ANALELE UNIVERSITATII BUCURESTI
Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
*p*ISSN: 1220-871X *e*ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com

EXPERIMENTAL AND QUANTUM CHEMICAL INVESTIGATION OF NEW ELECTROLUMINESCENT MATERIAL BASED ON THIOPHENE, PHENYLENE AND ANTRACENE

M. Bouachrine *, **O. Benaqqa** *,**, **H. Toufik** *, **M. Hamidi** ***, **J.-P. Lère-Porte******, **F. Serein-Spirau** **** **and A. Amine** ****

abstract: In this paper, we first report, the synthesis and physical properties of a recent soluble polymer based on thiophene, phenylene and antracene. Then, we present a detailed DFT study based on B3LYP/6-31G* 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 of the properties of copolymer.

key words: Conjugated polymers; thiophene-phenylene; antracene; DFT; electronic properties.

received: May 29, 2010 *accepted*: June 25, 2010

I. Introduction

Organic materials based on conjugated molecules have gained much interest as a novel class of semi-conductors and are frequently studied thanks to 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 and 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

---

* UMIM, Faculté Polydisciplinaire de Taza, Université Sidi Mohamed Ben Abdellah, B.P.1223/Taza Gare, Maroc, *corresponding author e-mail*: bouachrine@gmail.com

** LCBAE, Département de chimie, Faculté des Sciences de Meknes, Université Moulay Ismail, B.P. 4010 Beni M'hamed, Meknes, Morocco

*** URMM/UCTA, Faculté des Sciences et Techniques, B. P. 509 Boutalamine, 5200, Errachidia, Maroc

**** Hétérochimie Moléculaire et Macromoléculaire, UMR CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 05, France

exposed to the visible light. To improve the 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.

For a good understanding of 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. On the other hand, 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 the 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 antracene showing very good absorption properties. The schematic picture of the polymer can be seen in Fig. 1. Calculated results are compared with experimental data. Based on such comparison, we try first to investigate and suggest an oligomer model and then to obtain a qualitative understanding of the polymer's properties.

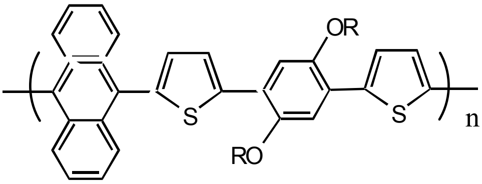

Fig. 1 *The chemical structure of the studied copolymer.*

II. Experimental and computations

Gel permeation chromatography (GPC) and Raman spectroscopy were used to determine the chemical structure of the resulting copolymers. Raman spectra were registered on a

Fourier Transformed (FTIR) 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 a 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 were investigated using ZINDO 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].

III. Results and discussion

III.1. Synthesis, characterization and properties

III.1.1. Copolymer synthesis

The synthesis of the thiophene/phenylene/antracene copolymer poly(**TPant)** was achieved, as shown in Fig. 2., by Stille coupling [13] using equimolar amounts of 9.10-dibromo anthracene stannyled (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.

