Research Article

Chemical Synthesis, Electronic Study, and Vibrational Analysis of a New Organic Copolymer Based on PVK and 3-nhexylthiophene

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Conjugated polymers containing carbazole moieties either in the main or in the side chains have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency, and thermal stability. The aim of this work is to study a new organic copolymer which combines the PVK properties and those of PHT. We will describe in this study the protocol synthesis, the chemical structure, and the electronic and vibrational properties of the resulting copolymer. The experimental and theoretical studies are combined in order to describe the properties of this material. These properties suggest this compound (PVK-PHT) to be a good candidate for optoelectronic application.

1. Introduction

Recently, more attention has been focused on the organic conducting polymers. Due to their specific properties, these compounds are widely used for optoelectronic device applications, such as organic light emitting diodes (OLEDs) [1, 2], field-effect transistors [3–5] (OTFTs), photovoltaic cells [6–8], portable electronic [9], and lasers [10, 11].

Among these conjugated materials, polythiophene and its derivative have received particular attention [12–14] and were also investigated for the realization of new hybrids with organic or inorganic materials, due to their interesting physical properties. In this family of polythiophene, poly(alkylthiophene) such as poly(3-hexylthiophene) (P3HT) has been the focus of great attention due to a combination of its relatively high chemical stability in ambient conditions, its high conductivity, and the fact that the electronic band gap of these materials generally falls within the visible region of the electromagnetic spectrum. On the other hand, several studies reported on the synthesis of a blend materials based on poly (N-vinylcarbazole) PVK [15–17], for its interesting physical properties. These materials form a subset of the organic materials under study for blue EL applications [18–21]. In fact PVK absorbs entirely in the UV region and as a consequence of its photoconductivity, its wide band gap. Conjugated polymers containing carbazole moieties either in the main or in the side chains have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency, and thermal stability. This family of materials can be prepared by electrochemical or chemical polymerization [22, 23]. By this way, copolymerization of, respectively, EDOT and 3-melthyl thiophene [24], pyrrole and N-substituted carbazole [25], PVK and 3-melthyl thiophene [26] and has been described. However, the copolymer PVK-PHT has not been synthesized yet.

The goal of this work is to study a new copolymer which combines the PVK properties and those of PHT. We will describe in this study the protocol synthesis, the chemical structure, and the electronic and vibrational properties of the resulting copolymer.

2. Methods and Calculation

2.1. Experimental Methods. Oxidative coupling is a straightforward and versatile method to synthesize conjugated polymers. It was developed by Yoshino and coworkers [27, 28], to synthesize poly(9, 9-dialkylflourene)s (PAFs) and poly(3-alkylthiophene)s (PATs). In this work, the copolymer (PVK-PHT) is dissolved and oxidatively polymerized with FeCl$_3$. The solvent was Chloroform (HPLC grade). The UV/Vis spectrum was recorded on an MC^2 Safas spectrometer. The FT-IR spectra were obtained with Bruker Vector 22 spectrophotometer. Samples were pellets of KBr mixed with organic compound under study. The optical density measurement was carried out at room temperature in solid state by using the MC^2 Safas spectrophotometer.

2.2. Computational Methods. The molecular geometry of (PVK-PHT) polymer was performed by Gaussview molecular visualization program [29] and the quantum calculations were performed using Gaussian 03 program [30]. The geometry of the studied compound was evaluated using the DFT level of the three-parameter compound functional of Becke (B3LYP) [31]. The geometrical parameters, infrared wavenumbers, and intensities were obtained for all atoms by the 3-21G* basis [32–35]. The geometry structure was optimized under no constraint. Additionally, Time-Depended DFT-B3LYP method with the 3-21G* basis set has been used to carry out electronic transitions of the optimized structure on the ground state. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO due to the MO energies. Furthermore, and due to the large number of heavy atoms, vibrational frequencies calculations have been carried out with semiempirical Austin Model (AM1) method [36].

