International Journal of Advanced Chemical Research
Vol. 3, No. 1, PP. 024-029, January, 2014
http://www.wrpjournals.com/IJARB

RESEARCH ARTICLE

Experimental and Quantum Chemical Investigation of New Organic Material Based on Thiophene, Phenylene and Bipyridine

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In this paper, we report first, a synthesis and physical properties of a recent soluble polymer based on thiophene, phenylene and bipyridine. Then, we present a detailed DFT study based on B3LYP/6-31G (d) of geometrical structures and electronic properties of this copolymer. Calculated results are compared with experimental data and based on such comparison we try first, to propose an oligomer model and then to obtain a qualitative understanding the properties of copolymer.

Key words: Conjugated polymers, thiophene-phenylene-bipridine, DFT, Electronic properties

INTRODUCTION

Organic materials based on conjugated molecules have gained much interest as a novel class of semi-conductors and are frequently studied because of their promising opto-electronic properties [1]. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are, in particular, desired in optoelectronic applications such as LEDS or solar cells [2]. Ones of the most important conjugated polymers which allow a very flexible structure and promising properties are polythiophene and polyphenylene. Copolymers containing both phenylene and thiophene units have also proved to be of interest in combining the properties associated with the two different conjugated rings [3]. These copolymers represent a very interesting class of materials and exhibit a strong fluorescence when exposed to the visible light. To improve solubility of copolymers, new substituted copolymers with different lateral alkoxy chains, have been synthesized. The effects of these alkoxy side chains are not only to give good solubility to the polymers, but also to improve their photoluminescence (PL) quantum yields [5]. The necessity of finding new organic materials has caused great concern in scientific community, in this regard; we are interested to develop new types of organic materials based on thiohpene, phenylene and bipyridine for eventual applications in optoelectronics. We must remember that bipyridines are a family of chemical compounds with the formula $(C_5H_4N)_2$, which are formed by the coupling of two pyridine rings. Six isomers of bipyridine exist, but two isomers are prominent:2,2'-bipyridine is a popular ligand in coordination chemistry and 4,4'-bipyridine is a precursor to the herbicide paraquat.

The bipyridines are colourless solids, which are soluble in organic solvents and slightly soluble in water. On the other hand and in order to understand well the optical and electronic properties and hence the improvement of such devices in which conjugated polymers are used as active layers, Raman spectra can provide structural information and photoluminescence can often be greatly enhanced by increasing the intrinsic stiffness of a polymer backbone or by inducing large bulky side groups to weaken intermolecular interactions. The emission spectrum of a conjugated polymer depends basically on its π–π^* band gap, which can be tailored using different structures [6].

In order to rationalize the experimentally observed properties of known materials and to predict those of unknown ones, theoretical investigations on the structures and electronic spectra and emissive properties of these materials are indispensable. In the past decades, ab initio and semi-empirical levels were applied to analyze various properties of thiophene-based molecules (oligomers and polymers). The semi-empirical PM3, AM1 and ZINDO approaches were used to calculate electronic structure of molecules based on thiophene and/or phenylene [7]. The conformational analysis and optical properties of symmetrically distributed terthiophenes were performed by Nicolas Dicésare and co-workers using the ab initio HF/3-21G* method [8]. However, it is very difficult to use a high level of theory with, the growing molecular size from monomer to oligomers, to treat these systems. Recently, methods based on Density Functional Theory (DFT) [9] were found attractive due to their features of including the electronic correlation in a computationally efficient manner and can be used in larger molecular systems. In this work we study the electronic structure and optical absorption of a recent soluble polymer based on thiophene, phenylene and bipyridine showing very good absorption properties. The schematic picture of the polymer can be seen

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in Fig. 1. Calculated results are compared with experimental data and based on such comparison. We try first to investigate propose an oligomer model and then to obtain a qualitative understanding of the polymer properties.

