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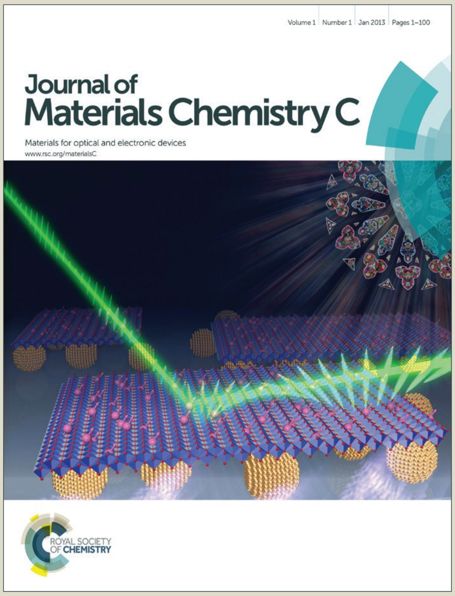

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ARTICLE

Synthesis, characterization and diode application of poly(4-(1-(2-phenylhydrazono)ethyl)phenol)

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Poly(phenoxy-ketimine)s, which have conjugated bond system, are a family of polyphenols and can be prepared by oxidative polycondensation reaction from a monomer containing both hydroxyl (-OH) and ketimine side groups. In this context, a novel poly(phenoxy-ketimine), poly(4-(1-(2-phenylhydrazono)ethyl)phenol) abbreviated as poly(4-PHEP), including a system of conjugated bonds and active hydroxyl groups, were synthesized and spectroscopically characterized by elemental analysis, FTIR (fourier transform infrared), NMR (nuclear magnetic resonance) absorption and fluorescence spectroscopy techniques. Optical band gap of the polymer is determined as 3.05 eV. In addition, electrical conductivity, solubility and thermal properties of poly(4-PHEP) were determined. Its electrical conductivity was found to be ~8.55×10^{-2} S/cm, which was the typical level for semiconductors. Afterwards, polymer/p-type Si junction device was fabricated and its rectifying behaviours, depending on some parameters including ideality factor, barrier height and series resistance values at room temperature, were examined by current-voltage(*I*–*V*) and capacitance-voltage(*C*-*V*) measurements. Consequently, these interesting properties of the polymer reveal that it would have potentially beneficial applications in various fields of electronics as semiconducting materials.

Introduction

Semiconductors are main components of electronic technology. While electronic and optoelectronic technology are developing rapidly, they demand new materials for popular devices. Hence, new semiconducting materials having superior quality are needed to satisfy arising requirements in device applications. Compared to conventional inorganic counterparts, organic semiconducting materials suggest various benefits, for instance, tuning properties via chemical synthesis, flexibility and solution processing in electronic applications. Furthermore, organic electronics are tremendously growing due to their low cost, lightweight and large area coverage by non-vacuum fabrication techniques compared to conventional inorganic counterparts.[1, 2] Hence, organic semiconductors have caught great attention from technological and scientific points of view. Conjugated polymers with semiconducting behaviour emerged as favourable alternative to inorganic electronic technology. In fact, conjugated semiconducting polymers constitute organic functional electronic materials that are employed in several plastic electronics/optoelectronics such as sensors, organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic solar cells, organic spintronics and so on.[3-6] Due to the fact that semiconducting performance of these polymers in device applications demands various properties, different polymers are designed and synthesized for novel electronic devices. Schottky diodes or heterojunctions, which have an important role in electronic technology, are the simplest structures of metal-semiconductor contacts.[7] A metal-semiconductor junction is formed by contacting a metal and semiconductor on a suitable substrate.[8] In current concept, polyphenols are the conjugated semiconducting polymers, which can be utilized as a semiconductor material.[9] Another class of conjugated polymers related to the polyphenols is namely poly(phenoxy-imine) and poly(phenoxy-ketimine), which have imine and ketimine groups in pendant groups, respectively (Scheme 1).

The conjugated poly(phenoxy-ketimine)s can be considered as simple derivatives of the corresponding poly(phenoxy-imine)s, in which the hydrogen atom of the azomethine group is replaced by an alkyl (R) group. Generally, polyphenols, obtained by oxidative polycondensation depending on different phenoxy-imine compounds, possess a

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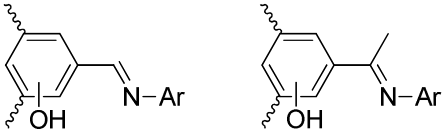
specific conductivity between 10^{-7}-10^{-13}S/cm at 20°C,[10, 11] which are typical levels for dielectrics. Therefore, many researchers have studied to enhance the conductivity of poly(phenoxy-imine)s and their conductivities were increased up to ~10^{-5}S/cm by iodine doping.[12] It has been reported that semiconducting properties of the polyphenols obtained by oxidative polycondensation of phenoxy-imines are enhanced by increasing the π-conjugation with the participation of extra nitrogen atoms in polymer pendent groups.[13] However, there are no simultaneous studies on the semiconducting properties and capacitive characteristics of poly(phenoxy-ketimine)s. In this regard, the synthesis of semiconducting polymers with higher level of semiconductivity by oxidative polycondensation is of interest.



(a) (b)

Scheme 1 The structures of poly(phenoxy-imine)s (a) and poly(phenoxy-ketimine)s (b)

In the present study, we report the synthetic routes, spectroscopic and semiconducting properties of the novel polymer with ketimine pendent group including extra nitrogen atoms namely poly(4-(1-(2-phenylhydrazono)ethyl)phenol, hereafter poly(4-PHEP). Conductivity, electrochemical and thermal properties of the newly synthesized compounds were determined and compared to the results given in the literature.[10-12] Poly(4-PHEP)/p-type Si junction device was fabricated by spin coating technique, and its rectifying behaviour at room temperature was examined by *I–V* and *C-V* measurements. Thus, the semiconducting properties of a poly(phenoxy-ketimine) have been put forward with this study for the first time.