3. Synthesis Procedure of the Copolymer PVK-PHT

The polymerization was been developed by a single procedure to prepare a mixture of PVK with PHT (Figure 1). The procedure adopted was to cross link PVK by reacting a CHCl$_3$ solution of PVK with anhydrous FeCl$_3$ and to add a known amount of HT (hexylthiophene) with undergo polymerization, and the resulting PHT would subsequently participate in copolymer formation process.

The details of the preparation of PVK-PHT is as follows: 0.8 g of PVK was dissolved in 100 mL of CHCl$_3$ and 4 g of anhydrous FeCl$_3$was added to the solution. The system was kept under stirring at ambient temperature for 1 hour, thereafter heated to 50°C for 10 minutes. The color of the solution changed from green to a dark color. Then (4 mL) of HT was added to the mixture. The system was kept under reflux for 3 hours. A solid mass separated was dried. The copolymer was extracted with boiling methanol and acetone successively in order to remove the low-molar mass homopolymer and dried under vacuum at 50°C.
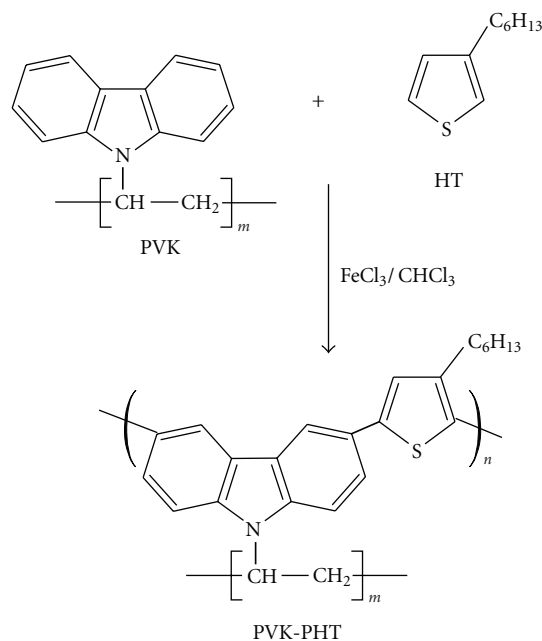

Figure 1: Synthesis of the (PVK-PHT).

4. Results and Discussion

4.1. Infrared Results. The vibrational assignments of the infrared spectra of the copolymer and the individual homopolymers are listed in Table 1. As mentioned, in IR spectroscopy, the PHT is essentially characterized by its IR principal bands centered at (720 cm^{-1}, 819 cm^{-1}, 1110 cm^{-1}, 1218.5 cm^{-1}, 1450 cm^{-1}, 1560 cm^{-1}, 1710 cm^{-1}, 2900 cm^{-1}). For the hompolymer PVK, it is essentially characterized by the principal bands observed at (718 cm^{-1}, 743.9 cm^{-1}, 1088.2 cm^{-1}, 1123.2 cm^{-1}, ...3044.8 cm^{-1}). However, when we compare the results, we note, in the vibrational spectra of the copolymer PVK-PHT, the presence of the principal characteristic bands of the PHT as well as those of PVK, which show the formation of PHT by polymerized of the HT monomers and its grafting into the Skelton of PVK to form a new back bone with the alternating of a motives of NVK and HT.

4.2. Electronic Properties. In Figure 2, we report the absorption spectrum of the new copolymer PVK-PHT recorded at ambient temperature in solid state. The synthesized copolymer absorbs in both the visible and UV-Violet region. In the visible region, we found a broad band centered at about 350 nm. The features are characteristic of organic conducting polymers [37–41]. As mentioned, PVK absorbs entirely in the UV region ($\lambda_{max} < 350$ nm) [42]. Furthermore the absorption detected in the UV-Visible spectrum of our copolymer centered at 350 nm is attributed to π–π^* transition, due to the presence of PVK in the copolymer PVK-PHT. On the other hand, the optical absorption spectrum of the PHT film exhibits a broad band centered at 500 nm [43]. We conclude that the transition located at 500 nm in the UV-V

TABLE 1: Experimental wavenumbers ($\overline{\nu}$) of infrared for PVK, PHT and PVK-PHT copolymer.