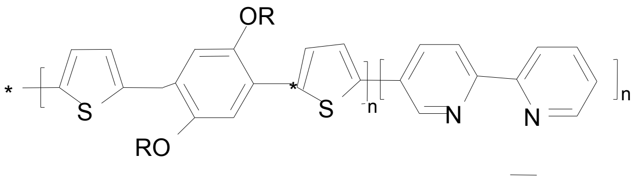


Fig. 1. The chemical structure of the studied copolymer

Experimental and computations

Gel Permeation Chromatography (GPC), infrared and Raman Spectroscopy were used to determine the chemical structure of the resulting copolymers. Raman spectra were registered on a Fourier Transformed (FTR) spectrometer Brüker RFS 100, using a laser wavelength at 1060 nm with a 4 cm^{-1} resolution. UV–Vis spectra were recorded on a MC^2 SAFAS spectrometer and emission spectra on an SLM-Aminco MC 200 spectrometer. Spectra of copolymers dissolved in chloroform ($CHCl_3$) were recorded at ambient temperature. The macromolecular characteristics were obtained by steric exclusion chromatography (SEC) or (GPC) in THF using polystyrene as standard. Concerning the theoretical part, the quantum calculations were performed using Gaussian 03 program [10]. The geometries were optimized at the DFT level of three-parameter compound functional of Becke (B3LYP) [11]. The 6-31G* basis set was used for all atoms. We have also examined the energy of HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using TD/DFT method starting with the fully optimized geometries obtained at B3LYP/6-31G* levels. In fact, these calculation methods have been successfully applied to other conjugated polymers [12].

RESULTS AND DISCUSSION

Synthesis, characterization and properties

Copolymer synthesis

The synthesis of the thiophene/phenylene/bipyridine copolymer poly (TPBip) was achieved, as shown in Fig. 2., by Stille coupling [13] using equimolar 9.10-dibromo anthracene amount of 1.4-bis(2-phenyl)-2.5-dioctoxy benzene, in a 1:1 THF:DMF mixture in the presence of $Pd(PPh_3)_4$ (1 mol%) as the catalyst. After reaction, the polymer was purified by precipitation upon addition of methanol. Our results are in agreement with the analytical data, elemental analysis, 1H NMR and FT-IR reported in ref [5] are consistent with the copolymer structure. The polymer was soluble in organic solvents (THF, CHCl3). The molecular weights of the copolymer were evaluated through gel permeation chromatography (GPC) calibrated by polystyrene standard. The number-average molecular weight ($\overline{\mathrm{M}}$n) of the synthesized copolymer poly(TPBip) was $\overline{\mathrm{M}}_w = 3104{,}66$. Thus, we note that this copolymer exhibits a relatively low molecular weight with polydispersity index ($\overline{\mathrm{M}}_w$ / $\overline{\mathrm{M}}_n$) value equal to 1,12. It indicates an average degree of polymerization (DPn) of 16 corresponding in average to 80 consecutive alternating aromatic rings (Table 1)