Experimental

Materials

Several chemicals, including *p*-hydroxyacetophenone, phenylhydrazine, sodium hypochlorite (NaOCl) (11%), hydrogen peroxide (H_2O_2) (30%), hydrochloric acid (HCl) (37%), sulphuric acid (H_2SO_4) (98%), potassium hydroxide (KOH), silver nitrate ($AgNO_3$), diethyl ether, dichloromethane (CH_2Cl_2), ethanol, ethyl acetate, acetone, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), methanol, chloroform ($CHCl_3$), *n*-hexane, and acetonitrile were purchased from Merck Schuchardt OHG (Hohenbrunn, Germany). All of these chemicals were used without further purification.

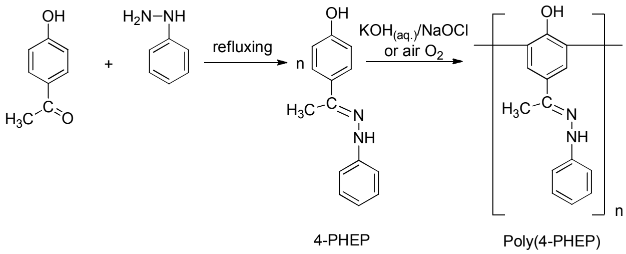
Synthesis

Preparation of 4-(1-(2-phenylhydrazono)ethyl)phenol (4-PHEP). The monomer was prepared by a standard condensation method.[14] Briefly, the solutions of phenylhydrazine (1.08 g, 10 mmol) in ethanol (2 mL) and *p*-hydroxyacetophenone (1.36 g, 10 mmol) in ethanol (3 mL) were mixed and stirred for ~5 hour at room temperature (Scheme 2). The reaction's progress was monitored by thin layer chromatography (TLC) technique until the starting material was all consumed. At the end of the reaction, distilled water (2 mL) was added to the reaction mixture. The precipitated product was filtered and washed with cold ethanol. The purity was confirmed by silica plates and melting point determination.

4-PHEP: Yield: 98%. R_f : 0.52 (SiO_2, *n*-hexane/ethyl acetate, v/v, 3:1). Melting point: 147°C. ^{1}H-NMR (600 MHz, DMSO-d_6, δ, ppm): 9.55 (1H, s, O$\underline{H}$), 9.03 (1H, s, N$\underline{H}$), 7.63 (2H, d, Ar$\underline{H}$), 7.19 (4H, d, Ar$\underline{H}$), 6.78 (2H, d, Ar$\underline{H}$), 6.72 (1H, dd, Ar$\underline{H}$), 2.19 (3H, s, C$\underline{H_3}$). FTIR (υ_{max}/1/cm): 3447 (O–H), 3370 (N–H), 3030 (C–H aryl), 2933-2860 (C–H aliphatic), 1598 (C=N), 1499-1445 (C=C), 1252 (C–N), 1177 (C–O), 1075 (N–N). Elemental analysis for $C_{14}H_{14}N_2O$: Theoretical mol/mol ratio C/N=6.00; C/H=11.91, found mol/mol ratio C/N=6.08; C/H=11.17.

The polymerization of 4-PHEP. 4-PHEP polymerization was carried out as described in the literature.[15] Oxidative polycondensation of phenol and substituted phenols are generally performed in a 50 mL three-necked glass flask equipped with a magnetic stirrer, a temperature control unit, a thermometer and a reflux condenser. In the experiments of oxidative polycondensation of phenol with atmospheric oxygen, an air inlet tube is attached. Before it was used in oxidative polycondensation, air was passed through 20% aqueous KOH (200 mL) to remove CO_2.

The flask was charged under stirring with aqueous solution of KOH (0.14 g, 2.5 mmol, 10%), and 0.56 g (2.5 mmol) 4-PHEP and it was heated to the required temperature. Then, air was bubbled in a rate of 0.25 L/h to 1 L/h. After the reaction was completed, the mixture was neutralized with HCl (1.0 M, 0.5 mL). The precipitate was filtered, thoroughly washed with hot distilled water (25 mL, three times) to remove inorganic salts, and thoroughly treated with diethyl ether (7 mL) to remove the unreacted 4-PHEP. Then the dark brown coloured powder product was dried at 105°C in a vacuum oven for about 24 h (Scheme 2). Oxidative polycondensation of 4-PHEP with 11% aqueous NaOCl and the subsequent work-up were performed similarly.



Scheme 2 The synthesis route of 4-PHEP and poly(4-PHEP)

Poly(4-PHEP): Yield: 65%. R_f : 0 (SiO_2, *n*-hexane/ethyl acetate, v/v, 3:1) and R_f : 0.85 (SiO_2, methanol). ^{1}H-NMR (600 MHz, DMSO-d_6, δ, ppm): 11.52-8.86 (2H, bs, O$\underline{H}$ and N$\underline{H}$), 8.45-6.09 (7H, m, Ar-$\underline{H}$), 2.53-1.10 (3H, bs, C$\underline{H_3}$). FTIR (υ_{max}/1/cm): 3435 (O–H), 3272 (N–H), 3066 (C–H aryl), 2921-2850 (C–H aliphatic), 1598 (C=N), 1501-1437 (C=C), 1252 (C-N), 1173 (C–O), 1071 (N–N). Elemental analysis for $C_{14}H_{12}N_2O$: Theoretical mol/mol ratio C/N=6.00; C/H=13.91, found mol/mol ratio C/N=5.98; C/H=13.49.