PVK Freq (cm^{-1})	I	PHT Freq (cm^{-1})	I	PV-PHT Freq (cm^{-1})	I	Assignments
526.2	w	—	—	590	w	Ring bending
616	m	—	—	632.8	w	Both peaks are for C–H out of plane vibration
718.7	vs	720	w	728.4	s	Aromatic structure for the ring deformation
743.9	vs	—	—	768.5	w	Rocking—wagging of methylene in polyvinyl
836.1	m	819	m	880	m	Out of plane deformation C–H
920.8	m	—	—	937.9	m	Aromatic out of plane C–H bending + aliphatic C–H rocking
1024.5	m	—	—	1023.6	w	ν(C–S) ring (Thiophene)
1088.2	s	1 110	w	1089.1	vs	Stretching vibration (C–H)
1123.2	m	—	—	1132	m	ν(C–N) carbazole
—	—	1218.5	m	1180	m	Stretching vibration (C=S)
1220.4	m	—	—	1232.1	s	In plane deformation (C–H)
1322.1	m	—	—	1331.9	m	C–H bending of vinyl group
1404.2	m	—	—	1400.6	m	Ring vibration of PVK moiety
1451.3	s	1450	s	1458.4	s	Symmetric stretching vibration (C=C)
1482.1	s	—	—	1486.8	s	Ring vibration of PVK moiety
—	—	1510	m	—	—	Aromatic (C=C) stretching
1595.8	m	1560	w	1598.8	m	Asymmetric deformation δ_{as}(N–H) and ν(C=C) ring in the Thiophene
1624.2	m	—	—	1628.3	w	Asymmetric deformation δ_{as}(N–H) and ν(C=C) ring in the Thiophene
1654.6	m	—	—	—	—	Asymmetric deformation N–H
1709	w	—	—	—	—	Symmetric stretching (C=C) of Carbazole
1763.6	w	1710	w	—	—	Symmetric stretching (C=C) of Carbazole
1920.2	w	—	—	—	—	Stretching vibration υ(C=C=C) of Carbazole group
2853.1	vw	2900	s	2850	w	Stretching of (C–N) group, aromatic ring of Carbazole
3022.3	w	—	—	2928.6	w	Symmetric stretching (C–H) of Carbazole group
3044.8	w	—	—	2978.1	m	Symmetric stretching (C–H) of Carbazole group
3435.9	m	3400	w	3400.3	m	Symmetric stretching (N–H) of vinylene group

vs: very strong; s: strong; m: mean; w: weak; vw: very weak.

spectrum of PVK-PHT is a result of a π–π^* transition due to the presence of the PHT moieties in our copolymer.

Optical absorption spectra (Figure 2) show a maximum peak at 350 nm (3.54 eV) and illustrate transition peaks at about 332.9 nm (3.72 eV) and 313.9 nm (3.95 eV). We reproduce the experimental gap value obtained from extrapolated absorption spectra (3.38 eV). These peaks correspond to the π–π^* interband transition. Moreover, the energy corresponding to the π–π^* transition is depending on the delocalization of the π-electrons system. This delocalization is determined by the effective conjugation length, which depends on the amount of structural and conformational defects in the polymer backbone and the interaction between polymer backbones.

4.3. ESR Studies. EPR spectra of the PVK-PHT copolymer were recorded at room temperature on Varian spectrometer operating at X-band frequency (9.7 GHz) using a dual sample cavity. The conformation of charge carriers is given by the experimental and theoretical ESR spectrum for the (PVK-PHT) powder (Figure 3). It is known that polaron
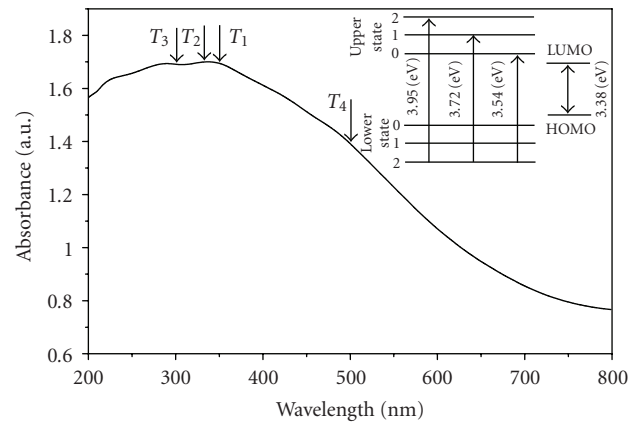

FIGURE 2: Experimental UV spectra of (PVK-PHT) powder. Inset representation of absorption between electronic ground state and first electronic excited state.