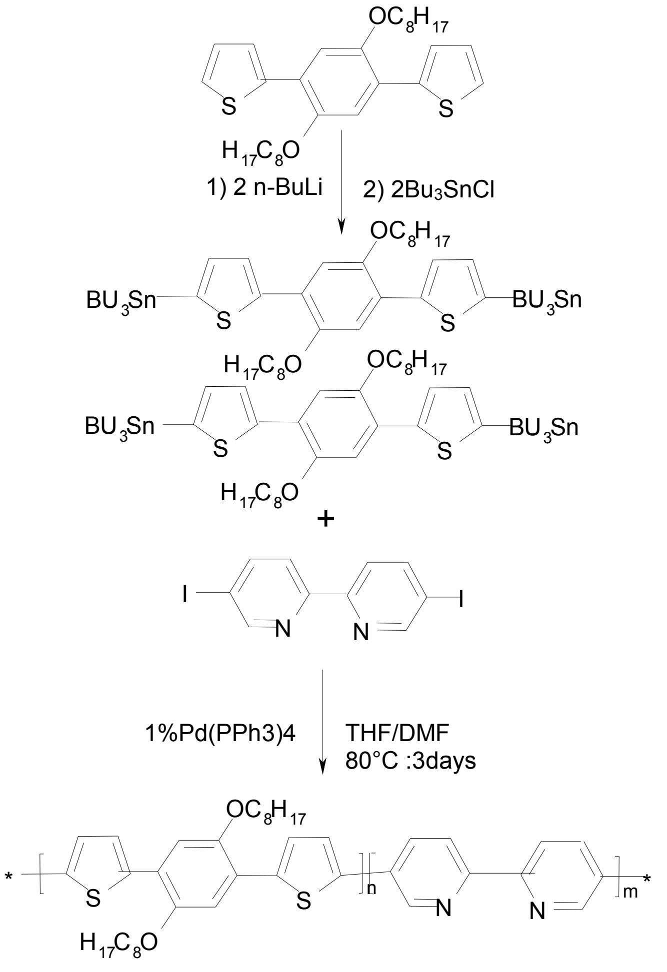


Fig. 2. Synthesis of the copolymer

Table 1. Gel Permeation Chromatography (GPC) analyses

GPC results	$\overline{\mathrm{M}}_n$	$\overline{\mathrm{M}}_w$	I= $\overline{\mathrm{M}}_w$ / $\overline{\mathrm{M}}_n$	DPn	Number of cycles
	3104,46	3477	1 .12	16	80

For a better understanding of the relationship between the copolymers structure and their vibrational or optical properties, we discuss in the following section Raman scattering, infrared absorption, UV–Vis absorption and PL emission results.

Spectroscopy results

We have studied the powder of the copolymer by IR and Raman. The IR spectrum showed in Fig 3. The main peaks and their attribution are reported in Table. We have showed that in the case of our copolymer, a very strong peak located at 1446 cm^{-1} dominates the normalized Raman spectra (Fig. 3). On this basis and from an examination of characteristic mode frequencies [13], we assigned this peak at 1446 cm^{-1} mainly to the symmetric ring-stretching mode of thiophene. The other peak at 1604 cm^{-1} is attributed to the para-phenylene ring-stretching mode. Peaks observed between 1000 and 1400 cm^{-1}

are much weaker in intensity than those observed at 1446 and 1605 cm^{-1}, leading then to alternative assignments in particular concerning C–C bridge rings. Furthermore, we note also the absence of C-N infrared vibration, situated at 1650–1670 cm^{-1}, which appear with broad absorption band in the Raman scattering spectra. The relative intensity changes in Raman could be related to the changes of the molecule structures.

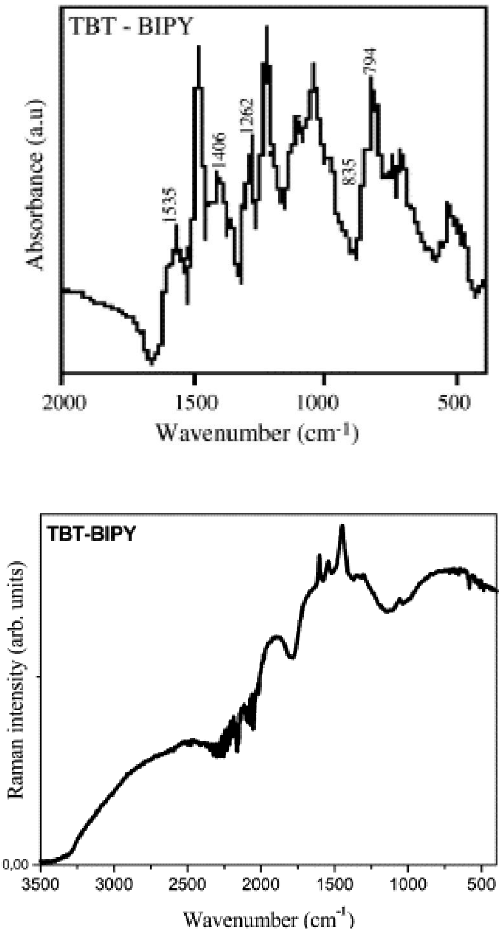


Fig. 3. IR and Raman spectra of the copolymer

In order to achieve the relationship between structural properties for different copolymers, we studied their optical characteristics (UV–vis absorption and PL emission) and even their optimization geometries with Density Functional Theory (DFT) calculations.