Characterization

Elemental analysis. Elemental analysis was accomplished on a LECO CHNS-932 (LECO Corporation, St Joseph, MI, USA).

FTIR spectra. FTIR spectra of the samples were measured by using a Perkin-Elmer FTIR Spectrum one (Perkin-Elmer, Llantrisant, UK) equipped with universal attenuated total reflectance sampling accessories (4000-450 cm^{-1}) whose brand is Pike GladiATR (Madison, WI, USA).

^{1}H-NMR spectra. NMR spectra were recorded by using ^{1}H-NMR spectra (Bruker ASCEND-600 NMR) at 25°C in DMSO via tetramethylsilane as an internal standard.

GPC analysis. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by Gel Permeation Chromatography-Light Scattering (GPC-LS) device of Malvern Viscotek GPC Dual 270 max. The GPC measurement was investigated by dual columns with 300 mm length and 8.00 mm in diameter. Addition1 g/L of lithium bromide in DMF (1 mL/min) was used as solvent. Light scattering (LS) detector and a refractive index detector (RID) were used to analyse the polymer at 55°C.[16]

Conductivity measurements. Electrical properties of the polymer were determined by four-point probe technique at room temperature and under atmospheric pressure using Four Point probe Measuring System FPP 470. The pellets were pressed on hydraulic press developing up to 100 bar/cm^2.

Excitation and fluorescence measurements. Excitation and fluorescence spectra of the samples in DMF were taken by Shimadzu RF-5301 PC Spectrofluorophotometer. To calculate the fluorescence lifetimes, fluorescence decays of the samples in DMF were recorded by using a Laser Strobe Model TM-3 lifetime fluorometer from Photon Technology International.[17] All spectroscopic measurements were executed by using a quartz cuvette of 1.0 cm^2.

Thermal analysis. Thermogravimetric analysis (TGA), derivative thermo gravimetric (DTG) and differential thermal analysis (DTA) of the materials were performed under nitrogen flow (100 mL/min) with a Perkin-Elmer Diamond Thermal Analyzer, heating from 20°C to 1000°C at a rate of 10°C/min.

Experimental procedure for heterojunction and diode applications. Common RCA1 and RCA2 chemical procedures have been used to remove the contamination of p-type Si surface.[18] To prepare a device, thermal evaporation technique was used to form ohmic contact by evaporating Al (Al has 5 N purity and it has been etched in diluted HCl (HCl/H_2O, v/v, 1:10)) on the back side of p-type Si at 10^{-5} Torr, and subsequently Si/Al has been annealed at 580°C for 3 minutes in N_2 atmosphere. Then, the polymeric samples in DMF were coated on the other side of p-type Si by spin-coating technique. Finally, Au has been evaporated on polymer at 10^{-5} Torr as the measurement electrode. The *I–V* and *C-V* measurements of the junction were performed by using Keithley 487 Picoammeter/Voltage Source and HP 4192A LF Impedance Analyzer, respectively. Measurements were depicted in Figure S3 (see Supplementary Information) and performed in dark and at room temperature.

Results and discussion

Synthesis conditions of the polymer

The oxidative polycondensation of 4-PHEP was investigated in various media such as neutral, acidic and alkaline aqueous solutions. Under ambient conditions in neutral and acidic aqueous solutions, 4-PHEP is not oxidized with atmospheric oxygen and NaOCl. However, the addition of an alkali immediately caused red-brown coloration, suggesting the oxidation of 4-PHEP to the corresponding phenoxyl radical.

The effects of reaction parameters, such as the initial concentrations of KOH and NaOCl, the flow rates of air oxygen, reaction time and temperature, on the yield of oxidative polycondensation products were also examined. According to these results, desired product yield was 65% under the optimum reaction conditions: $[\text{4-PHEP}]_0=[KOH]_0=[NaOCl]_0=$ 0.26 mol/L at 50°C for 24 h. Replacement of NaOCl with atmospheric oxygen, under equal other conditions, decreases the polymerization yield (43%). The optimum reaction conditions with atmospheric oxygen were obtained as $[\text{4-PHEP}]_0=0.26$ mol/L, $[KOH]_0=0.26$ mol/L, flow rate of air oxygen=0.5 L/h at 50°C for 24 h. In brief, the yield of the polymer was dependent on temperature, time, initial concentrations, and type of oxidant. Comparing the obtained data, NaOCl was observed to be more active than air (O_2) for the synthesis of the polymer.

Characterization of the Synthesized Compounds

FTIR spectra. The polyphenols obtained by the oxidative polycondensation of phenol and its derivatives had a structure consisting of a mixture of phenylene and oxyphenylene units.[19, 20] In the current study, structures of the synthesized compounds were analysed by FTIR and ^{1}H-NMR spectroscopies.

In the comparison of the FTIR spectra of 4-PHEP and poly(4-PHEP), the differences were observed in the reduction of band strength and peak numbers (Fig. 1).