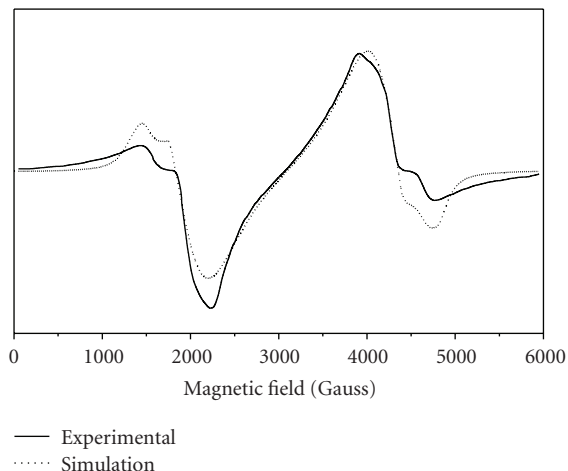states play a dominant role in the charge transport in π-conjugated heterocyclic chains [44, 45]. The spectra of

Figure 3: ESR spectra of the (PVK-PHT) powder ($F = 9.7$ GHz).

Table 2: ESR parameters of the (PVK-PHT) copolymer.

Compound	$g_{//}$	$\Delta g_\perp$	$\Delta g_{//}$	$\Delta g_\perp$	$A_{//}$	$A_\perp$	ΔH (en Gauss)
PVK-PHT	2.264	2.244	0.45	0.002	3250	2350	550

(PVK-PHT) have been described by the spin Hamiltonian formed by the Zeeman term perturbed by the hyperfine one that consists of an anisotropy of g and A tensors:

$$H_s = \beta SgB + SAI,$$

$$g_{//} = g_z,$$

$$g_\perp = \frac{g_x + g_y}{2} \qquad (1)$$

$$A_{//} = A_z,$$

$$A_\perp = \frac{A_x + A_y}{2},$$

where β is the Bohr magneton, B the static magnetic field, and g and A the g-factor and the hyperfine term A tensors, respectively.

Two hyperfine lines occur; they are attributed mainly to the interaction between a free radical composed of the polaron of the electronic spin ($S = 1/2$) and the nuclear one ($I = 1/2$) of H^- ion. The simulation of the spectrum was obtained by a program using a spin Hamiltonian made up of the electronic Zeeman term perturbed by the hyperfine one and a Lorentzian form for which the EPR parameters are presented in Table 2. In this spectrum (Figure 3), a broad signal ($\Delta H = 550$ Gauss) is observed, whereas no ESR signal in pure PVK is detected, and thus indicating the nonexistence of unpaired electron or free radical. The initial PHT sample demonstrates a Lorentzian nearly symmetrical line with $g = 2.0029$ [46]. As the PHT modified by PVK, two lateral lines appear in its spectrum ; this broad signal observed in the case of PVK-PHT is attributed to the interaction between the thiophene molecule and the corresponding near-neighboring carbazole group in the copolymer.
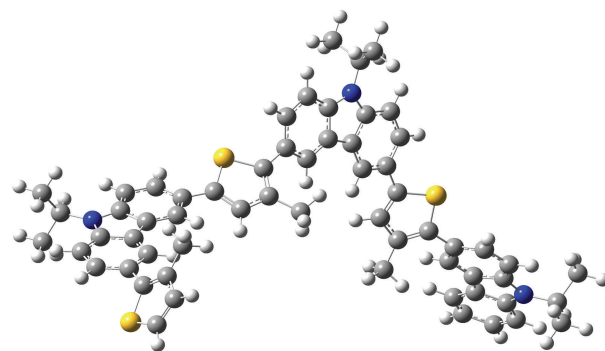

Figure 4: Optimized structure of (Cbz-Mth)$_3$, by B3LYP/3-21G* level.