Optical and photoluminescence properties

Fig. 4 shows the absorption and the emission spectra recorded measured in $CHCl_3$ at room temperature. The UV–vis absorption and PL emission maxima of the copolymer are quoted in Table 2 together with their optical band gap estimated by the absorption onset wavelengths. The poly(TPBip) exhibits an absorption spectra where the maximum absorption λ_{abs} appears at 419,22 nm, which is assigned to the electron donating alkoxy substituents on the phenylene ring [14]. This value is very similar to those observed for regioregular polyalkylthiophenes [15]. On the other hand, the onset of absorption, which corresponds to an approximation of the band gap, is estimated to be 3,2 eV. An important red shift of the absorption maximum was recorded and attributed to a higher mean conjugation length in the solid state and to interchain electronic coupling λab= (453 nm). Truly in the solid state, intermolecular interactions favor the coplanar arrangements of the aromatic rings that may be responsible for the observed enhanced conjugation

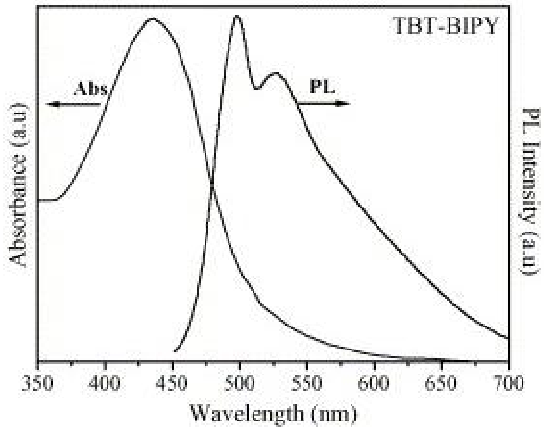


Fig. 4. Optical absorption and photoluminescence spectra of the copolymer

Table 2. Optical properties of the copolymer

absorption	emission	Optical
λ_{abs} (nm)	λ_{em} (nm)	Band gap (eV)
419,22	496,7	3,2

Concerning the PL emission properties of the copolymer (Fig. 4), spectra show typical vibronically structured bands with a maximum, a shoulder and a tail. The PL spectra of poly(TPBip) are red-shifted (λ_{em}= 496,7 nm) resulting in a green emission. The red shift of the PL spectra could be related to interchain interactions. As observed for absorption, the photoluminescence maximum is red-shifted in the solid state in comparison to the solution. An orange-red photoluminescence maximum appeared in the range 610–625 nm in the solid state. It should be noted that these values of λ_{ab} and λ_{em} are sufficient to consider applications of this material in the optoelectronic field [16].

Theoretical results

Geometric parameters

The optimized ground state geometries of the chosen model (One motif TBTBIP and two motifs (TBTBIPTBTBIP) obtained at the B3LYP/6-31G* level are given in Fig. 5. The optimized inter-ring bond lengths and dihedral angles between the subunits are summarized in Table 3 and Table 4.

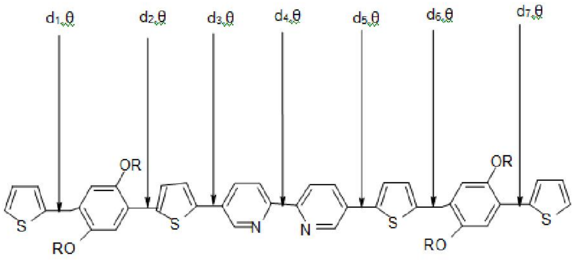
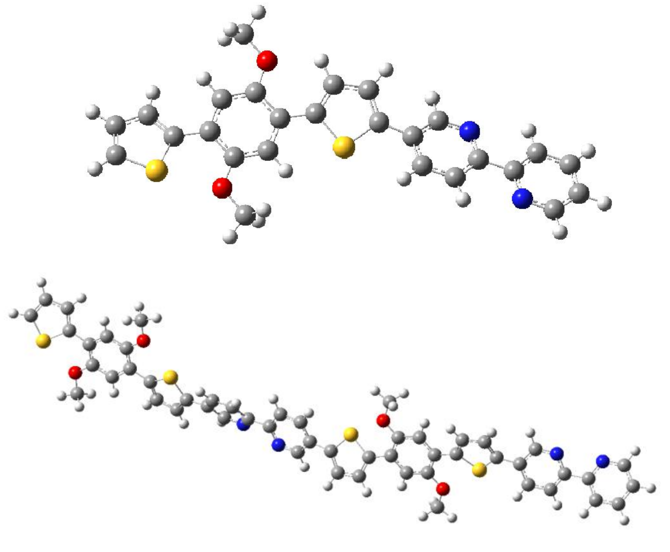


