Chapter 5

Phenazine Containing Poly(phenylene vinylene): Synthesis, Characterization and Application to Field Emission

Phenazine-containing poly(phenylene vinylene) (PHN-PPV) was synthesized using Wittig-Horner polycondensation of the appropriately designed monomers. This conjugated polymer has been explored for the application of field emission study. The design embraces the specific motivation of incorporating the nitrogen-containing heterocycle viz. phenazine in the polymeric backbone. PHN-PPV showed reversible redox properties. For PHN-PPV turn-on field for 1 µA/cm$^2$ was observed at 1.68 V/µm in the field emission measurements. The maximum current density of ~4.9 mA/cm$^2$ was achieved at the applied field of 3.6 V/µm. The emission current showed very good stability for 6 h at constant current of 1 µA.
5.1 Introduction

In recent years there has been a tremendous surge of research activity in the field of next generation device systems in view of the exacting demands of the emerging application sectors. In this field particular emphasis is being laid on light weight, flexible, multifunctional and low cost device platforms based on earth abundant materials.¹ Thus, the choice of material systems is as important as the novelty of the device concept or the corresponding architecture. Towards this end, several classes of materials such as elemental and compound semiconductors, metal oxides/sulfides/selenides, low dimensional carbon forms and other 2D inorganic and hybrid materials, as well as small molecules and polymers are being intensely researched.²⁻⁶ In this context, polymers stand out for their intrinsically light weight character, flexibility, low temperature processability, easy scalability, but perhaps most importantly, the ability afforded by the well established polymer synthesis methods to design them to meet a specific performance objective. In this work, we address the issue of field emission, which is central to many applications, especially the modern display systems capable of rendering good luminosity with lower electrical energy inputs; and explore whether a polymer system could be suitably designed to yield a good performance in this respect.

Field emission (FE) is also called as cold cathode emission, in which electrons are emitted in the presence of an applied electric field at the ambient temperature. The applied electric field causes band-bending leading to the formation of a triangular barrier near a tip feature of a material with locally highly intensified electric field causing electron tunneling (emission). Field emission display devices have the ability to provide flat-panel visual displays with upright picture quality at much lower power consumption and low cost than the conventional display systems; hence are regarded as energy saving devices. Since the realization of the significance of field emission displays, the materials used as cathodes in such architectures have evolved from metals to semiconductors to oxides/sulfides. Unfortunately, the volume of work on the use of polymers is rather limited thus far although some excellent papers have shown the promise of this class of materials in the field emission context.⁷⁻¹⁵
Use of specific micro-tipped array-like morphologies hold the key to high intensity emission at low applied potential between the electrodes because the electric field is highly enhanced at the tip. FE studies of carbon nanotubes, silicon nanowires, metal oxide nanowires and other forms of tapering morphologies like nanorods, nanotubes, nanoneedles etc. have been widely reported.\textsuperscript{16,17} Wide band gap, good electrical properties, low work function, low electron affinity etc. are the essential quality factors for the material to be applicable as a cathode for field emission. Conducting polymers satisfy several of these requirements and can thus be considered as potentially promising candidates for field emission. However, the consideration of long-term stability, which is based on the electrical, thermal and morphological property domains, is a more serious concern in so far as realistic application goals are concerned.

Pi-conjugated polymers have attracted tremendous attention of researchers in the wide range of areas like solar cell, organic light emitting diodes (OLED), organic field effect transistors (OFET), electromagnetic (EMI) interface shielding, etc. The attributes for this recognition lie in their properties like lightweight, film forming ability, flexibility, stability, relatively high conductivity, etc. Amongst the reported conjugated polymers till date, some conjugated polymers like polyaniline, polypyrrole, PEDOT, polythiophene and their composites with carbon nanostructures and other metal oxides have been synthesized in various ways with interesting morphologies and explored for the field emission application.\textsuperscript{18-31} The advantage of such polymers is that they can be synthesized to get specific morphologies like rods, arrays, fibers etc. Unfortunately, some of these materials are not solution processable and are therefore difficult to scale-up for flexible large area display panels. Conjugated polymers, which are solution processable are therefore regarded as technologically more desirable materials for the field emission application.\textsuperscript{17} Also, there have been reports on thin film cathodes consisting of nitrogen doped, chemical-vapour-deposited diamond films,\textsuperscript{32} and amorphous carbon films.\textsuperscript{33}

Poly(phenylene vinylene) (PPV) is a particular class of conjugated polymers, which shows high luminescence, good conductivity, film forming nature, and most importantly, good solubility in common organic solvents, rendering it to be solution processable. A range of PPV series of polymers has
been synthesized and modified till date for diverse end applications such as solar cells, OLEDs, OFETs, etc.