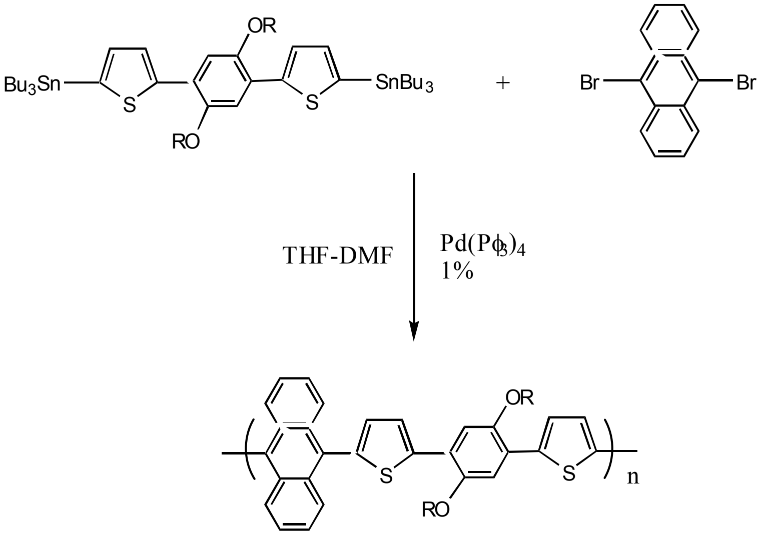

Fig. 2 *Synthesis of the copolymer.*

Our results are in agreement with the analytical data, elemental analysis, ^{1}H NMR and FTIR reported in ref [5] are consistent with the copolymer structure. The polymer is soluble in organic solvents (THF, $CHCl_3$). The molecular weights of the copolymer are evaluated through gel permeation chromatography (GPC) calibrated by polystyrene standard. The average- number molecular weight (Mn) of the synthesized copolymer poly(TPanth) was 4942 (Mw/Mn = 102). Thus, we note that this copolymer exhibits a relatively low molecular weight with polydispersity index (Mw/Mn) value equal to 102. It indicates an average degree of polymerization (DPn) of 7 corresponding in average to 42 consecutive alternating aromatic rings (Table 1).

Table 1 *Gel permeation chromatography (GPC) analyses.*

GPC results	M_n	M_w	I= M_n/M_w	DPn	Number of cycles
	4342	5080	1.02	7	42

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

III.1.2. Spectroscopy results

We have studied the powder of the copolymer by Raman. The Raman spectrum is showed in Fig 3. 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 have 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.

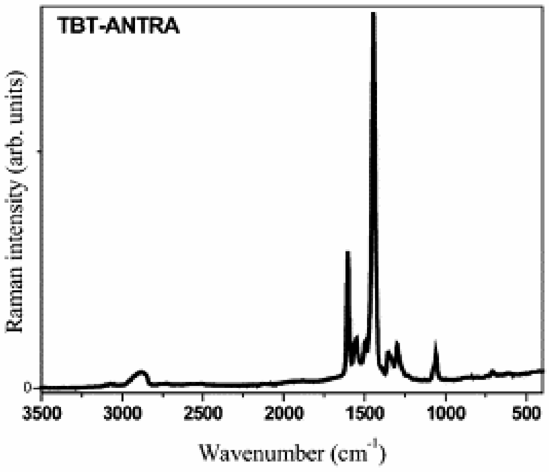

Fig. 3 *Raman spectra of the copolymer.*

In order to achieve the relationship between structural properties for different copolymers, we have studied their optical characteristics (UV-VIS absorption and PL emission) and even their optimization geometries with density functional theory (DFT) calculations.

III.1.3. Optical and photoluminescence properties

Fig. 4 shows the absorption and the emission spectra recorded 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(TPant) exhibits an absorption spectra where the maximum absorption λ_{ab} appears at 453 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 ~2.52 eV. An important red shift of the absorption maximum is recorded and attributed to a higher mean conjugation length in the solid state and to interchain electronic coupling λ_{ab}= (453 nm). In fact, in the solid state, intermolecular interactions favor the coplanar arrangements of the aromatic rings that may be responsible for the observed enhanced conjugation.

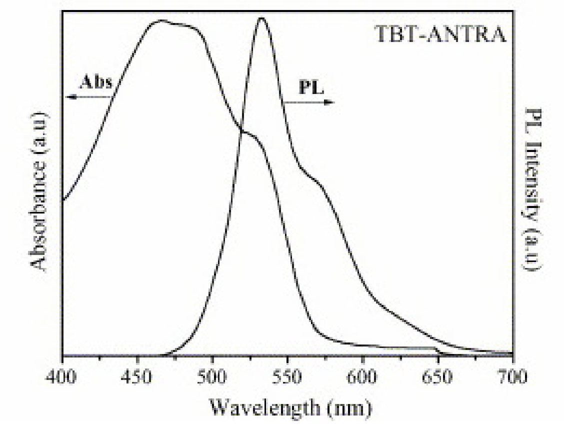

Fig. 4 *Optical absorption and photoluminescence spectra of the copolymer*

Table 2 *Optical properties of the copolymer*

absorption λ_{ab} (nm)	emission λ_{em} (nm)	Optical band gap (eV)
453	533	2.52

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(TPant) are red-shifted (λ_{em}= 533 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 appears 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].