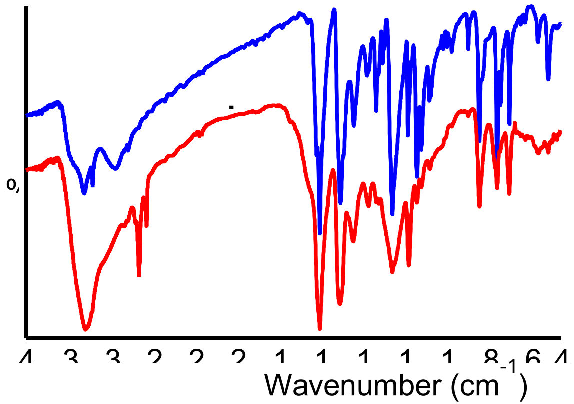
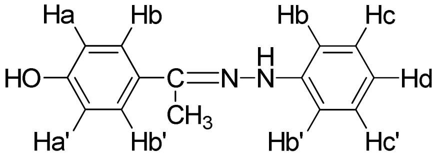


Fig. 1 FTIR spectra of 4-PHEP (a) and poly(4-PHEP) (b)

In the FTIR spectrum of poly(4-PHEP), the peak at 1598 cm^{-1} was assigned to the characteristic absorption of C=N vibration. A broad peak centred at 3435 cm^{-1} was due to the vibration of the O-H linkage of the phenolic group, and a peak at 3272 cm^{-1} was attributed to the strength vibrations of the N-H linkage. Since no additional peaks at 1100-1250 cm^{-1} for C-O-C linkages were observed in FTIR spectrum of the polymer, it was clearly observed that poly(4-PHEP) consists of phenylene units in accordance with the reported value in the literature.[21, 22]

In addition, polyphenols obtained by the oxidative polycondensation of phenol and its derivatives showed a small peak at ~1660 cm^{-1}, which was attributed to the carbonyl (C=O) stretching vibration due to the oxidation of the imines groups at the polymer pendent groups.[23, 24] In the FTIR spectrum of the synthesized polymer, a peak originated from the carbonyl group could not be detected. Moreover, the peaks at 650-900 cm^{-1} correspond to different substitution patterns in the aromatic ring.[25, 26] In the FTIR spectrum of 4-PHEP, the peaks at 694 and 752 cm^{-1} showed the presence of five adjacent aromatic hydrogen atoms of the benzyl ring. This means that the oxidative polycondensation leaves the monomer core intact.

^{1}H-NMR spectra. ^{1}H-NMR spectra of the 4-PHEP and its polymer were given in Fig. 2. In the NMR spectrum of poly(4-PHEP), the signals were shown broadly and it was one of the proofs for polymerization. The signals in the 8.80-11.50 ppm range presented the protons of the hydroxy proton (O<u>H</u>) and secondary amine proton (N<u>H</u>) groups. The broad multiplet signals centred at 7.30 ppm could be attributed to the aromatic protons (Ar-<u>H</u>). FTIR and ^{1}H-NMR results show the formation of polymeric macromolecules from the 4-PHEP residue via polymerization on H_a *and* H_a' positions (Scheme 3). This suggests that the polymerization proceeds primarily through *ortho-ortho* coupling.



Scheme 3 The phenyl C-H groups of 4-PHEP

GPC analysis. GPC analysis chromatograms of poly(4-PHEP) were given in Figures S1 and S2 (see Supplementary Information). Molecular weight distribution parameters of poly(4-PHEP) were calculated according to a PMMA standard calibration curve. M_n, M_w and PDI values of poly(4-PHEP) were found to be 40650, 85230, and 2.096, respectively, for NaOCl oxidant. In the case of atmospheric oxygen oxidant, M_n, M_w and PDI values of poly(4-PHEP) were found to be 73850, 122500, and 1.659, respectively. According to total values, synthesized polyphenol had high molecular weights. These results confirmed the polymeric structure of poly(4-PHEP) and showed that poly(4-PHEP) had higher M_n and M_w values than poly(phenoxy-ketimine)s with similar structure such as poly(3-PHEP).[27]

Thus, our data on the composition, structure and chemical properties of 4-PHEP polymers are compatible with the published data on the mechanism and products of oxidative polycondensation of hydroaromatic compounds[28] suggest that the poly(phenoxy-ketimine) prepared by oxidative polycondensation of 4-PHEP mainly consist of phenylene units as seen from Scheme 2.

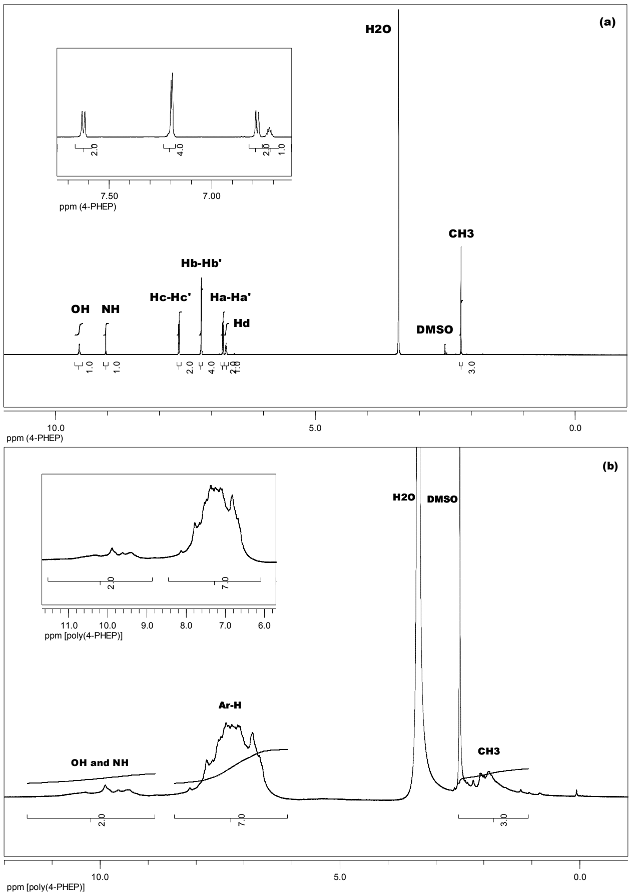


Fig. 2 ^{1}H-NMR spectra of 4-PHEP (a) and poly(4-PHEP) (b)