Herein, we have synthesized the PPV system with alkylated phenazine moiety. Phenazine is an important class of nitrogen containing hetero-cycle, which is known for decades for applications in chemical and biological sectors and such systems are widely used for various applications such as pharmaceuticals, agro-chemicals, pigments, dyes etc. It is a completely conjugated tricyclic molecule with pyrazine as a central ring. It is dibenzo annulated pyrazine. The fascinating structure of nitrogen containing stable ring makes researchers unfold its properties for other applications platforms. Furthermore, it has also been explored for OLEDs, solar cells (conjugated polymers and small molecules for DSSC), and sensing applications.

Herein, we report for the first time the insertion of reduced phenazine (dihydrophenazine) in the poly(phenylenevinylene) system. Phenazine containing poly(phenylenevinylene) shows film forming ability, good reversible oxidation-reduction properties, ambient condition stability, as well as adequate conductivity. These characteristic features are the key to the field emission properties.

5.2 Experimental

Materials:
Hydroquinone (Sigma Aldrich), potassium carbonate (Merck), 2-ethyl hexyl bromide (Sigma Aldrich), paraformaldehyde (Sigma Aldrich), HBr in acetic acid (Sigma), triethylphosphite (Spectrochem), phenazine (Sigma), sodium dithionite (Merck), 1-bromoocetane (Spectrochem), tetrabutyl ammonium bromide (TBAB) (Merck), phosphoryl chloride (Spectrochem), and potassium tertiary-butoxide solution (Sigma) were purchased from commercial sources and were used as received. Solvents were purchased from local sources and used after distillation. Reactions were carried out in oven-dried glassware under a positive pressure of argon atmosphere unless otherwise mentioned. Silica gel (Thomas Baker, 100–200 and 230–400 mesh) was used for column chromatography. Aluminium oxide (neutral) was procured from Spectrochem for column chromatography.
### 5.2.1 Synthesis

#### 5.2.1.1 Synthesis of 5,10-dihydrophenazine (1)

Into a 250 mL two-necked round-bottom flask, was dissolved phenazine (5.68 g, 31.5 mmol) in ethanol (120 mL) under argon atmosphere. The solution was refluxed for 30 min and then to this solution was added sodium dithionite (54.88 g, 31.5 mmol) dissolved in water at the same temperature. The color of the reaction mixture turned dark blue, and then precipitate formed in the reaction mixture. The reaction mixture was refluxed for additional 1 h and then cooled to room temperature. The precipitate was filtered, washed with water (300 mL), and dried in vacuum for 30 min. A light green solid was obtained (7.2 g) and was directly used for the next step because of its instability in air.

#### 5.2.1.2 Synthesis of [5,10-dioctyl-5,10-dihydrophenazine] (2)

Into a 250 mL round-bottom flask, was dissolved 5,10-dihydrophenazine (1) (7.2 g, 39.5 mmol) in dimethyl sulphoxide (~100 mL). To this solution, sodium hydroxide (4.74 g, 0.119 mol), tetra n-butyl ammonium bromide (0.76 g, 2.4 mmol), and 3 mL of water were added under argon atmosphere. The reaction mixture was stirred for 15 min., and then 1-bromooctane (13.65 mL, 79.0 mmol) was added drop-wise. The mixture was then heated at 40 °C for 4 h. After cooling to room temperature, the reaction mixture was poured into ice water (400 mL) and it was extracted with ethyl acetate (2 x 200 mL). The organic layer was washed with water (200 mL), saturated brine solution (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by neutral aluminium oxide chromatography using pet ether as an eluent to afford pure compound (2) (yield 11.0 g, 69 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta 0.91\) (t, 6H), 1.15-1.50 (m, 24H), 3.16 (broad s, 4H), 6.24 (s, 4H), 6.64 (s, 4H). \(^13\)C NMR (Benzene \(d_6\)): 137.93, 121.63, 111.45, 45.84, 32.53, 30.05, 27.54, 25.15, 23.41, 14.73.

