

Synthesis of Functionalized Polythiophene as a Potential Organic Semi-Conductor

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Abstract. The synthesis Poly[1,5-naphthyridine-(3-hexylthiophene)] (PN₃HTh) semi-conducting polymer has been accomplished by adopting both conventional and microwave-assisted Suzuki-Miyaura cross-coupling reaction between 3-hexylthiophene-2,5-diboronic ester and 2,6-dibromo-1,5-naphthyridine. The electrochemical and transport properties of PN₃HTh were investigated both in the bulk as well as in thin film form. These properties can be further tuned by changing the solvent and the nature of the electrode used. Consequently, cyclic voltammetry (CV) measurements were conducted using a potentiostat coupled with an electrochemical cell. The CV results of PN₃HTh as a bulk form in H₂SO₄ solution indicated that the concentration of the polymer in the solution is not well defined because of polymer poor solubility in aqueous solutions. On the other hand, the sulfur group which works as electron donating makes the system more electron-rich. This can explain by the absence of the reduction peak. For the thin film, two single oxidation peaks were obtained at around 0 V and 0.3 V for both cases. Different solvents can tune the transport properties of the polymer as can be seen from the two CVs where BF₃ exhibited enhanced transport properties over ACN. The synthesized polymers were characterized by modern spectroscopic methods including IR and NMR.

1 Introduction

During recent years, conjugated polymers and oligomers have been under intensive research and development as new functional materials for electronics [1-5]. These electronic polymers, inherently (or intrinsically) conductive polymers (ICPs) contain an extended π -conjugated organic backbone, rendering unique opto-electrical properties. The ICPs possess the electrical properties of metals or semiconductors while exhibiting the mechanical properties and processibilities of polymers. Applications of ICPs include, photonics, advanced coatings, electromagnetic-interference (EMI) shielding, light-emitting diodes (OLEDs), organic field effect-transistors (OFETs), and anti-corrosion coatings for iron and steel. Several classes of polyconjugated molecules of high molecular weight (polymers), and of relatively low molecular weight (oligomers), have been synthesized. Polythiophenes, polypyrroles and other polymers with heteroatoms in the polymer main chain are considered among the most important classes of heterocyclic polymers with extended n -conjugation [6-10]. The preparation of such polymeric materials often involves metal-catalyzed cross-coupling reactions, and frequently requires long reaction time to yield high-molecular-weight material.

Since the electronic properties of semiconducting polymers are often strongly molecular weight dependent, research to develop high molecular weight regioregular

polythiophenes (RPTs) have been a matter of great significance. There is an ever-increasing body of work, which shows that microwave heating is efficient in reducing reaction times and, consequently, increases reaction yields and reduces the amount of side products. The real advantage of microwave radiation is that it is generally 'quicker and cleaner' than conventional heating, reducing reaction times by more than a factor of 10 and yielding products in high yield with less side-products.

In this study, the synthesis of poly[1,5-naphthyridine-(3-hexylthiophene)] (PN₃HTh) semi-conducting polymer was accomplished by adopting both conventional and microwave-assisted Suzuki-Miyaura cross-coupling reaction between 3-hexylthiophene-2,5-diboronic ester and 2,6-dibromo-1,5-naphthyridine. The synthesized polymers were characterized by modern spectroscopic methods including IR and NMR. The electrochemical and transport properties of PN₃HTh were investigated both in the bulk as well as in thin film form.

2 Experimental work

Instrumentation: Melting Points were determined on a Büchi apparatus (Büchi Labortechnik AG, Switzerland) and are uncorrected. Elemental analysis was carried out on a Perkin Elmer Elemental Analyzer Series 11 Model 2400 (PerkinElmer Inc. USA). IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrophotometer (PerkinElmer Inc. USA). ¹H and ¹³C NMR spectra were

measured in CDCl_3 and d_6 -DMSO using TMS as internal standard on a JEOL JNM-LA 500 MHz spectrometer (JEOL USA Inc.). Mass spectra were recorded on Agilent Technologies 6890N GC-MS system (Agilent Technologies Inc. USA). Analytical TLC was carried out on silica gel 60 F254 plates (E. Merck); column chromatography was carried out on silica gel (200-400 mesh, E. Merck).

Synthesis of 6-Chloro-2-methyl-3-nitropyridine (2): To a solution of 6-methyl-5-nitropyridin-2-amine (20 g, 130.72 mmol) in water (330 ml) at 0°C was added sulfuric acid (23.6 ml) slowly followed by the dropwise addition of an ice-cold solution of sodium nitrite (12.0 g, 173.91 mmol) in water (30 ml). The resulting solution was allowed to react, with stirring, for 20 at 0°C and then allowed to warm to room temperature and stirred for an additional one hour. The resulting slurry was filtered and the solids collected by vacuum filtration to afford the title compound 6-Chloro-2-methyl-3-nitropyridine **2** as a brown solid [11].