Properties of the synthesized compounds

Absorption and Fluorescence properties of poly(4-PHEP). Energy dependent absorption coefficient is given in Tauc equation;[29]

$$(\alpha h\nu)^n = A(h\nu - E_G) \qquad (1)$$

where α, ν, h, and A are the absorption coefficient, frequency of light, Planck's constant and optical constant, respectively. The value of exponent n denotes the type of the band gap. Regarding a direct band gap, a plot of $(\alpha h\nu)^2$ versus hν has a linear region with slope A and its extrapolation to the abscissa yields the optical band gap value of the sample. The inset of Fig. 3 shows Tauc plot. By extrapolating this behaviour to the abscissa, one can be able to determine the direct optical band gap which is around 3.05 eV. Semiconductors possessing 3 eV or higher band gap values are generally considered as wide band gap semiconductors. Due to emitting visible colour range, they are promising materials for optoelectronic applications like solid state lightening.

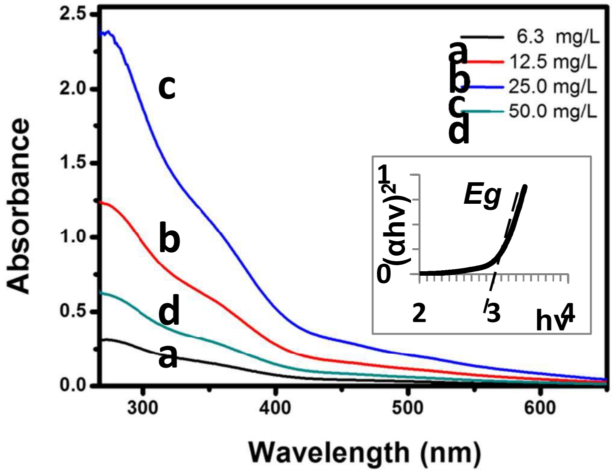


Fig. 3 UV spectra of poly(4-PHEP) and Tauc plot

Fluorescence properties of poly(4-PHEP) in DMF were investigated at room temperature. In order to analyse the effect of the polymer concentration on its fluorescence property, the fluorescence spectra of the polymer were taken at various concentrations. The concentration of poly(4-PHEP) from 200.0 mg/L to 6.3 mg/L in DMF were gradually altered, and then their spectroscopic measurements were done. Fig. 4 presented the excitation and fluorescence spectra of poly(4-PHEP) in DMF.

In the excitation spectra (Fig. 4a), a wide excitation band appeared at the range of 260 nm-400 nm, and its shape and relative intensity were changed by increasing the amount of polymer in DMF. As seen from Fig. 4b, the intensity of fluorescence were dependent on the concentration of poly(4-PHEP), which the strong fluorescence at ~430 nm was observed from the diluted concentration of poly(4-PHEP) in DMF. The fluorescence maximum of poly(4-PHEP) was red-shifted from ~430 nm to ~465 nm, and its fluorescence intensity was noticeably quenched when its concentration reached up to 200 mg/L. This could be attributed to π-π stacking poly(4-PHEP) molecules in DMF by increasing the concentration of polymer. Additionally, we evaluated the fluorescence lifetime of poly(4-PHEP) in DMF at diluted polymer concentration (6.3 mg/L). To measure the fluorescence lifetime of poly(4-PHEP) in DMF, fluorescence decay spectrum of the diluted polymer sample (6.3 mg/L) was obtained with an excitation wavelength of 337 nm. Single-exponential analysis of the fluorescence decay of poly(4-PHEP) in DMF revealed that its lifetime was 2.77 ns with the acceptable statistical χ2 value (χ2=1.12).

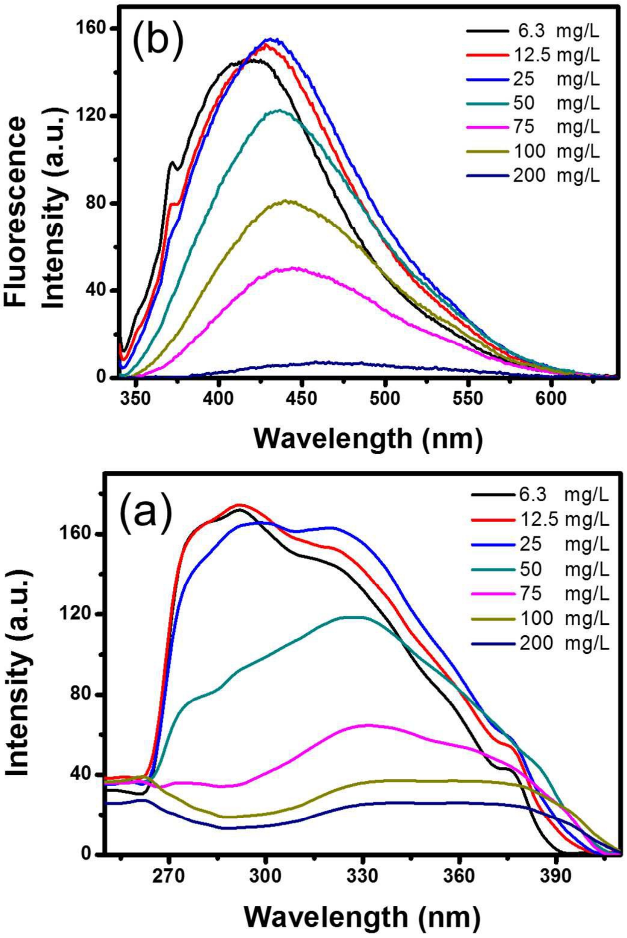


Fig. 4 The excitation (a) and fluorescence spectra (b) of poly(4-PHEP) in DMF at various concentrations. λ_{em}=430 nm for excitation spectra and λ_{ex}=337 nm for emission spectra

Thermal properties. TGA-DTG-DTA curves of the 4-PHEP and poly(4-PHEP) were plotted in Fig. 5, and the results were listed in Table 1.