Table 3: Geometric parameters of optimized structure of (Cbz-Mth)$_3$.

Geometric parameters	
d_1	1.473 Å
d_2	1.468 Å
d_3	1.473 Å
d_4	1.468 Å
d_5	1.472 Å
θ_1	45.74°
θ_2	29.74°
θ_3	47.20°
θ_4	31.81°
θ_5	48.29°

5. Theoretical Study

Like in most polymers these materials are amorphous. And due to the absence of X ray spectra and without reliable microanalyses it was not possible to infer their architecture experimentally.

In order to predict the unknown properties of our prepared copolymer and to find a model that reflects the polymer properties, theoretical investigation on the structure and electronic properties are indispensable. For that matter, it is commonly believed that DFT theoretical methods are able to describe the geometry of organic macromolecules as well as their electronic properties in a satisfactory manner [47]. In order to facilitate the calculation efficiency, the methyl and the isopropyl groups were used to replace, respectively, the hexyl and polyvinyl groups present in the synthesized copolymer.

5.1. Geometric Parameters. The (PVK-PHT) copolymer prepared in this research is sufficiently long to consider the translation as a symmetry operation. In order to be coherent with experimental results, and in the geometric structure of this copolymer, we have chosen an oligomer model with six successive monomers units. The optimized geometry structure of this model is illustrated in Figure 4. The optimization process (the global minimum energy information of the
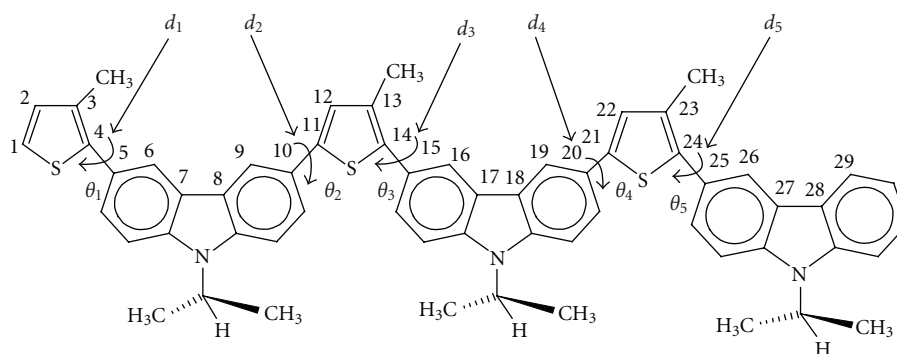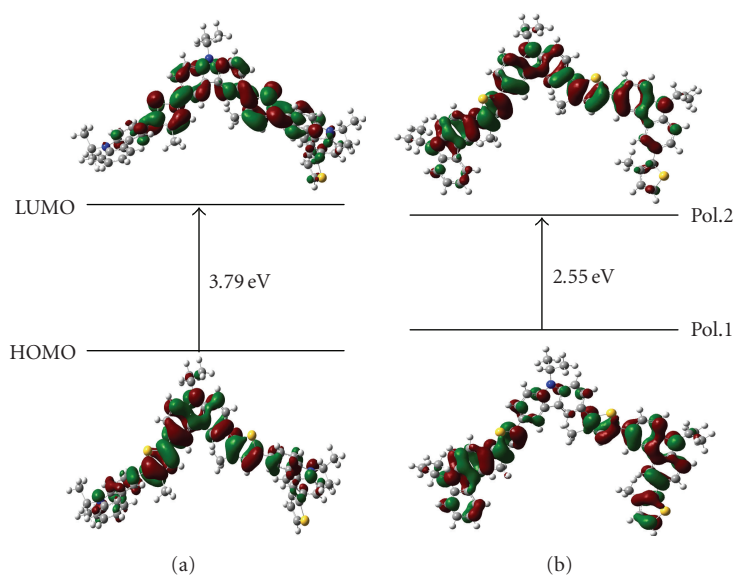
FIGURE 5: Structures of studied (Cbz-Mth)$_3$ and their geometric parameters.