Synthesis of 6-Methoxy-2-methyl-3-nitropyridine (3): A roundbottom flask was charged with a solution of 6-chloro-2-methyl-3-nitropyridine (12.0 g, 69.36 mmol) in methanol (100 ml). Sodium methanolate (5.6 g, 103.70 mmol) was added and the resulting solution was stirred at room temperature for 24 hours. The mixture was poured into 100 ml of water and the solids that formed were collected by filtration to afford the title compound as light yellow solid.

Synthesis of ethyl 3-(6-methoxy-3-nitropyridin-2-yl)-2-oxopropanoate (4): A roundbottom flask was charged with ethanol (54 ml). To this was added potassium (8.2 g, 0.21 mol) and mixture was stirred until all the potassium dissolved. Diethyl oxalate (30.6 g, 0.21 mol) was then added. The mixture was stirred for 5 minutes and then 6-methoxy-2-methyl-3-nitropyridine (32.0 g, 0.19 mol) was added. The resulting solution was stirred at room temperature for 36 hours. The slurry was filtered and the collected solids were washed thoroughly with ether and dried under reduced pressure. The solid was then suspended in 30 ml of water acetic acid was added until the pH - 4. The solids that formed were collected by filtration to afford the title compound as a light yellow gum.

Synthesis of 3-hydroxy-6-methoxy-3,4-dihydro-1,5-naphthyridin-2(1H)-one (5): A roundbottom flask was charged with a solution of ethyl 3-(6-methoxy-3-nitropyridin-2-yl)-2-oxopropanoate (3.73 mmol) in a solution of ethyl acetate (50 mL) and methanol (20 mL). The mixture was cooled to 0°C and a solution of sodium borohydride (0.5 mg, 0.01 mmol) in methanol (30 ml) was added. Aluminum trichloride (50 mg, 0.37 mmol) was then added and the resulting solution was stirred for 4 hours at 0°C . The reaction mixture was then quenched by the addition of ice water. The resulting solution was diluted with 100 ml of water and extracted two times with 100 ml of ethyl acetate. The combined organic layers were concentrated under reduced pressure to afford the ethyl 2-hydroxy-3-(6-methoxy-3-nitropyridin-2-yl)propanoate as a light yellow solid. A roundbottom flask was charged with a solution of ethyl 2-hydroxy-3-(6-methoxy-3-nitropyridin-2-yl)propanoate (37 mmol) in

methanol (500 ml). To the mixture was added 10% palladium on carbon (3 g). The solution was shaken under 40 psi of hydrogen for 12 hours. The resulting solution was then allowed to react, with stirring, for 5 hours while the temperature was maintained at room temperature. The mixture was then filtered and the filtrate was diluted with 100 ml of water. Hydrochloric acid was added until the pH = 5. The mixture was filtered and the filtrate was adjusted to pH = 8 by the addition of sodium carbonate. The solids that formed were collected by filtration to afford the title compound 3-hydroxy-6-methoxy-3,4-dihydro-1,5-naphthyridin-2(1H)-one **5** as a thick gum.

Synthesis of 2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-3-hexylthiophene (8): Under nitrogen atmosphere, n-Butyllithium (3.8 mL of a 2.5 M solution in hexane, 9.5 mmol) was slowly added to a solution of 2,5-dibromo-3-hexylthiophene (1.30 g, 4.0 mmol) in THF (30 mL) at -78°C and the mixture was stirred for 2 h at the same temperature. Afterward, 2-Isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (2.4 mL, 11.6 mmol) was promptly injected into the reaction mixture and the reaction was stirred for 1 h at -78°C followed by stirring continued overnight at room temperature. The mixture was poured onto ice-water and extracted with dichloromethane (50 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Column chromatography of the light orange oily material, using boric acid impregnated silica gel, eluting with acetate/hexane, 1/10, v/v) gave the title compound **8** as a colorless viscous oil (0.84 g, 50% yield). $^1\text{H-NMR}$ [500 MHz] (CDCl_3 , δ/ppm): 7.52 (s, 1H), 2.88 (t, 2H), 1.60 (m, 2H), 1.34 ~1.28 (m, 30H), and 0.88 (t, 3H). $^{13}\text{C-NMR}$ [500 MHz] (CDCl_3 , δ/ppm): 155.084, 139.592, 84.013, 83.583, 31.768, 31.669, 29.919, 28.978, 24.769, 22.598, and 14.130. FTIR: 3032 cm^{-1} (=C-H, m), 2922.5 cm^{-1} (-C-H,s), 1575.3 cm^{-1} (C=C, m), 1473.8 cm^{-1} (-CH₂, s), 1322.5 cm^{-1} (-CH₂, s), 1060 cm^{-1} (-C-O, m), 697 cm^{-1} (C-S, s).