Table 1 Thermal decomposition values of the monomer and the polymer

Compounds	$T_{initial}$ (°C)	50% mass loss (°C)	Carb. Res.(%) at 1000°C
4-PHEP	165	288	3.4
Poly(4-PHEP)	150	600	41.2

According to the literature, polyphenols contain absorbed water molecules in their structures with hygroscopic nature.[30, 31] The presence of water can be seen in TGA curves of 4-PHEP (7.7%) and poly(4-PHEP) (2.7%) (Fig. 5).

50% mass loss of 4-PHEP and poly(4-PHEP) were observed at 288°C and 600°C, respectively. Likewise, the level of carbine residue quantity of poly(4-PHEP) was higher than that of the monomer. Moreover, in DTA curve of the monomer, endothermic peak was observed at 147°C (Fig. 5a).

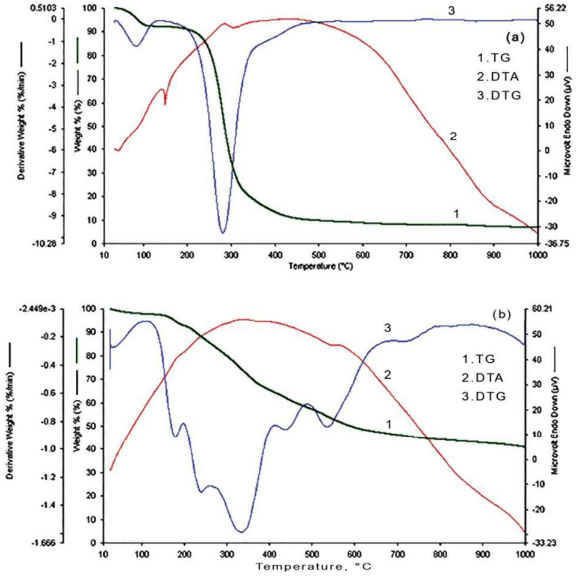


Fig. 5 TGA-DTG-DTA curves of the monomer (a) and the polymer (b)

Solubility. Solubility of the synthesized compounds was investigated in 12 types of solvents in detail. Table 2 demonstrated that the synthesized compounds exhibited an enhanced solubility in highly polar solvents such as DMSO, DMF, and solutions of KOH and concentrated H_2SO_4. The monomer was completely soluble in diethyl ether, CH_2Cl_2, ethyl acetate, DMSO, DMF and $CHCl_3$. Conversely, poly(4-PHEP) due to their high molecular weight were completely insoluble in these solvents except highly polar DMSO and DMF.

Molecular weights of polymers are one of the important parameters for solubility in organic solvents. Generally, solubility of a polymer decreases when its molecular weight increases. Consequently, because of long polymer chains from not being transported into polar solution, the solubility of polymer chains is limited with only highly polar solvents.

Table 2 The solubility tests of the synthesized compounds

Compounds	Diethyl ether	CH_2Cl_2	Ethanol	Methanol	*n*-Hexane	Ethyl acetate	DMF	DMSO	$CHCl_3$	THF	$KOH_{(aq)}$	conc. H_2SO_4
4-PHEP	+	+	+	+	-	+	+	+	+	+	+	+
Poly(4-PHEP)	-	-	±	±	-	-	+	+	-	±	+	+

Symbols: +, soluble; ±, partly soluble; -, insoluble.

Conductivity of poly(4-PHEP). The conductivity value for poly(4-PHEP) was found to be approximately 8.55×10^{-2} S/cm. This value revealed that poly(4-PHEP) had higher conductivity values than poly(phenoxy-imine)s with similar structure.[32, 33] The highest electrical conductivity belonging to these poly(phenoxy-imine)s was reported in the range of 10^{-9}-10^{-10} S/cm.[32] This is because of the polyconjugated structures of the polymers with phenylhydrazono pendent groups that increase the electrical conductivity values. Obtained results are compatible with the values in the literature.[32, 33]

Electrical Characterization of Poly(4-PHEP)/p-Silicon Heterojunction Device. In heterojunctions or Schottky type devices there may be various current transport mechanisms such as thermionic emission (TE) of the electrons from the semiconductor into the metal over a barrier, tunnelling through the barrier, recombination of the carriers in the depletion region of the device and injection and diffusion of the carriers. In general, the first is dominant in the rectifying junctions. The current-voltage (*I-V*) relation, according to the TE theory is given by;[34]

$$I = AA^*T^2\exp[-(q\Phi_b)/(kT)]\{\exp[(qV)/(nkT)]-1\} \tag{2}$$

where A is the effective diode area, A^* is the effective Richardson constant for semiconductor ($A^*=32$ A/cm^{2}K^2 for *p*-type Si), Φ_b is the effective barrier height at zero bias, T is the absolute temperature, I_0 is the saturation current, n is the ideality factor which equals unity for ideal rectifier. Furthermore, I_0 is given by;

$$I_0 = AA^*T^2\exp[-(q\Phi_b)/(kT)] \tag{3}$$

Regarding non-ideal heterojunction devices, a variety of phenomena may lead to an ideality factor greater than unity. High values of n can be attributed to the interfacial layer between the semiconductor and metal, and a wide distribution of low-barrier height patches, series resistance effect at higher forward voltages and, therefore, to the bias voltage dependence of barrier height. In addition, barrier height inhomogeneities may be a reason for the higher n values. Namely, barrier height inhomogeneities can cause the ideality factor to increase with the decreasing temperature.[34] The values of n and Φ_b are respectively given by;

$$n = (q/kT)[dV/d(\ln I)] \tag{4}$$

and

$$\Phi_b = kT/q\ln(AA^*T^2/I_0) \tag{5}$$

Fig. 6a shows the experimental *I-V* plot of the poly(4-PHEP)/p-Si junction device, at room temperature.