#### 5.2.1.3 Synthesis of [5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde] (3)

Into a 100 mL round-bottom flask, 5,10-dioctyl-5,10-dihydrophenazine (2) (0.5 g, 1.22 mmol) was dissolved in freshly distilled N,N-dimethyl formamide (7 mL) under argon atmosphere at 0 °C. POCl\(_3\) (0.25 mL, 2.7 mmol) was added
drop-wise to the solution at the same temperature. The reaction mixture was stirred at 90 °C for 12 h, then cooled to room temperature and poured into ice water. The pH of reaction mixture was adjusted to 7 by adding dilute NaOH solution drop-wise. The color of the reaction mixture became red orange. The precipitate was filtered and dried in vacuo. The crude product was purified by column chromatography using pet ether: dichloromethane (50:50, v/v) to afford an orange solid (3) (yield 0.35 g, 61 %). $^1$H NMR (CDCl$_3$): $\delta$ 0.91 (t, 6H), 1.32-1.68 (m, 24H), 3.43 (t, 4H), 6.27 (d, 2H), 6.71 (d, 2H), 7.12 (d, 2H), 9.60 (s, 2H). $^{13}$C NMR (Benzene d$_6$): 189.25, 142.68, 135.95, 131.45, 130.10, 110.35, 108.80, 45.92, 32.49, 29.96, 29.80, 27.19, 25.01, 23.42, 14.73.

5.2.1.4 Synthesis of [1,4-bis((2-ethylhexyl)oxy)benzene] (4)
Into a three-necked 500 mL round bottom flask equipped with an addition funnel and a reflux condenser, were added activated K$_2$CO$_3$ (43.9 g, 0.317 mol) and hydroquinone (10 g, 0.09 mol). The mixture was evacuated and then purged with argon. Dry DMF (150 mL) was added to it and the mixture was stirred at 60 °C for 2 h. 2-Ethylhexyl bromide (48.45 mL, 0.27 mol) was added drop-wise through the addition funnel. After the completion of addition, the reaction mixture was refluxed for 12 h at 150 °C. After cooling, the reaction mixture was poured into ice water and the product was extracted with ethyl acetate (500 mL). The ethyl acetate solution was further washed with water (800 mL), separated and dried over anhydrous sodium sulfate. The organic phase was concentrated and the product was purified by column chromatography using pet ether: ethyl acetate 95:5 (v/v) to get colorless viscous liquid (4) (yield 25 g, 82 %). $^1$H NMR (CDCl$_3$): $\delta$ 0.94 (m, 12H), 1.31-1.56 (m, 16H), 1.76 (m, 2H), 3.80 (d, 4H), 6.84 (s, 4H).

5.2.1.5 Synthesis of [1,4-bis(bromomethyl)-2,5-bis((2-ethylhexyl)oxy)benzene] (5)
Into a two necked 250 mL round bottom flask equipped with a reflux condenser, a liquid addition funnel and a magnetic stirrer were added bis-1,4-(ethylhexyloxy) benzene (4) (5 g, 0.014 mol), paraformaldehyde (0.92 g, 0.03 mol) and glacial acetic acid (50 mL). The reaction mixture was stirred at room temperature for 30 min. HBr (33 wt % in acetic acid) (5.63 mL, 0.031 mol) was
added drop-wise to the reaction mixture. The reaction mixture was stirred at 70 °C for 8 h in the argon atmosphere. After cooling it to room temperature, the reaction mixture was poured into ice water to obtain a white precipitate. The precipitate was then filtered, washed several times using cold water and dried in vacuum. The crude product was purified by column chromatography (pet ether: ethyl acetate (1%)) (Yield 6.9 g, 88 %) \( ^1 \text{H} \) NMR (CDCl\(_3\)): \( \delta 0.96 \) (m, 12H), 1.32-1.56 (m, 16H), 1.76 (m, 2H), 3.88 (d, 4H), 4.53 (s, 4H), 6.86 (s, 2H).

5.2.1.6 Synthesis of [tetraethyl ((2,5-bis(2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene)bis(phosphonate)] (6)

Into a 100 mL single neck round bottom flask were added 1,4 bis(ethylhexyloxy)-2,5 dibromomethyle benzene (5) (1 g, 1.9 mmol) and triethylphosphite (1.6 mL, 0.0046 mol) at once. The reaction mixture was then stirred at 90 °C for 12 h under argon atmosphere. The excess triethylphosphite was removed by vacuum distillation to obtain oily viscous liquid. The product was purified by column chromatography using dichloromethane: methanol, 99:1 (v/v). (Yield 0.85 g, 85 %). \( ^1 \text{H} \) NMR (CDCl\(_3\)): \( \delta 0.92 \) (m, 12H), 1.23-1.52 (m, 28H), 1.71 (m, 2H), 3.19 (d, 4H), 3.81 (d, 4H), 4.01 (q, 8H), 6.94 (s, 2H). \( ^{13} \text{C} \) NMR (CDCl\(_3\)): 150.17, 114.42, 70.93, 61.55, 39.41, 30.33, 28.85, 27.05, 25.33, 23.64, 22.77, 16.07, 13.78, 10.88.