Synthesis of Poly[1,5-naphthyridine-(3-hexylthiophene)] (9) by conventional method: Under an argon atmosphere, to a solution of compound **8** (0.25 g, 0.6 mmol), compound **9** (0.17 g, 0.6 mmol) in toluene (18 mL) was sequentially added Pd(PPh₃)₄ (70 mg, 0.06 mmol) and 2 M K₂CO₃ (3 mL). After bubbling argon through the solution for 2 minutes, the reaction mixture was at 90°C for 72 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (20 mL) and the organic layer was washed with water and then dried with Na₂SO₄. Evaporation of volatiles under reduced pressure yielded crude powder which was washed with methanol and acetone by Soxhlet extraction for a day. The obtained precipitate was collected to give dark green solids in a yield of (yield 89%). $^1\text{H-NMR}$ [500 MHz] (CDCl_3 , δ/ppm): 7.69 (aromatic, -CH=N), 7.55 (thiophene, -CH=C), 7.49 (aromatic, -CH=C), 2.66 (=C-CH₂-CH₂), 1.69 ((=C-CH₂-CH₂-CH₂), 1.33 ~1.26 (CH₂-CH₂-CH₂-CH₂-; -C-(CH₃)₂), and 0.90 (-CH₂-CH₃). FTIR: 3037 cm^{-1} (=C-H, m), 2995 cm^{-1} (-C-H, s), 1581 cm^{-1} (C=C, m), 1467 cm^{-1} (-CH₂, s), 1387 cm^{-1} (-CH₂, s), 697.6 cm^{-1} (C-S, s).

Synthesis of Poly[1,5-naphthyridine-(3-hexylthio-phenyl)] (9) by microwave assisted method: In a microwave tube, to a solution of mixture of compound **8** (0.1 g, 0.24 mmol), **6** (0.07 g, 0.24 mmol) in H₂O (2 mL) was added tetra-n-butylammonium bromide (0.18 g, 0.56 mmol) followed by the addition of Na₂CO₃ (0.06 g, 0.56 mmol). After the nitrogen gas was bubbled through the solution for two minutes, [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride (10 mol %) was added and the mixture was heated for 15 minutes at 80 °C at. The product was isolated by washing with methanol and decanting to get the desired **9** in 52% yield. ¹H-NMR and FTIR of the synthesized material were in full agreement with the previously synthesized material through conventional methods.

Raman Spectroscopy of Poly[1,5-naphthyridine-(3-hexylthio-phenyl)] (9): Raman spectra were recorded on HORIBA LabRam HR high resolution spectrometer with Ar⁺ polarized laser green line. To avoid thermal effects of the laser beam on the films, intensity was adjusted to an excitation power of 50 μW. The acquisition time is 400 s. Spectra fitting was done with LabSpec© software supplied with the apparatus.

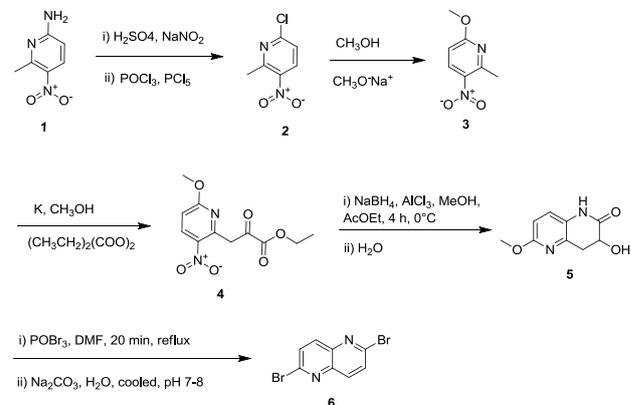
Field - Emission Scanning Electron Microscope (FESEM) of Poly[1,5-naphthyridine-(3-hexylthio-phenyl)] (9): The morphological and detailed microstructural attributes of the materials were discerned with the aid of Field Emission Dual Beam (Electron/ Focused Ion Beam) system, and that combines a high - end field - emission scanning electron microscope (FESEM) and a high - performance focused ion beam (FIB) system in one chamber (Tescan Lyra-3). Electron guns are used to produce a fine, controlled beam of electrons which are then focused at the specimen surface. The electron gun omits electrons from field-emission gun to produce the image and number of other characteristics.