Fig. 5. Studied geometric parameters

Table 3. Inter-ring bond lengths (d_i) Dihedral angles (θ_i) of the proposed oligomer obtained by B3LYP/6-31G*

d_i (Å)	(θ_i)(°)
1,49098	32,11
1,46125	156,47
1,46417	18,31
1,46404	18,94
1,46099	156,12
1,48758	29,47
1,46092	155,83
1,46470	16,19
1,46654	21,15

The results of the optimized structures for the copolymeric molecules show that all molecules possess non-planar structures. We have demonstrated in the precedent works that the inter-ring bond lengths and bond angles do not suffer appreciable variation with the oligomer size and it suggests that we can describe the basic structures of the polymers as their oligomer. As shown in Table 3, the inter-ring bond length (d_i) phenylene and thiophene ring are in the average of 1,469018 Å. The dihedral angles (θ_i, i = 1 – 9) are also collected in Table 3. The inter-ring torsions between thiophene and phenylene were evaluated to be about θ_1 = 32,11°, θ_2 =156,47°, θ_3 = 18,31°, θ_4 = 18,94°, rather than θ_7 = 21,15° as occurs for poly (thiophene-phenylene). It is obvious that the torsion angle constitutes a compromise between the effect of conjugation on crystal packing energy, which favours a planar structure, and the steric repulsion between hydrogens which favours a non planar structure [16]. The effect of alkoxy groups grafted on 2 and 5 position of phenyl ring is clearly seen. We believe that the difference between the values of θ_i is owing to attractive interaction forces taking place between the oxygen atom and the sulphur atom in the opposite thiophene ring as suggested previously by Meille et al and Lerich et al [17]. (Fig. 6). The effect will reduce the effective conjugation of the polymer. On the other hand, the stronger electron donating effect of alkoxy groups is responsible for the reduction of the dihedral angles θ_i. The conjugation across phenylene and thiophene agrees very well with experimental results [18].



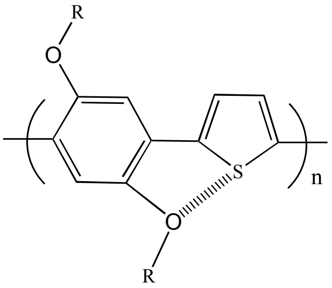


Fig. 6. Optimized structure at B3LYP/6-31G(d,p) level for TBTBIP and TBTBIPTBTBIP Intramolecular interactions between S and O are indicated by dotted lines.

Electronic properties

Front molecular orbitals and HOMO–LUMO gaps

It is important to examine the HOMO and the LUMO orbitals for these two oligomers (TBTBip et TBTBipTBTBip) because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and the ability of electron hole transport. In general, as plotted in Figure 7, the HOMO possesses an antibonding character between the consecutive subunits; whereas the LUMO of all oligomers generally shows a bonding character between the subunits.