5.2.1.7 Synthesis of phenazine containing poly(phenylene vinylene) (PHN-PPV)

The Wittig-Horner polycondensation was carried out according to the reported protocol\(^{55}\) using potassium tertiary butoxide as a base. A dry two necked 50 mL round bottom flask was fitted with a rubber septum and an argon balloon. The mixture was purged with argon after addition of both the monomers viz. (3) (0.3 g, 0.64 mmol) and (6) (0.41 g, 0.64 mmol) followed by the addition of dry THF (25 mL) under argon atmosphere. Potassium tertiary butoxide solution (1.29 mL, 1M in THF, Sigma Aldrich) was added to the reaction mixture drop-wise with constant stirring. After completion of the addition, the reaction mixture was allowed to stir at room temperature for 4 h. The polymer was precipitated into the cold methanol (200 mL). The red colored precipitate was filtered and was subjected to successive washings of methanol (200 mL). The polymer was
purified by Soxhlet extraction method using the solvents methanol, acetone and chloroform. Yield = 0.4 g. $^1$H NMR (CDCl$_3$): $\delta$ 0.90-1.0 (CH$_3$), 1.26-1.81 (aliphatic CH$_2$), 3.41-3.95 (O-CH$_2$, N-CH$_2$), 6.24-7.06 (ArH). Molecular weight obtained by GPC (with respect to polystyrene standard): $M_n$ = 6.12 * 10$^3$, $M_w$ = 1.2 *10$^4$ and PDI = 1.7.

**PHN-PPV** is soluble in various organic solvents like chloroform, dichloromethane (DCM), toluene, benzene, dichlorobenzene.

### 5.2.2 Characterization

$^1$H NMR spectra were recorded on a Bruker-AV 500 MHz spectrometer in solvents as indicated with TMS as an internal standard. The chemical shift values are reported and the coupling constants ($J$) measured in Hz. The molecular weight and the molecular weight distribution was determined by Gel Permeation Chromatography (GPC) which was performed using Thermo Separation Products equipped with UV 100 and RI 150 detectors (Spectral Series) and chloroform as an eluent at a flow rate of 1 mL min$^{-1}$ at 25 °C. The concentration of the polymer sample used was 2 mg mL$^{-1}$ and polystyrenes with a narrow molecular weight distribution were used as the calibration standards. Thermogravimetric analysis (TGA) was accomplished using TGA-7 Perkin Elmer instrument. **PHN-PPV** sample weight taken was ~6 mg for TGA measurements. The film of polymer was characterized by using Field emission scanning electron microscope (FESEM) with FEI Nova nanoSEM 450 for structural and morphological analysis.

### 5.2.3 Preparation of the polymer film for field emission study using spray coating

![Figure 5.1: Polymer film preparation](image)
The polymer film, which was used as cathode for field emission study, was made on a clean single crystal n-Si substrate (Sigma Aldrich N-Silicon wafer (111)) by spray coating method. The polymer solution of 10 mg/mL in chloroform was used for the film formation. The spray gun (Airbrush set, single action, Paasche, USA) was used for the spray coating. The spray coated film was then subjected to vacuum annealing at 40 °C.

5.2.4 Field Emission Studies
The field emission (FE) measurements of PHN-PPV thin film on Si substrate prepared by spray pyrolysis were carried out in an all-metal field emission microscope (FEM) system equipped with load lock facility. The metal FEM system was evacuated to ultra high vacuum (UHV) employing a set of vacuum pumps: a turbo molecular pump backed by a rotary pump, a sputter ion pump, and titanium sublimation pump with liquid nitrogen cooled jacket. The FE studies were performed at the base pressure of \( \sim 1 \times 10^{-8} \) mbar. The FE measurements were carried out in 'planar diode' (also termed as 'close proximity') configuration. In a typical experiment, the cathode (PHN-PPV film on Si substrate) was pasted onto a stainless steel stub (diameter \( \sim 30 \) mm) using UHV compatible silver paste. A semitransparent cathodoluminescent phosphor screen (an anode) connected to a high precision linear motion drive was held parallel to the cathode. The cathode anode separation was maintained at 2500 \( \mu \)m for all the experiments. For measurements of the emission current as a function of the applied voltage, a Keithley 485 Picoammeter and a Spellman high voltage DC power supply were used. Special care was taken to avoid any leakage current using shielded cables with proper grounding.