Cyclic Voltammetry of Poly[1,5-naphthyridine-(3-hexylthio-phenyl)] (9): The electrochemical and transport properties of **9** were investigated both as a bulk form and as a thin film form. Therefore, CV measurements were conducted using a potentiostat / galvanostat coupled with an electrochemical cell. The supporting electrolyte was a 1.0 mol L⁻¹ sulfuric acid solution. The cell was composed of an Ag/AgCl as reference electrode, a glassy carbon electrode (GCE) as working electrode, and a platinum wire as counter electrode. The scan rate was fixed at 50 mV s⁻¹.

3 Results and discussion

The synthesis of polymer **9** necessitated the synthesis of monomer **6** which in turn was synthesized as outlined in scheme I. In short, reaction of pyridine **1** with a mixture of phosphoryl chloride and phosphorous pentachloride rendered the known **2** [11] in high yield. Displacement of the chloro group of **2** with a methoxy group, using sodium methoxide in methanol finished intermediate **3** which was in turn transformed to the desired **4** by the action of treatment with a base followed by condensation of the resultant carbanion with diethyl oxalate. Reduction of the nitro and carbonyl functions of intermediate **4** with

aluminium borohydride, generated in situ by the reaction of sodium borohydride and aluminium trichloride, followed by concomitant lactamization furnished **5** in good yield. The aromatization of **5** was ensued by the action of phosphoryl bromide in refluxing DMF to generate the desired **6** in good yield (Scheme I).



Scheme I. Synthesis of 2,6-dibromo-1,5-naphthyridine (**6**)

The characteristic FTIR, proton and carbon spectra of 2,6-Dibromo-1,5-naphthyridine (**6**) are given below in Figures 1–3.

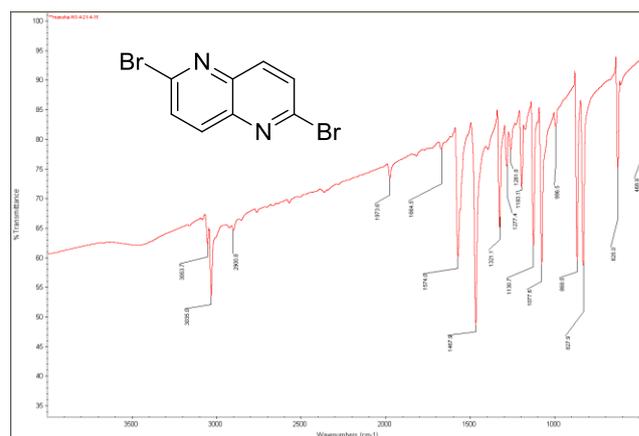


Figure 1. FTIR spectra of 2,6-Dibromo-1,5-naphthyridine (**6**)

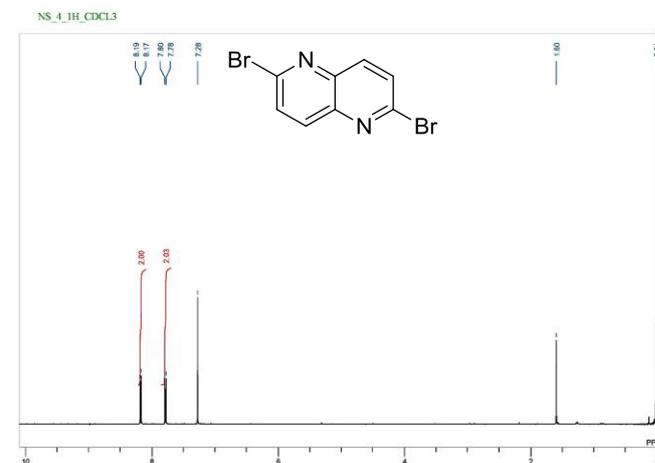


Figure 2. Proton NMR spectra of 2,6-Dibromo-1,5-naphthyridine (**6**)