IV. Theoretical results

IV. 1. Geometric parameters

The optimized ground state geometries of the chose model obtained at the B3LYP/6-31G* level are given in Fig. 5. The optimized inter-ring bond lengths and dihedral angles between the subunits (θ_1=1-2-3-4; θ_2= 4-5-6-7; θ_3= 8-9-10-11) are summarized in Table 3.

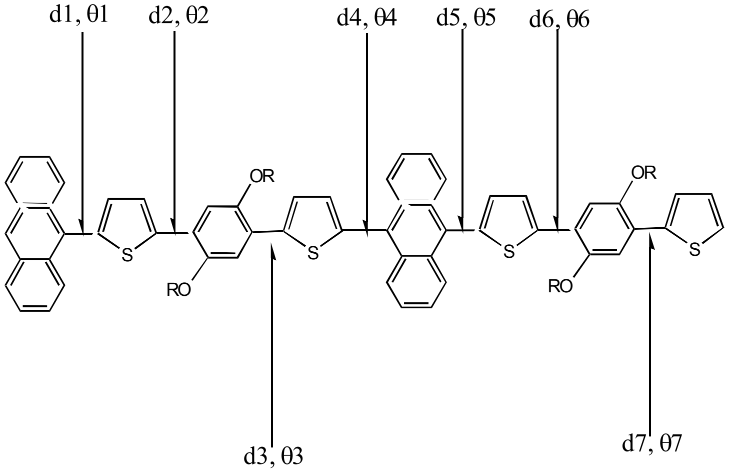

Fig. 5 *Structure for a chosen model of the studied copolymer.*

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

d1(d5) (Å)	d2 (d6) (Å)	d3 (d7) (Å)	d4 (Å)
1.484	1.467	1.466	1.484
θ1 (°)	θ 2 (°)	θ 3 (°)	θ 4 (°)
–94.93	159.55	155.55	–93.94

The results of the optimized structures for the copolymeric molecules show that all molecules possess non-planar structures. We 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 1.467 Å. The dihedral angles (θ_i, i = 1 – 4) are also collected in Table 3. The inter-ring torsions between thiophene and phenylene are evaluated to be about $\theta_{1\,=}\,94.93°$, $\theta_{2\,=}\,159.55°$, $\theta_{3\,=}\,155.55°$, $\theta_{4\,=}\,93.94°$, rather than $\theta = 27.7°$, the same thing occurring 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's of phenyl ring is clearly seen. We believe that the difference between the values of θ_i is due 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].

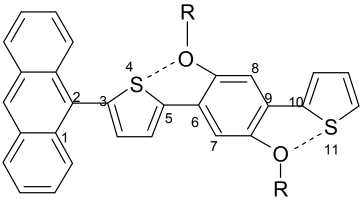

Fig. 6 *Intramolecular interactions between S and O are indicated by dotted lines.*

IV. 2. Electronic properties

IV. 2. 1. Frontier molecular orbitals and HOMO–LUMO gaps

It is important to examine the HOMO and the LUMO orbitals for this oligomer because the relative ordering of the occupied and virtual orbitals provides a reasonable qualitative indication of the excitation properties and the ability of electron hole transport. In general, as plotted in Fig. 7, HOMO is localized on the entire chain while LUMO is localized on cycle.