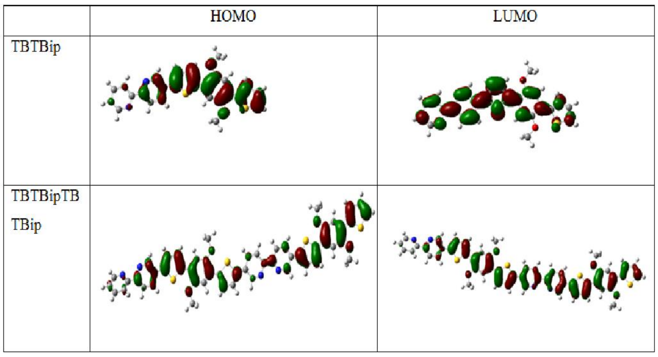


Fig 7. The HOMO and LUMO orbital's obtained by B3LYP/6-31G*

The experiment showed that the HOMO and LUMO energies were calculated from an empirical formula proposed by Bredas et al. [19], based on the onset of the oxidation and reduction peaks measured by cyclic voltammetry. But theoretically speaking, the HOMO and LUMO energies can be calculated by DFT calculations. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tends to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers. For a better understanding of the electronic properties of the studied oligomer, we present in Table 5, the DFT calculated HOMO and LUMO energies, E_{gap} = LUMO-HOMO. The band gaps in conjugated polymers are governed by their chemical structures. This value is obtained for one chain (monomer), band gap for infinite chains (polymer) can be determinate by plotting band gaps in oligomers against the inverse of the number (n) of monomer units and extrapolating the number of units to infinity. The predicted band gaps are for the isolated gas-phase chain [21]. Interestingly, for our proposed models, the obtained value 3,2 eV and 2,946 eV, these values are sufficient to consider applications of these oligomers in optoelectronic devices.

Table 4. The HOMO, LUMO and HOMO–LUMO gaps energies (eV) by B3LYP/6-31 G*

Compounds	E_{LUMO}(ev)	E_{HOMO}(ev)	Gap(ev)
TBTBip	-1,8151518	-5,0138599	3,2003419
TBTBipTBTBip	-1,9801656	-4,9261793	2,946013

Absorption properties

The TD/DFT method has been used on the basis of the optimized geometry to obtain the energy of the singlet–singlet electronic transitions and absorption properties All electronic transitions are of the π–π* type and no localized electronic transitions are exhibited among the calculated singlet–singlet transitions. The maximum absorption wavelength λ_{abs} for the proposed oligomers and the available experimental data of the studied copolymer are exhibited in Table 5.

Table 5. Absorption λ_{abs} (nm) obtained by the ZINDO et TD/DFT methods and the experimental values of the copolymer poly (TPTBIP)

	E_{ex}(ev)	λ_{abs} (nm) (TD)	O.S	MO/character
TBTBip	0,66041 0,56791 0,50090	419,22 341,2 331,08	1,2433 0,3700 0,1033	HOMO→ LUMO HOMO→ LUMO+1 HOMO-1→ LUMO
TBTBipTBTBip	0,64423 0,65984 0,66319	461,55 422,42 401,42	2,9673 0,1049 0,66319	HOMO→ LUMO HOMO-1→ LUMO HOMO→ LUMO+1

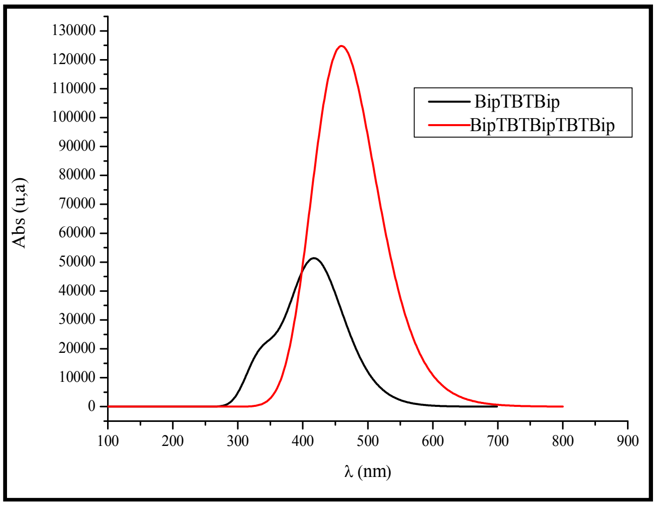


Fig. 8. UV visible of BipTBTBip and BipTBTBipTBTBip

Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbitals. As in the case of the oscillator strength, the absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition and as analyzed above that with. The results are a decrease of the LUMO and an increase of the HOMO energy.

These values are calculated by and TD method starting with optimized geometry obtained at B3LYP/6-31G* level. However, we believe that the bulk of intermolecular effect must be taken into account when considering the polymers with long chain. After considering this effect, our calculations are in good agreement with the experimental values (λ_{max} = 453nm). The deviation between the calculation and the experiment data is not more than 35 nm. Therefore, the procedures of theoretical calculations give good descriptions of opto-electronic properties of the proposed oligomers TBTBip and can be employed to predict the electro-luminescence characteristics of other materials. These results lead us to suggest that the proposed structure is a good model to reflect optoelectronic properties for the parent polymer.