(a)   (b)

FIGURE 6: Schematic representation molecular orbitals.

materials is achieved) was fully done using B3LYP/ 3-21G* calculation.

The geometric characteristics set as interring distances (d_i) and dihedral angles (θ_i) are listed in Table 3. The optimized geometrical structure of (Cbz-Mth)$_3$ model and their geometric parameters are displayed in Figure 5. An accurate representation of the bond rotations in the chain is extremely important, since especially the properties of polymer depend strongly on the conformational statistics of polymer chains.

The theoretical calculations show that the interring torsion angles were evaluated to be about 45.74° for θ_1, 29.74° for θ_2, 47.20° for θ_3, 31.81° for θ_4, and 48.29° for θ_5. The interring distance was evaluated to be about 1.473 Å. In fact, the torsional angle constitutes a compromise between the effect of conjugation and the steric repulsion between hydrogen which favors a nonplanar structure. In comparison with the torsional angles obtained in the case of PEDOT [48, 49] ($\theta_i = 180.0 \pm 5.0°$) and in the case of n-THP (oligothiophenes) [50, 51]

($\theta_i \approx 150.0°$) where the anticonformation was predicted as the global minimum at different levels of theory, that is, HF, B3LYP, B3PW91, and MP2 combined with different basis sets, the effect of insertion of PVK motive is clearly seen. However, the introduction of charges carriers into carbazole enhances the π-conjugated structures.

On the other hand, we have also calculated the infrared frequencies of the (Cbz-Mth)$_3$ copolymer for semiempirical-AM_1 method, when comparing the experimental and theoretical values of frequencies, Tables 1 and 4, respectively. We find that the mode positions are almost similar.

Examining the structure of (Cbz-Mth)$_3$ molecule, we find bands related to infrared modes of methylene in polyvinyl groups (Rocking- wagging of 734.1 cm^{-1}), stretching vibration ν(C–S) in the thiophene (1212.8 cm^{-1}), ring vibration of Cbz moiety (1431.5 cm^{-1}), asymmetric deformation δ_{as}(N–H) and ν(C=C) ring in the thiophene (1621.6 cm^{-1}), and in stretching of (C–N) group (3190.4 cm^{-1}).

TABLE 4: Comparison of the observed IR of (PVK-PHT) copolymer and calculated (by DFT-B3LYP/3-21G* level) vibrational wavenumbers (cm^{-1}) of $(Cbz-Mth)_3$.

Exp. Freq. (cm^1)	I	Calc. Freq. (cm^1)	I	Assignments
—	—	537.2	w	Ring bending + wagging CH_3
590	w	614.57	w	Ring bending
632.8	w	719.8	m	Both peaks are for C–H out of plane vibration
728.4	s	734.1	m	Wagging rocking—of methylene in polyvinyl
768.5	w	811.5	w	Out of plane deformation C–H
937.9	m	930.5	w	Aromatic out of plane C–H bending + aliphatic C–H rocking
1023.6	w	—	—	ν(C–S) ring (thiophene)
1089.1	vs	1030.1	w	ν(C–H) stretching vibration
1132	m	1098.8	m	ν(C–N) Carbazole
1180	m	1212.8	m	Stretching vibration ν(C–S) thiophene
1331.9	m	1312.2	m	C–H bending of vinyl group
1400.6	m	1358.6	m	Ring vibration of PVK moiety
—	—	1403.6	s	Stretching N–H + deformation and rocking C–H + wagging CH_3 + deformation CH_3
1458.4	s	1431.5	s	Ring vibration of PVK moiety
1598.8	m	1529.9	m	Aromatic C–C stretching
1628.3	w	1621.6	vs	Asymmetric deformation δ_{as}(N–H) and ν(C=C) ring in the Thiophene
—	—	1776.4	vs	In plane C=C aromatic stretching
—	—	1868.1	s	C–C inter-ring stretching
2850	w	3190.4	w	Stretching of (C–N) group, aromatic ring of Carbazole
3400.3	m	3326.8	w	Aromatic C–H stretching (terminal group)

vs: very strong; s: strong; m: mean; w: weak; vw: very weak.