5.3 Results and Discussion
5.3.1 Polymer Design and Synthesis
As stated above, in this work we have synthesized phenazine containing poly(phenylenevinylene) with the incorporation of 5,10-dialkyl-substituted dihydrophenazine viz. poly(5,10-octyl- dihydrophenazine)-phenylenevinylene (PHN-PPV). The long alkyl chains were introduced in order to achieve the solubility in organic solvents. The alkyl chain substituted 5,10-dihydrophenazine
has the strong electron donating ability and hence it has been used as an electron donor in many organic charge transfer crystals.\textsuperscript{56} This electron donor property motivated us to select phenazine. Highly electron-rich and redox-active compounds are valuable building blocks in material science.\textsuperscript{57} 5,10-Dihydrophenazine systems are attractive as they satisfy such conditions. Due to presence of two tertiary nitrogens, this system is a good redox active system. As 5,10-dialkyl-substituted dihydrophenazine system opens up many possibilities to tune the design, we decided to introduce this moiety into the polymer.

\textbf{Scheme 5.1} represents the synthesis of monomers and \textbf{Scheme 5.2} depicts the synthesis of phenazine containing poly(phenylenevinylene). Phenazine was reduced using sodium dithionate followed by N-alkylation.\textsuperscript{54} The N-alkylated phenazine was then treated with DMF and POCl\textsubscript{3} to get 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde (3).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme_5.1.png}
\caption{Synthesis of monomers (3) and (6)}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme_5.2.png}
\caption{Synthesis of PHN-PPV}
\end{figure}
On the other hand; hydroquinone was subjected to O-alkylation reaction followed by bromomethylation to yield 1,4-bis(bromomethyl)-2,5-bis(2-ethylhexyl)oxy)benzene (5). Compound (5) was then reacted to thriethylphosphite to get tetraethyl ((2,5-bis (2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene)) bis (phosphonate) (6)\(^{58,59}\).

**PHN-PPV** is a polymer formed by the condensation of 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde moiety (3) and the tetraethyl ((2,5-bis ((2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene)) bis (phosphonate) (6), synthesized by Wittig-Horner polycondensation reaction. Using potassium tert. butoxide as the base for Wittig-Horner polycondensation of (3) and (6), yielded red colored **PHN-PPV**, which was purified by re-precipitation followed by Soxhlet extraction method.

### 5.3.2 \(^1\)H NMR Spectra of Monomers

\(^1\)H spectrum of 5,10-dioctyl-5,10-dihydrophenazine is shown in the **Figure 5.2**. In the \(^1\)H spectrum of 5,10-dioctyl-5,10-dihydrophenazine, the broad singlet is appeared at 3.16 \(\delta\) ppm due to the four protons next to nitrogen confirming the N-alkylation. The remaining alkyl chain protons are appeared at 0.9 - 1.5 \(\delta\) ppm.

The aromatic protons are of two types as the molecule is symmetric and they appeared as two separate broad peaks at 6.64 \(\delta\) ppm and 6.24 \(\delta\) ppm.

**Figure 5.3** represents the \(^1\)H spectrum of 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde. In the \(^1\)H spectrum of 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde, the appearance of the singlet at 9.60 \(\delta\) ppm due to two aldehyde protons. Due to the presence of aldehyde group, the aromatic protons appeared at 6.26 \(\delta\) ppm, 6.72 \(\delta\) ppm, 7.10 \(\delta\) ppm.
Figure 5.2: $^1$H spectrum of 5,10-dioctyl-5,10-dihydrophenazine (in benzene d$_6$)

Figure 5.3: $^1$H NMR spectrum of 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde recorded in CDCl$_3$
Figure 5.4 depicts the $^1$H NMR spectrum of tetraethyl ((2,5-bis((2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene))bis(phosphonate. In the spectrum, singlet was appeared at 6.94 δ ppm due to two aromatic protons. Quintet appeared at 4.01 δ ppm due to $\text{CH}_2$ of phosphonate group. Also, peak at 1.23 δ ppm appeared due to $\text{CH}_3$ of phosphonate.

Figure 5.4: $^1$H NMR spectrum of tetraethyl ((2,5-bis((2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene))bis(phosphonate) recorded in CDCl$_3$

5.3.3 $^{13}$C NMR Spectra of Monomer (3)

Figures 5.5 and 5.6 represent $^{13}$C NMR spectra of 5,10-dioctyl-5,10-dihydrophenazine and 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde recorded in benzene d$_6$. The peaks are in good agreement with the respective structures.
Figure 5.5: $^{13}$C spectrum of 5,10-dioctyl-5,10-dihydrophenazine recorded in Benzene $d_6$

Figure 5.6: $^{13}$C NMR spectrum of 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde recorded in Benzene $d_6$
5.3.4 MALDI Characterization of Monomers (3) and (6)

Figure 5.7 shows the MALDI spectrum of monomer (3) - 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde. The peak at m/z of 463 characterizes the monomer (3) mass value.

Figure 5.7: MALDI spectrum of monomer (3) 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde.