Conclusion

A new soluble copolymer based on thiophene, phenylene and bipyridine was prepared by condensation of Stille. This new material exhibits lower molecular weight and high photoluminescence, making it as an attractive candidate for light-emitting diode applications. Theoretical studies, based mainly on Density Functional Theory (DFT) calculations, are performed for an oligomer model. The obtained values are (gap = 3.23eV, λ_{abs} = 419,22 nm , λ_{em}=496,7). These results lead us to suggest that the proposed state is a good model to reflect optoelectronic properties for the parent polymer. Calculated results are in good agreement with experimental data. Therefore, the procedures of theoretical calculations give good descriptions of opto-electronic properties and can be employed to predict the electro-luminescence characteristics of other materials. Further theoretical investigations are necessary in order to advance our understanding of the interface phenomena in polymer LEDs.

Acknowledgements

This work has been supported by the AUF organization (Ref. 63/3PS589) and by CNRST/CNRS cooperation (Project chimie1009). We are grateful to the “Association Marocaine des Chimistes Théoriciens” (AMCT) for its pertinent help concerning the programs

REFERENCES

[1] T.A. Skotheim (Ed.), Handbook of conducting Polymers, Marcel Dekker, New York, (1986); Advances in Synthetic Materials, Twenty Years of progress in Sciences and Technology, Edité par Bernier, Lefrant et Bidan, Elsevier (1995); Special issues on molecular materials for electronic and optoelectronic devices Acc. Chem. Res., 32 (1999) 191.

[2] H.J. Snaith, N.C. Greenham and R.H. Friend, Adv. Mater. 16 (2004) 1640 ; Y. Kim, S. Cook, S.A. Choulis, J. Nelson, J.R. Durrant and D.D.C. Bradley, Chem. Mater. 16 (2004) 4812 ; H. Spanggaard and F.C. Krebs, Sol. Energy Mater. Sol. Cells, 83 (2004) 125.

[3] P. Damman, M. Dosière, M. Brunel and J.C. Wittmann, J. Am. Chem. Soc., 119 (1997) 4633 ; Shu Hotta, Midori Goto, Reiko Azumi, Masamitsu Inoue, Musubu Ichikawa, and Yoshio Taniguchi, Chem. Mater., 16 (2) (2004) 237; S. Hotta; Kimura, H. Lee, S. A. Tamaki, T. J. Heterocycl. Chem., 37 (2000) 281; S. Hotta, T. J. Katagiri, Heterocycl. Chem., 40 (2000) 845.

[4] M. Bouachrine, S. Bouzakraoui, M. Hamidi, S. Ayachi, K. Alimi, J-P.Lère-Porte, J. Moreau, Synth., Met., 145 (2004) 237.

[5] H. Sarker, I. Ong, S. Shuker, P. C. Searson, T. O. Poehler, Synth. Met., 108 (2000) 33; Haripada Sarker, Ivan W. Ong, Peter C. Searson and Theodore O. Poehler, Synth. Met., 113 (2000) 151.

[6] J. Pei, W. L. Yu, W. Huang, Macromolecules, 33 (2000) 2462; Jian Pei, Wang-Lin Yu, Wei Huang and Alan J. Heeger, Synt. Met., 105 (1999) 43; J. Pei, W. L. Yu, W. Huang, Macromolecules, 33 (2000) 2462 ; M. Nisoli, V. Pruneri, S. De Silvestri, V. Magni, A. M. Gallazzi, C. Romanoni, G. Zerbi, G. Zotti, Chem. Phys. Lett., 220 (1994) 64; M. Mushrush, A. Facchetti, M. Lefenfeld, H. E. Katz, T. J. J.Marks, Am. Chem. Soc., 125 (2003) 9414 ; M. C. Gallazzi, L. Tassoni, C. Bertarelli, G. Pioggia, F. Di Francesco, E. Montoneri, Sensors and Actuators B: Chemical, 88 (2003) 178.