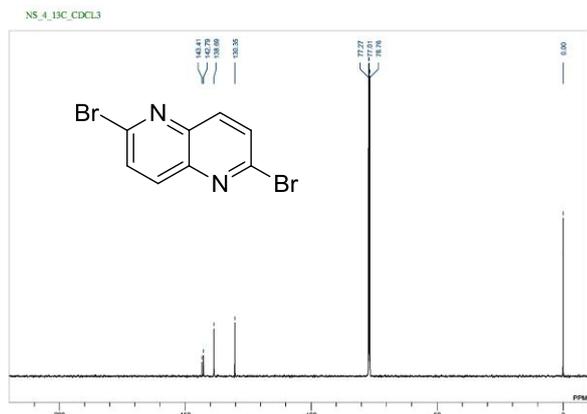
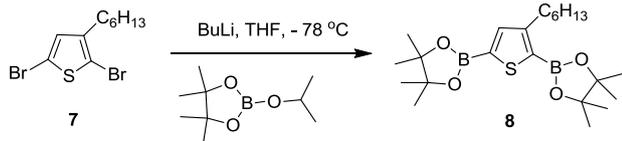
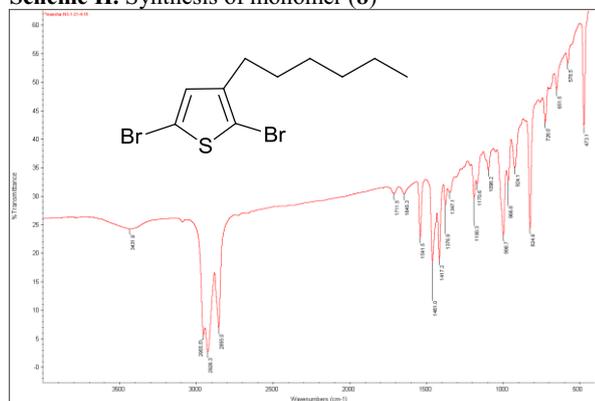


Figure 3. Carbon NMR spectra of 2,6-Dibromo-1,5-naphthyridine (6)

Having secured the synthesis of monomer **6** we next moved towards the synthesis of the monomer **8**. To this end, lithium bromine exchange of compound **7** at lower temperature followed quenching the anion with isopropoxy borolane gave monomer **8** in good yield (Scheme II). The characteristic FTIR, proton and carbon spectra of 2, 5-Dibromo-3-hexylthiophene (**7**) are given below in Figures 4–6.



Scheme II. Synthesis of monomer (**8**)



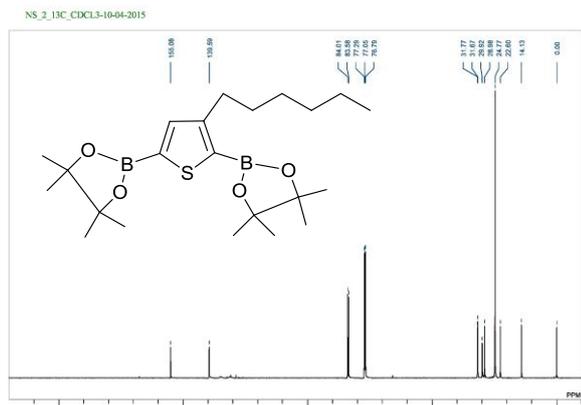
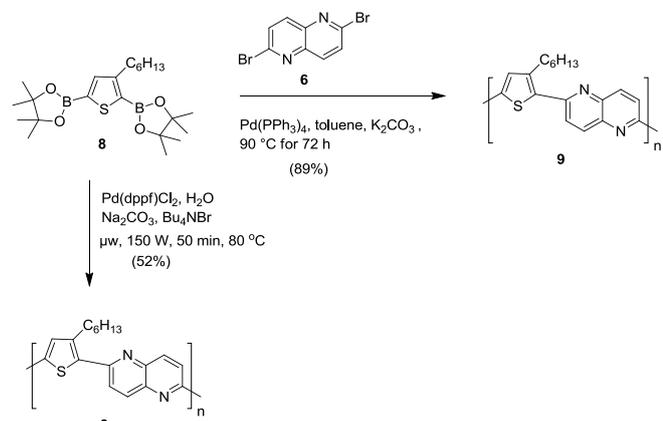


Figure 9. Carbon NMR spectra of 2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-3-hexylthiophene (8).

For the polymerization reaction we first tried microwave assisted polymerization by treating the monomers under microwave heating at 80 °C for 20 minutes, using 1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) dichloride as a catalyst. Unfortunately this reaction was very sluggish leading to several side products along with the desired polymer in a low yield. Another attempt towards the microwave assisted synthesis of polymer **9** was made when polymer bound catalyst Pd(OAc)₂-PEG was used. Unfortunately that was attempt was also not successful, leading to the formation of very little **9** in the reaction. Finally reaction of monomers **6** and **9** in water in a microwave reactor was tried where [1,1'-bis-(diphenylphosphino)-ferrocene]palladium(II) dichloride was used as a catalyst and tetra-*n*-butylammonium bromide as a phase transfer catalyst. [J. Org. Chem, Vol. 68, No. 14, 2003 5667]. This attempt was reasonably successful as the desired polymer **9** could be isolated in 52% yield (Scheme III).