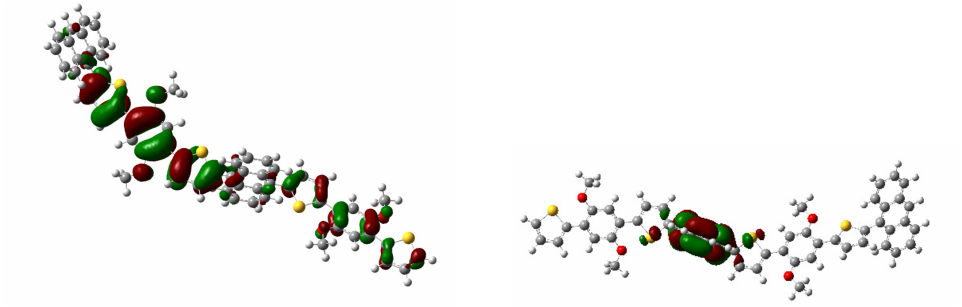
HOMO LUMO

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

The HOMO and LUMO energies may be 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. Also, the HOMO and LUMO energies can be obtained 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.

We present, in Table 4, the DFT calculated the HOMO and LUMO energies and the HOMO-LUMO energy gap E_{gap} = LUMO-HOMO.

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

E(HOMO)	E(LUMO)	E(Gap)
–5.00215	–1.7625	3.239

The band gaps in conjugated polymers are governed by their chemical structures. Band gap for infinite chains (polymer) can be determined 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 oligomer, the obtained value (3.23 eV) is sufficient to consider applications of this oligomer in optoelectronic devices.

IV. 2. 2. Absorption properties

The ZINDO method has been used 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_{ab} for the proposed oligomer and the available experimental data of the studied copolymer are exhibited in Table 5.

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

Experimental λmax of the copolymer in Chloroform	Calculated λmax (ZINDO)	Calculated λmax (TD/DFT)
453 nm	425.67 nm	428.17 nm

The 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. This is reasonable, since HOMO→LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition as analyzed above. The results are a decrease of the LUMO and an increase of the HOMO energy.

These values are calculated by ZINDO and TD method starting with optimized geometry obtained at B3LYP/6-31G* level. We believe that the bulk of intermolecular effect must be taken into account when considering the polymers with long chains. After considering this effect, our calculations are in good agreement with the experimental values (λ_{max} = 453 nm). 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 optoelectronic properties of the proposed oligomer and can be employed to predict the electro-luminescence characteristics of other materials. However, the problem is that the first experimental large absorption band is the result of three overlapping absorption bands due to three electronic transitions. That is why the first transition S1 → S0 is probably located at above 525 nm and not 453 nm.

These results lead us to suggest that the proposed structure is a good model which reflects the optoelectronic properties for the parent polymer.

V. Conclusions

A new soluble copolymer based on thiophene, phenylene and antracene 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, $\lambda_{abs} =$ 428.15 nm). 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, however 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.) (1986) **Handbook of conducting Polymers**, Marcel Dekker, New York.
2. Bernier, Lefrant and Bidan (Eds.) (1995) **Advances in Synthetic Materials, Twenty Years of progress in Sciences and Technology**, Elsevier,
3. ***Special issues on molecular materials for electronic and optoelectronic devices (1999) *Acc. Chem. Res*. **32** 191.
4. H.J. Snaith, N.C. Greenham and R.H. Friend, (2004) *Adv. Mater*. 16, 1640.
5. Y. Kim, S. Cook, S.A. Choulis, J. Nelson, J.R. Durrant and D.D.C. Bradley, (2004) *Chem. Mater*. 16**,** 4812.
6. H. Spanggaard and F.C. Krebs, (2004) *Sol. Energy Mater. Sol. Cells* 83**,** 125.
7. P. Damman, M. Dosière, M. Brunel and J.C. Wittmann, (1997) *J. Am. Chem. Soc*. 119**,** 4633.
8. Shu Hotta, Midori Goto, Reiko Azumi, Masamitsu Inoue, Musubu Ichikawa, and Yoshio Taniguchi, (2004) *Chem. Mater*. **16**(2), 237.
9. S. Hotta; Kimura, H. Lee, S. A. Tamaki, T. (2000) *J. Heterocycl. Chem*. **37**, 281.
10. S. Hotta, T. J. Katagiri, (2000) *Heterocycl. Chem*. **40**, 845.
11. M. Bouachrine, S. Bouzakraoui, M. Hamidi, S. Ayachi, K. Alimi, J-P.Lère-Porte, J. Moreau, (2004) *Synth., Met.* **145**, 237.
12. H. Sarker, I. Ong, S. Shuker, P. C. Searson, T. O. Poehler, (2000) *Synth. Met*. **108**, 33.
13. Haripada Sarker, Ivan W. Ong, Peter C. Searson and Theodore O. Poehler, (2000) *Synth. Met.* **113**, 151.
14. J. Pei, W. L. Yu, W. Huang, (2000) *Macromolecules* **33**, 2462.
15. Jian Pei, Wang-Lin Yu, Wei Huang and Alan J. Heeger, (1999) *Synt. Met.* **105**, 43.
16. J. Pei, W. L. Yu, W. Huang, (2000) *Macromolecules* **33**, 2462.