Figure 5.8 represents MALDI spectrum of monomer (6)- tetraethyl ((2,5-bis((2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene))bis(phosphonate). The peak at 635 m/z value signifies mass value of monomer (6).
Figure 5.8: MALDI spectrum of monomer (6) - tetraethyl ((2,5-bis((2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene))bis(phosphonate)

5.3.5 NMR Spectrum of PHN-PPV

Figure 5.9 shows $^1$H NMR spectrum polymer PHN-PPV. For the polymer the spectral lines appeared broader. A small peak at 9.69 δ ppm appeared due to presence of aldehyde end group of the polymer. The peaks at 3.86 δ ppm and 3.14 δ ppm are due to $-\text{OCH}_2$ and $-\text{NCH}_2$, respectively. The doublet at 7.89 δ ppm was attributed to vinylic protons of PHN-PPV ($-\text{CH}=$CH-) and coupling constant of 16 Hz confirmed the trans configuration of PHN-PPV.
Figure 5.9: $^1$H NMR spectrum polymer PHN-PPV

5.3.6 UV-Vis and Photoluminescence Spectroscopy

Figure 5.10 (a) represents UV visible spectrum of PHN-PPV solution in chloroform. The spectrum clearly reveals that the polymer absorbs in the visible range. The absorption maximum peak at 490 nm is broad in nature with the absorption band edge at 600 nm. The peak appearing at lower wavelength (330 nm) is due to $\pi-\pi^*$ transitions in the conjugated polymer.

Figure 5.10: (a) UV visible spectrum of the PHN-PPV polymer in chloroform solution, (b) Photoluminescence spectrum of PHN-PPV polymer in chloroform solution.
The photoluminescence of the polymer solution in chloroform was recorded which is shown in Figure 5.10 (b). The broad PL was observed with the emission peak at 623 nm when the polymer solution was excited at its maximum absorption value i.e. 490 nm.

### 5.3.7 Electrochemical Properties

To understand the energy levels of the polymer, cyclic voltammetry (CV) study was performed, the result of which is indicated in Figure 5.8.

![Figure 5.11: Cyclic voltammetry for PHN-PPV at the scan rate of 100 mV/s](image)

The CV was recorded at the scan rate of 100 mV/s using ferrocene as the internal standard. From the CV it is clear that polymer shows reversible oxidation-reduction nature. The oxidation onset potential value, which is 0.15 V, was used for the calculation of HOMO. The HOMO level value was turned out to be -4.19 eV. The band gap was calculated from the UV-Vis spectrum and it turned out to be 2.5 eV. The oxidation potential in the polymer may correlate with the concept of work function in the case of metals or semiconductors. The lower work function is one of the prerequisite for the field emission application, as it is directly relevant to the value of the turn-on voltage of the field emission device. As stated in the introduction, wide band gap, good electrical properties, low work function, low electron affinity etc. are important parameters to take into consideration. The data indicate that PHN-PPV fulfills these requirements at satisfactory level. The lower oxidation onsets and reversible redox properties with wide band gap of 2.5 eV, indicated that PHN-PPV could be a potentially useful candidate for field emission device.
5.3.8 Thermogravimetric analysis (TGA)

The thermogravimetric analysis was performed on the sample at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TG) curve of PHN-PPV is shown in Figure 5.12. The T$_{10}$ value is found to be 373 °C indicating its good thermal stability.

5.3.9 Theoretical Studies

To acquire extra insight into the electronic structure, theoretical calculations of repeating unit of PHN-PPV were implemented by density functional theory (DFT) with the Gaussian 09 program at B3LYP/6-311 G* level. DFT calculations clearly revealed that the electron density of HOMO is distinctly distributed over 5,10-dioctyl-5,10-dihydrophenazine moiety in the polymer backbone. This implies that the 5,10-dioctyl-5,10-dihydrophenazine moiety is acting as a strong donor. The HOMO value obtained from this theoretical calculation was -4.3 eV, which is close to the experimental value (-4.2 eV). The LUMO was shown to spread over the phenylenevinylene part of the polymer caused by the absence of any strong accepter group into the polymer. Moreover, the band gap of 2.8 eV was obtained by the DFT calculations while the experimental optical band gap observed was 2.5 eV.

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**Figure 5.12:** TG curve of PHN-PPV in the nitrogen atmosphere
Figure 5.13: HOMO and LUMO levels of the monomer of PHN-PPV

5.3.10 Mott-Schottky and Conductivity Measurements

To interpret whether the polymer exhibit p-type or n-type nature, the Mott-Schottky experiment was performed (Figure 5.14 (a)) in 1 M H$_2$SO$_4$ with three-electrode system, in which Ag/AgCl was used as the reference electrode and the carbon as counter electrode.

