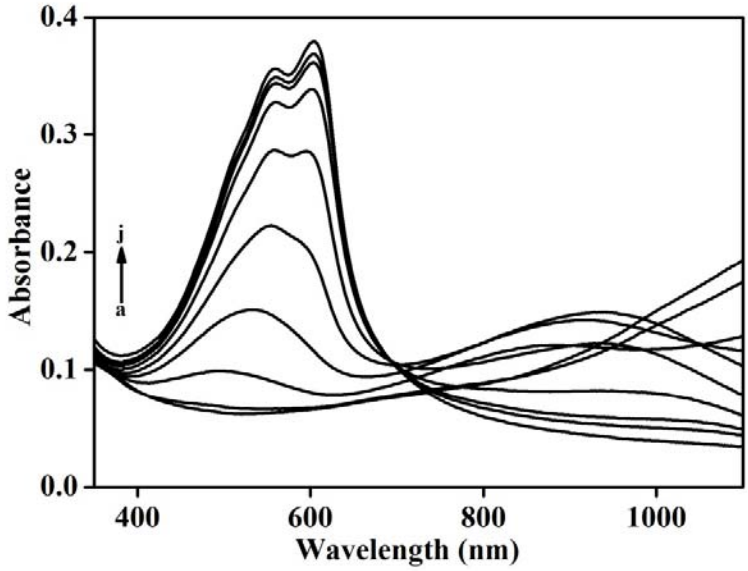

Figure S8. Spectroelectrochemical analysis of PProDOT-Hex$_2$: UV-vis-NIR spectra at a potential of 1 (a), 0.8 (b), 0.6 (c), 0.4 (d), 0.35 (e), 0.3 (f), 0.25 (g), 0.2 (h), 0.15 (i) and -1 (j) V versus Ag wire.