Having not satisfactory synthesis from the microwave assisted approach, we next tried the synthesis of polymer **9** by using conventional method. Therefore, monomers **6** and **9** were treated under Suzuki-Miyaura conditions, using, 1'-bis(diphenylphosphino)ferrocene]-palladium(II) dichloride as a catalyst and K₂CO₃ as a base. The reaction yielded the desired polymer **9** in very high yield (89%) (Scheme III).



Scheme III. synthesis of Poly[1,5-naphthyridine-(3-hexylthiophene)] (**9**)

The characteristic FTIR and proton NMR spectra of Poly[1,5-naphthyridine-(3-hexylthiophene)] (**9**) are given below in Figures 10-11.

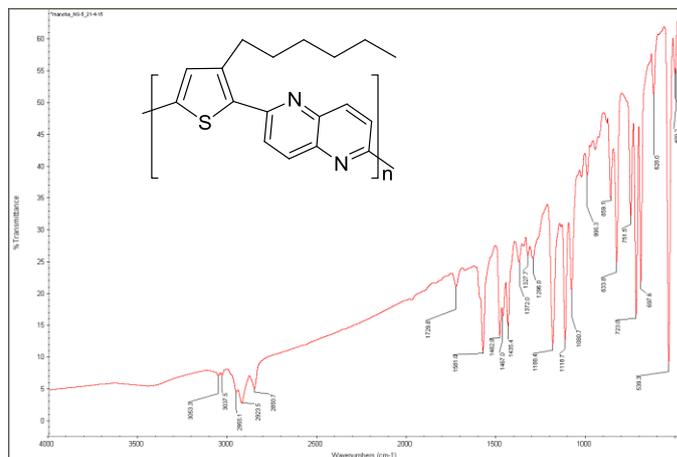


Figure 10. IR spectra of Poly[1,5-naphthyridine-(3-hexylthiophene)] (**9**).

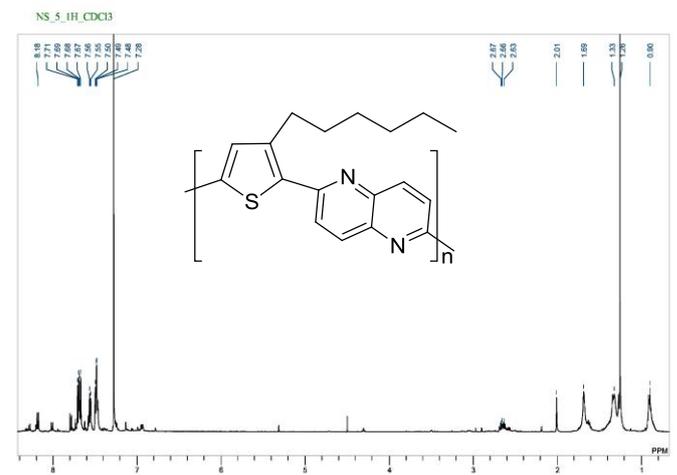


Figure 11. Proton NMR spectra of Poly[1,5-naphthyridine-(3-hexylthiophene)] (**9**).

Field emission scanning electron microscope (FESEM) was used to characterize the morphology and microstructure of the synthesized polymer. The FESEM confirms the uniform structure of the synthesized polymer, Poly[1,5-naphthyridine-(3-hexylthiophene)] (**9**), as shown in figures 12 a-c.

Raman spectrum of Poly[1,5-naphthyridine-(3-hexylthiophene)] is shown in Figure 13. The peaks corresponding to wave number 1465, 1369, and 1099 cm⁻¹ can be seen which corresponds to thiophene unit. The C-C bonding stretching peak at ~ 1272. C-N stretching causes some shifts in peak position. The band at 913 cm⁻¹ is due to the ring-breathing mode of the N=C bond. The bands at 1099 cm⁻¹ correspond to ring mode of C=N bond. The positions of these peaks are in good agreement with the adsorption of S-C, C=C and N=C surfaces reported in previous SERS work.