PHN-PPV film coated on n-silicon substrate made the working electrode. Mott-Schottky measurements were performed at the frequency of 10 KHz. The nature of the slope signifies that PHN-PPV is p-type. The flat band potential estimated from the intercept on the X-axis of the linear portion of Mott-Schottky plot is 0.058 V.

Figure 5.14: (a) Mott-Schottky measurements, (b) AC conductivity measurements
The conductivity of PHN-PPV was measured using frequency dependent (AC) conductivity measurements; the corresponding data is shown in Figure 5.14(b). The freestanding 0.11 mm thick polymer film was cast and it was directly placed in-between the silver/aluminium electrodes for the electrical conductivity measurements. The conductivity decreases from higher to lower frequency range, which is common for the semiconducting conjugated polymers.

### 5.3.11 Field Emission Studies

For a planar emitter comprised of a thin film of nanostructures deposited on flat substrate, the modified Fowler – Nordheim F-N equation\(^60\) is given as,

\[
J = \lambda_M \alpha \phi^{-1} E^2 \beta^2 \exp \left( -\frac{b \phi^2}{\beta E} \nu_F \right) \quad \ldots \ldots \ldots (1)
\]

Where, \(J\) is the emission current density obtained for the applied electric field \(E\), \(\lambda_M\) pre-exponential correction factor, \(\beta\) represents local electric field enhancement factor, \(a\) and \(b\) are constants having values \((1.54 \times 10^{-6} \text{ A eV V}^{-2})\) and \((6.83 \text{ eV}^{-3/2} \text{ Vnm}^{-1})\) respectively, \(\nu_F\) (correction factor) is a particular value of the principal Schottky-Nordheim barrier function \(\nu\), and \(\phi\) is the work function of the emitter material. The value of HOMO is observed to be \(~ -4.2\) eV.

**Figure 5.15 (a)** depicts the plot of emission current density \((J)\) versus applied electric field \((E)\). The values of the onset and threshold fields, corresponding to emission current densities of 10 \(\mu\)A/cm\(^2\) and 1 mA/cm\(^2\) are observed to be 1.93 and 2.88 V/\(\mu\)m, respectively. The J-E curve exhibits exponential behavior indicating that the emission is due to tunneling of electrons through the deformed potential barrier. Interestingly, a maximum current density of \(~4.9\) mA/cm\(^2\) could be drawn from the emitter at an applied field of 3.6 V/\(\mu\)m.

The field emission characteristics were further analyzed by plotting a graph of \(\ln (J/E^2)\) versus \((1/E)\), known as the Fowler-Nordheim (F-N) plot, shown in **Figure 5.15 (b)**. The F-N plot of PHN-PPV/Si emitter exhibited overall linear behavior, over the entire range of applied electric field values. Numerous reports can be found in which field enhancement factor \(\beta\) has been calculated from the
slope of the F-N plot. It has been observed that \( \beta \) value is overestimated for multi-tip emitter. An attempt to estimate local field \( (E_{\text{local}} = \beta E_{\text{av}}) \) using the \( \beta \) value calculated from F-N plot results in very high magnitude than that required for field emission. Therefore, in this case, we have not estimated the value of \( \beta \) from the F-N plot analysis.

**Figure 5.15:** (a) Emission Current density versus applied electric field \((J-E)\) plot, (b) F-N plot.

From the practical application point of view, emission current stability is very important and a decisive parameter. The emission current-time (I-t) stability recorded at a pre-set value of 1 \( \mu \)A over the duration of 6 h is shown in **Figure 5.16.** The emission current exhibits good stability characterized with some excursions superimposed with 'spike' type fluctuations. Instantaneous variations in the ‘local’ work function, or the ‘local’ electric field that lead to fluctuations in the emission current \( I \). The variation in the ‘local’ work function occurs due to field-induced adsorption, migration and desorption of residual gas species. Also the continuous ion bombardment over several hours changes the local radius of curvature (geometrical factor, \( \beta \)) and hence the strength of the ‘local’ electric field during the emission current stability tests. In the case of a multi-tip emitter in thin film form the fluctuation in \( I \) arises due to combined effect of both these processes.

In fact due to very high aspect ratio of the nanostructures, the constant ion bombardment of the nanostructure can alter the local radii of curvature significantly, thereby causing even ‘extinction’ and/or ‘generation’ of emission
sites. The concurrent ‘appearance’ and ‘disappearance’ of ‘emission spots’ observed in the phosphor screen image supports this argument.