TABLE 5: Calculated HOMO (eV), LUMO (eV), $\triangle E_g$ (=LUMO-HOMO) (eV), absorption λ_{max} (nm), and oscillator strength (O.S) of the model $(Cbz-Mth)_3$ as well as experimental gap E_g (eV) and absorption λ_{max} (nm) for undoped and doped (PVK-PHT).

Compound			calculated value			experimental result	
	HOMO	LUMO	$\triangle E_g$	UV λ_{max}	O.S	UV λ_{max}	E_g
Undoped	−4.85	−0.82	4.03	347.65	1.617	350	3.38
Doped	−6.74	−3.58	3.16	1332.65	0.011	—	—

In parallel we have calculated the electronic transition. In Table 5, we present HOMO and LUMO energy and the calculated energy differences between LUMO and HOMO, as a result of all theoretical methods in comparison to those of experimental data, where the DFT method was the well reproduced one. In fact, the band gap obtained with DFT method is in close agreement with the extrapolated band gap from experimental absorption spectra. In fact, the density functional calculation method, which accounts for electron correlation, yielded much more accurate values for the HOMO-LUMO gap than other methods. Generally, we argued that the theoretical band gaps calculated for isolated chains are expected to be about 0.2 eV larger than the condensed phase values [52]. However, it is believed that the bulk or intermolecular effects must be taken into account when considering the polymers with long chains [53, 54]. After correcting this effect, our theoretical band gaps agree well with experiment.

In order to gain greater insight into the difference between the pristine and the doped copolymer, it is worthwhile to plot their highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital. In our case, the HOMO possesses a π-bonding character within subunit and a π-antibonding character between the consecutive subunits; whereas the LUMO possesses a π-antibonding character within subunit and a π-bonding character between the subunits, the energy diagram of neutral and oxidized (Cbz-Mth)$_3$ model is shown in Figure 6.

In Table 5, we present a calculated neutral and polaronic HOMO and LUMO energy, $\triangle E$ (the calculated energy differences between LUMO and HOMO), absorption λ_{max} (nm), and oscillator strength (O.S), compared with the experimental E_g (eV) and absorption λ_{max} (nm) for (PVK-PHT), where the DFT method was the well-reproduced one.

Traditionally, charged states in conjugated polymers have been discussed in terms of a one-electron band model. One singly charged defect leads to the appearance of two new levels inside the band gap (Pol.1 and Pol.2) (Figure 6). The lower level is occupied by one electron. After doping, the gap energy of the polymer is weak, and the structure has a quinoidic character. The effect of doping on the decrease in the gap energy is very clear.

6. Conclusion

In this work, a new organic conjugated copolymer has been prepared from PVK and 3-nhexylthiophene (HT). The structural parameters, infrared wavenumbers and intensities, electronic transitions, gap energy, and ESR parameters of (PVK-PHT) copolymer have been determined. The IR and UV.Visible spectroscopies indicate that we have synthesized a new copolymer (PVK-PHT) using PVK and HT as starting materials. Due to molecular modeling, a structural model was elaborated and made it possible to determine the geometrical properties having a relationship with the conjugation (interring distances and dihedral angles). There is an excellent agreement between experimental and theoretical infrared wavenumbers in the region of (400–3600 cm^{-1}). The gap energy calculated with the DFT method decreases when passing from the neutral to the doped structure, and the gap energy value calculated in the neutral state correlated with the experimental value of the copolymer. The experimental ESR spectrum confirms the presence of charge carriers.

This structural and optoelectronic information can be applied in the design of novel conducting polymer materials PVK-based PHT. These properties suggest this compound (PVK-PHT) to be a good candidate for optoelectronic applications.

Acknowledgments

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