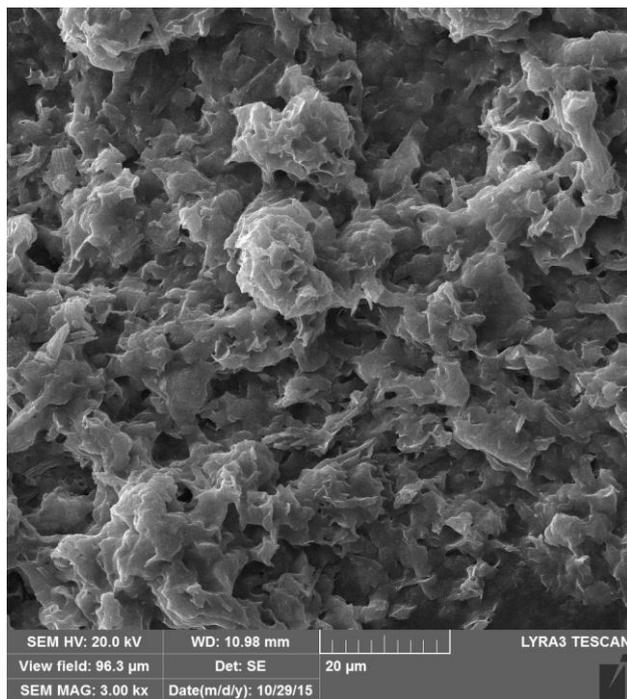


Figure 12-a. FESEM of Poly[1,5-naphthyridine-(3-hexylthiophene)] (9).

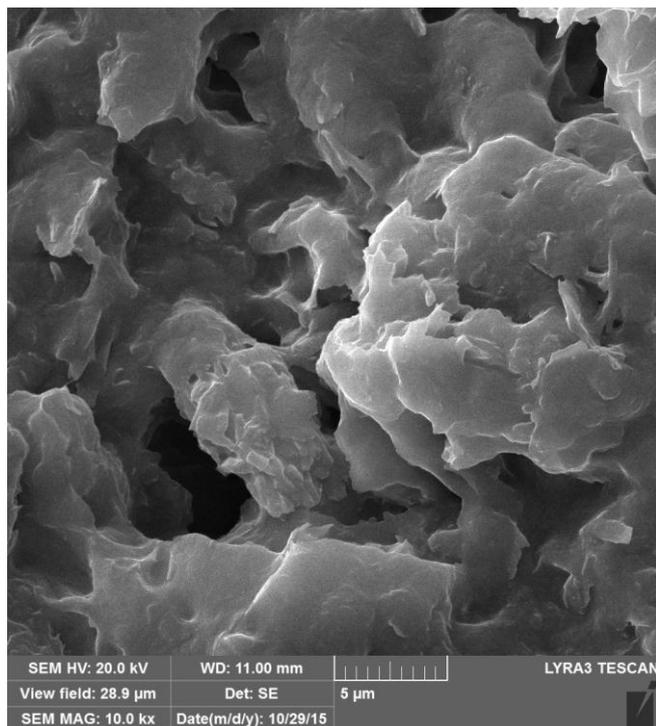


Figure 12-c. FESEM of Poly[1,5-naphthyridine-(3-hexylthiophene)] (9).

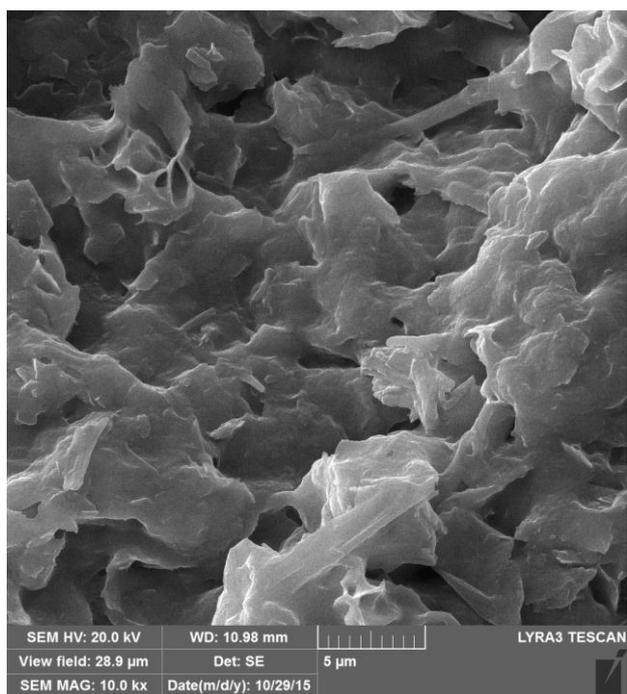


Figure 12-b. FESEM of Poly[1,5-naphthyridine-(3-hexylthiophene)] (9).