[7] Muzaffer Can, Fatma Sevin and Attila Yildiz, Applied Surface Science, 210 (2003)338 ; D.A. dos Santos, D.S. Galvao, B. Laks and M.C. dos Santos. Synth. Met. 51 (1992) 203 ; M. Belletête, M. Leclerc and G. Durocher. J. Phys. Chem., 98 (1994), 9450 ; C. Aleman, V.M. Domingo, L. Fajari, L. Julia and A. Karpfen. J. Org. Chem., 63 (1998) 1041.

[8] Nicolas DiCésare, Michel Belletête, Mario Leclerc and Gilles Durocher, Journal of Molecular Structure (THEOCHEM), 467 (1999) 259 ; Nicolas DiCésare, Michel Belletête, Anne Donat-Bouillud, Mario Leclerc and Gilles Durocher, Journal of Luminescence, 81 (1999) 111.

[9] F.C. Grozema, LP. Candeias, M. Swart, P. Van Duijnen, J. Wildemen, G. Hadzianon, J. Chem. Phys., 117 (24) (2002) 11366; Jean-Francois Briere and Michel Cote, J. Phys. Chem. B, 108 (10) (2004) 3123; Yunqiao Ding, Dacheng Feng, Shengyu Feng, Jie Zhang and Ju Xie, Polymer, 47 (2006) 368 ; Kotaro Honda, Yukio Furukawa and Hiroyuki Nishide Vibrational Spectroscopy, 40 (2006) 149; S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, J. Mol. Struct. (THEOCHEM), 725 (2005) 39; S.M. Bouzzine, S. Bouzakraoui, M. Bouachrine, M. Hamidi, J. Mol. Struct. (THEOCHEM), 726 (2005) 269.

[10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.R. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Promelli, C. Adamo, S. Clifford, J. Ocherski, A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W.Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN98, Revision A 7, Gaussian Inc., Pittsburgh, PA, (2003).

[11] C. Lee, W. Yang, R. G. Parr, Phys. Rev., B 37 (1993) 785.

[12] L Yang, J. Feng, A. Ren, Polymer, 46 (2005) 10970.

[13] The handbook on Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, Inc. Harcourt Brace Jovanovich Publishers, New York, (1989).

[14] H. Zgou, M. Hamidi, M. Bouachrine, J. Mol. Struct. (THEOCHEM), in press, 2007

[15] J-P, Lère-Porte, J.J.E Moreau and C. Torreilles, Synt. Met., 101(1999) 588.

[16] E. Faulgnes, W. Wallufer, H. Kuzmany, J. Chem. Phys., 90 (12) (1989) 7585.

[17] S.V. Meille, A. Farina, F. Bezziccheri and M.C. Gallazzi. Adv. Mater., 6 (1994) 848; Philippe Leriche, Mathieu Turbiez, Vincent Monroche, Pierre Frère, Philippe Blanchard, Peter J. Skabara and Jean Roncali, Tetrahedron Letters, 44 (2003) 649.

[18] J-F. Pan, S.L. Chua, W. Huang. Chem. Phys. Lett., 363 (2002) 18.

[19] JL. Bredas, R. Silbey, DS. Boudreaux, RR. Chance, J. Chem. Soc., 105 (1983) 6555.

[20] J. P. Hay, J. Phy. Chem., A 106 (2002) 1634; S. Hong, D. Y. Kim, C. Y. Kim, R. Hoffmann, Macromolecules, 34 (2001) 6474; Li Yang, Ji-Kang Feng, Ai-Min Ren and Jia-Zhong Sun, Polymer 47 (2006) 1397 ; Songwut Suramitr, Supa Hannongbua and Peter Wolschann, J. Mol. Struct. (THEOCHEM), 807 (2007) 109.

[21] U. Salzner, J. B. Lagowski, P.G. Pickup, R.A. Poirier, Synth. Met., 96 (1998) 177 ; P. Puschning, C. Ambrosch-Draxl, G. Heimel, E. Zojer, R. Resel and G. Leising., Synth. Met., 116 (2001) 327; Puschnig and C. Ambrosch-Draxl. Phys. Rev., B 60 (1999) 7891.

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