Ideality factor and barrier height of poly(4-PHEP)/Si were calculated from *I-V* measurement *as* $n=1.54$ and $\Phi_b=0.78$ eV, respectively. The high value of the ideality factor confirms that the poly(4-PHEP)/Si is not an ideal junction device and it might be attributed to the barrier height inhomogeneities and the effect of series resistance R_s at higher forward biases.

In fact, series resistance R_s is dependent on the device structure so, it leads to power loss. Hence, its value should be determined. The value of series resistance can be determined from the forward bias *I-V* curves at high voltages. Norde method[35] is one of the methods which are used to determine

R_s value. According to this method a *F(V,I)* vs *V* curve is plotted and the relation is written as;

$$F(V, I)=(V/2)-(kT/q)\ln[I(V)/(AA^{*}T^{2})] \quad (6)$$

Then the minimum value of *F(V,I)* is determined so, Φ_b and R_s values can be calculated by using following formulas;

$$\Phi_b=F(V_0)+(V_0/2)-(kT/q) \quad (7)$$

$$R_s=[kT(2-n)]/qI \quad (8)$$

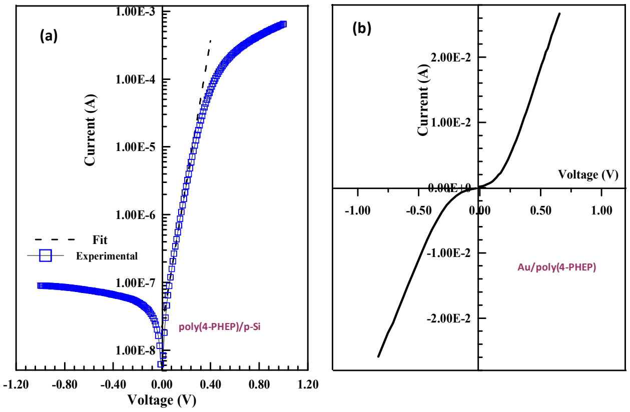


Fig. 6 (a) Experimental *I-V* plot of the poly(4-PHEP)/p-Si heterojunction device, at room temperature and (b) Ohmic *I-V* characteristics of Au/poly(4-PHEP) structure.

As a matter of fact, there is no depletion layer between two metals which are contacted to each other. Furthermore, the width of the depletion layer is inversely proportional to the doping density. Hence, regarding heterojunctions the depletion layer penetrates primarily into the lower doping material, and the width of the depletion layer in the heavily doped material can often be neglected. So, it may be consider that a heavily doped material (the degenerate material) behaves like a metal. When there is no depletion layer between two contacted materials, then the current-voltage characteristic is ohmic behaviour. For this purpose, current-voltage characteristics of Au/poly(4-PHEP) and poly(4-PHEP)/p-Si structures were compared. The *I-V* characteristic of poly(4-PHEP)/p-Si was investigated by forming circular Au electrodes with area of 7.85×10^{-3} cm^{-2} on poly(4-PHEP) side and depositing Si side with Al. Thus, it was observed the ohmic behaviour for Au/poly(4-PHEP) structure and the rectifying (Schottky type) behaviour for poly(4-PHEP)/p-Si structure (see Supplementary Information). Both characteristics have been presented in Fig. 6. Consequently, Schottky type *I-V* characteristic of the poly(4-PHEP)/p-Si confirms that the main depletion region occurs only in p-Si side not in poly(4-PHEP).

Fig. 7 shows the *F–V* plot of the poly(4-PHEP)/p-Si structure. From the *F–V* plot we calculated Φ_b=0.78 eV, R_s=460 Ω and F(V_0)=0.69 V, V_0=0.25 V values. It is seen that the barrier heights determined by forward *I-V* extrapolation and Norde-plot are exactly the same.

Therefore, for the further determination of barrier height as an alternative method to current-voltage characteristics, capacitance-voltage (*C-V*) measurement should be performed. The value of barrier height is determined from the reverse bias *C-V* plot.