**Figure 5.16:** Stability of the field emitter over the duration of 6 hrs.

### 5.3.12 Field Emission Scanning Electron Microscopy (FESEM)

**Figure 5.17:** SEM images of the film before (a) and after (b) the FE measurement.

We have also recorded FESEM images of the films before and after field emission experiment in order to see whether the surface morphology of the emitter sustains the ion bombardment induced effects (**Figure 5.17 (a-b)**). It is observed that the spray-coated film is deposited quite uniformly on the Si-substrate and post field emission experiment the SEM image does not show any
noticeable change in the surface morphology of the emitter. This clearly indicates its mechanical robustness against the ion bombardment.

5. 3.13 Field Emission Images

Figure 5.18 depicts the field emission images recorded at different applied voltages (corresponding to different emission current densities). All the FE images show the presence of very tiny bright spots, indicating a large number of emission sites. The increase in the number of spots along with their respective intensities with increase in the applied voltage is quite obvious. For such a multi-tip emitter, intensity as well as the emission current from the prevailing emitters also increases making them brighter.

Figure 5.18: Field emission images

The promising FE behavior of the PHN-PPV/Si emitter can be attributed to its nanometric dimensions and moderate electrical conductivity. The lower oxidation potential (~ 0.2 V) lowers the field required to eject the electron from the material. In case of inorganic materials (metals/semiconductors) the FE properties are decided by the work function value. By altering the surface morphology of the polymer emitter, the FE characteristics can be further improved. The synthesis plays important role in the modification of the polymeric systems that could potentially be used as FE material. Incorporation
of electron rich moieties in the material can improve FE properties as it mainly depends on the ejection of electron to the vacuum.

It is further useful to point out that the observed values of applied electric fields corresponding to the onset, threshold and maximum current density in the case of our polymeric system are comparable with those reported for various conducting polymer nanostructures and their nanocomposites. Table 5.1 depicts the comparative performance of different planar emitters comprising of conducting polymers and their composites.

**Table 5.1**: Turn on field and maximum current density values of the different conducting polymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Turn on field V/µm</th>
<th>Max. Current Density</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHN-PPV</td>
<td>1.93 (10 µA/cm²)</td>
<td>4.9 mA/cm² (3.6 V/µm)</td>
<td>Present studies</td>
</tr>
<tr>
<td>PEDOT-co-T34bT</td>
<td>1.83 (10 µA/cm²)</td>
<td>4 mA/cm² (3.6 V/µm)</td>
<td>20</td>
</tr>
<tr>
<td>PEDOT-DBSA</td>
<td>~3.5 – 4 (10 µA/cm²)</td>
<td>100 µA/cm² (~4.5 V/µm)</td>
<td>18</td>
</tr>
<tr>
<td>PANI nanofibrils</td>
<td>~3 – 5 (10 µA/cm²)</td>
<td>5 mA/cm² (27 V/µm)</td>
<td>8</td>
</tr>
<tr>
<td>PANI/HClO₄</td>
<td>5.5 (~1 µA/cm²)</td>
<td>~5 µA/cm² (~6 V/µm)</td>
<td>14</td>
</tr>
<tr>
<td>PPy/TBAPF₆</td>
<td>~3.5 – 4 (~1 µA/cm²)</td>
<td>50 µA/cm² (~6 V/µm)</td>
<td>14</td>
</tr>
</tbody>
</table>

**5.4 Conclusions**

We have successfully designed and synthesized two monomers viz. 5,10-dioctyl-5,10-dihydrophenazine-2,7-dicarbaldehyde and tetraethyl ((2,5-bis((2-ethylhexyl) oxy)-1,4 phenylene) bis(methylene))bis(phosphonate. The monomers were characterized fully and the Wittig - Horner polycondensation was performed in order to achieve a conjugated polymer <i>viz</i> phenazine.
containing poly(phenylene vinylene) (PHN-PPV). PHN-PPV exhibited M_n of 6 *10^3 and PDI of 1.7. PHN-PPV showed lower oxidation potential of ~ 0.2 V and redox properties indicating its suitability as an emitter in the filed emission studies. PHN-PPV demonstrated acceptable field emission behavior. The lower turn on voltage of 1.68 V/µm was observed for 1 µA/cm^2. The maximum current density measured was of ~4.9 mA/cm^2 for the applied filed of 3.6 V/µm. Also, the polymer was found to be stable up to 6 h at constant current of 1 µA. Thus, PHN-PPV is a welcome addition to the family of polymeric emitter materials available for practical field emission applications.
References


2. Organic Nanomaterials: Synthesis, Characterization, and Device Applications By Tomas Torres, Giovanni Bottari, John Wiley & Sons, 05-Aug-2013,