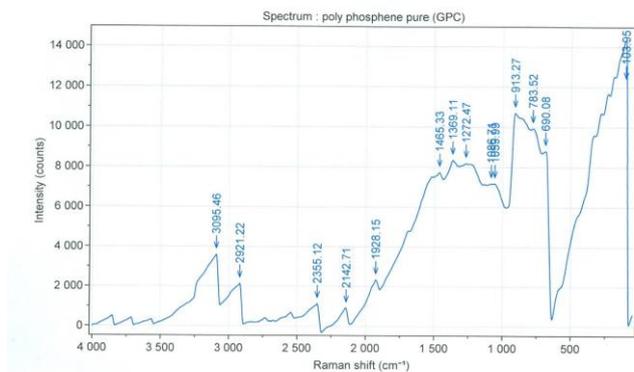


Figure 13. Raman spectra of Poly[1,5-naphthyridine-(3-hexylthiophene)] (9).

The cyclic voltammetry studies of polymer **9** are summarized in figures 14 and 15.

Figure 14 indicates CV results obtained for **9** as a bulk form in H₂SO₄ solution. The concentration of the polymer **9** in the solution was not well defined because the polymer had a low solubility in aqueous solutions. A well-defined oxidation peak at around 0.01 V is due to the slow transport of counter anions [1, 2]. The irreversible peak can be attributed to the conjugated system that has been disturbed by the lone pairs of the two nitrogen atoms. On the other hand, the sulfur acts as an electron donor which makes the system more electron-rich. This can also be explained due to the absence of the reduction peak.

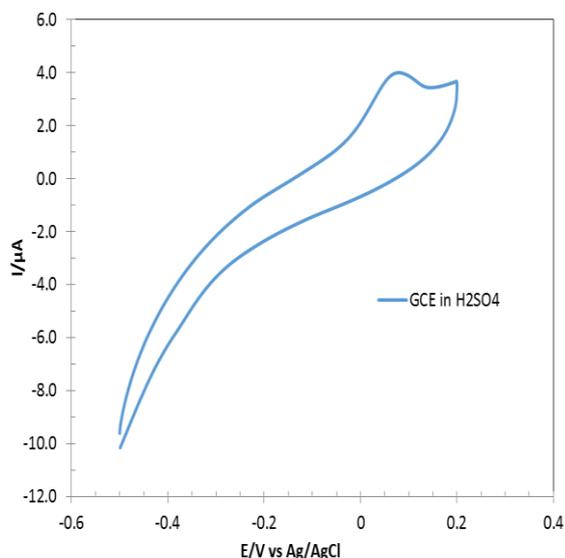


Figure 14. Cyclic voltammogram of PN₃HTh in 1.0 M H₂SO₄

Figure 15 shows the CV results obtained for polymer **9** as a thin film form in H₂SO₄ solution. The polymer was dissolved in acetonitrile (ACN) and boron trifluoride diethyl etherate (BF₃.OEt₂) before casting on a glassy carbon electrode. Two single oxidation peaks were obtained at around 0 V and 0.3 V for both cases. The potential scan started at -0.5 V and cycled to +0.5 V shows two-electron transport process which indicated the ability of p-doping. Different solvents can tune the transport properties of the polymer as can be seen from the two CVs where BF₃ exhibited enhanced transport properties over ACN.

It also showed electroactivity that can be improved further by addition/optimization of the functional groups on the skeleton of the polythiophenes structure. In order to make conjugated system at the same plane, the polythiophenes system should have structures where pi-electron can delocalized easily.

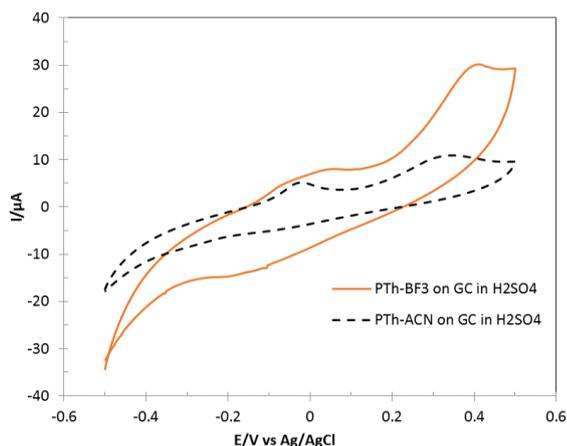


Figure 15. Cyclic voltammogram of PN₃HTh casted on GCE from BF₃ solution (solid line) and ACN solution (dash line) in 1.0 M H₂SO₄

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