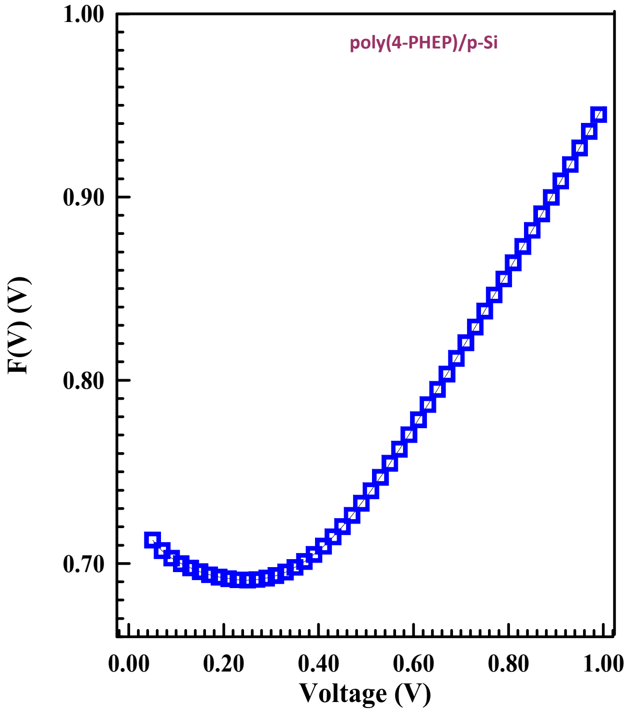


Fig. 7 The *F–V* plot of the poly(4-PHEP)/p-Si heterojunction device

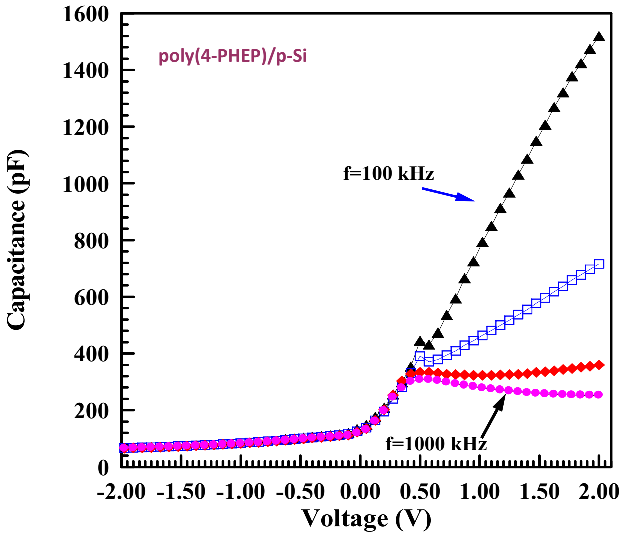


Fig. 8 *C-V* plots of the poly(4-PHEP)/p-Si heterojunction device at various frequencies

Fig. 8 depicts the *C-V* plots of the poly(4-PHEP)/p-Si device at various frequencies. The forward bias *C-V* measurements show a strong dependence of frequencies. At low frequencies, higher values of *C* can be attributed to the excess capacitance arising from the interface states in equilibrium with the *p*-Si. Under these conditions, interface states can follow the alternative current (AC) signal or vice versa.

Fig. 9 presents the reverse bias $1/C^2$-*V* plots of the poly(4-PHEP)/p-Si device. It is seen that the $1/C^2$-*V* plots are almost independent frequencies. The value of barrier height can be determined by the relation

$$\Phi_b(C\text{-}V)=V_d+V_P \qquad (9)$$

where V_P is the potential difference between the Fermi level and the bottom of the valance band of *p*-Silicon and it is determined from the following relation:

$$V_P=(kT/q)\ln[(N_v/N_a)] \qquad (10)$$

where $N_v=1.04\times10^{19}$cm^{-3} is the effective density of states in the valance band of p-Si.[34] From the $1/C^2$-*V* plots, the values of barrier heights calculated as 0.81 eV at 500 kHz. Barrier height (*C-V*) is higher than that of *I-V* plots since *C-V* plots give only a mean barrier or flat band conditions.

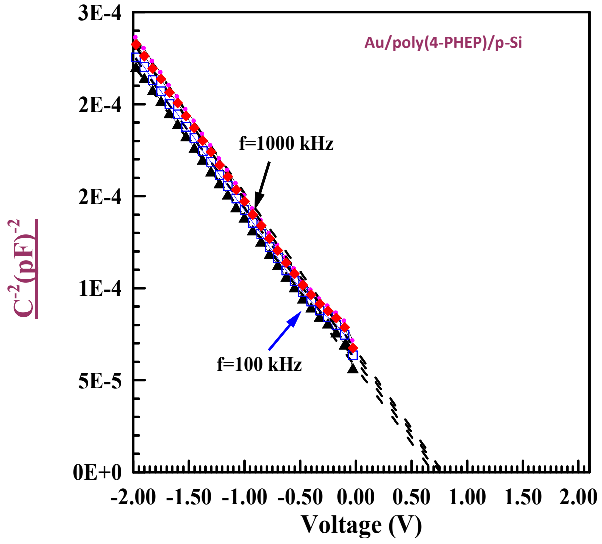


Fig. 9 The reverse bias $1/C^2$-*V* plots of the poly(4-PHEP)/p-Si heterojunction device

Conclusions

Synthesis of a new polyphenol with phenylhydrazono pendent groups, poly(4-PHEP), was achieved by oxidative polycondensation method. Reaction temperature, time and initial concentrations of alkaline and NaOCl had great effects on the yield of polymer. The resulting polymer was a powdery material, readily soluble in DMSO and DMF with molecular weight up to 1.5×10^4. Structural studies of poly(4-PHEP) by FTIR and ^{1}H-NMR spectroscopy indicated that the major linkage was the C-C coupling thorough *ortho*-positions. The C-O linkage was not involved. This novel polymer also exhibited reasonable electrical conductivity and wide optical direct band gap. *I-V* characteristics of poly(4-PHEP)/p-Si junction was analysed and the device showed good rectifying behaviour. Furthermore, *C-V* characteristics of the device were obtained as a function of frequency. As expected in the most of the Schottky type devices, barrier height obtained from the capacitance measurement was higher than that of *I-V*. These data suggested that the conjugated polymer presents properties good enough for a semiconducting material. Based on the discussion of semiconducting properties as well as 3.05 eV wide band gap, poly(4-PHEP) is a novel organic semiconductor candidate for electronic and optoelectronic device applications. Thus, further understanding about electronic and electrochemical study is needed to nominate this polymer in optoelectronics.

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GRAPHICAL ABSTRACT

Highlight

Novel poly(phenoxy-ketimine) containing both free hydroxyl and ketimine side groups was successfully synthesized *via* oxidative polycondensation method. Afterwards, the poly(phenoxy-ketimine)/p-type Si junction device was fabricated by spin coating technique, and its diode behavior at the room temperature was examined by *I–V* and *C-V* measurements.