17. M. Nisoli, V. Pruneri, S. De Silvestri, V. Magni, A. M. Gallazzi, C. Romanoni, G. Zerbi, G. Zotti, (1994) *Chem. Phys. Lett.* **220**, 64.
18. M. Mushrush, A. Facchetti, M. Lefenfeld, H. E. Katz, T. J. J.Marks, (2003) *Am. Chem. Soc.* **125**, 9414.
19. M. C. Gallazzi, L. Tassoni, C. Bertarelli, G. Pioggia, F. Di Francesco, E. Montoneri, (2003) *Sensors and Actuators B: Chemical* **88**, 178.
20. Muzaffer Can, Fatma Sevin and Attila Yildiz, (2003) *Applied Surface Science* **210**, 338.
21. D.A. dos Santos, D.S. Galvao, B. Laks and M.C. dos Santos. (1992) *Synth. Met.* 51**,** 203.
22. M. Belletête, M. Leclerc and G. Durocher. (1994) *J. Phys. Chem*. 98, 9450.
23. C. Aleman, V.M. Domingo, L. Fajari, L. Julia and A. Karpfen. (1998) *J. Org. Chem*. 63**,** 1041.
24. Nicolas DiCésare, Michel Belletête, Mario Leclerc and Gilles Durocher, (1999) *Journal of Molecular Structure* (THEOCHEM) **467**, 259.
25. Nicolas DiCésare, Michel Belletête, Anne Donat-Bouillud, Mario Leclerc and Gilles Durocher, (1999) *Journal of Luminescence* **81**, 111.
26. F.C. Grozema, LP. Candeias, M. Swart, P. Van Duijnen, J. Wildemen, G. Hadzianon, (2002) *J. Chem. Phys.* **117**(24), 11366.
27. Jean-Francois Briere and Michel Cote, (2004) *J. Phys. Chem. B* **108**(10), 3123.
28. Yunqiao Ding, Dacheng Feng, Shengyu Feng, Jie Zhang and Ju Xie, (2006) *Polymer* **47**, 368.
29. Kotaro Honda, Yukio Furukawa and Hiroyuki Nishide (2006) *Vibrational Spectroscopy* **40**, 149.
30. S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, (2005) *J. Mol. Struct*. (THEOCHEM) **725**, 39.
31. S.M. Bouzzine, S. Bouzakraoui, M. Bouachrine, M. Hamidi, (2005) *J. Mol. Struct*. (THEOCHEM) **726**, 269.
32. ***Gaussian Inc. (2003) *GAUSSIAN 98*, Revision A 7, Pittsburgh, PA.
33. C. Lee, W. Yang, R. G. Parr, (1993) *Phys. Rev. B* **37**, 785.
34. L Yang, J. Feng, A. Ren, (2005) *Polymer* **46**, 10970.
35. Harcourt Brace Jovanovich Publishers (1989) **The handbook on Infrared and Raman Characteristic Frequencies of Organic Molecules**, Academic Press, Inc., New York.
36. H. Zgou, M. Hamidi, M. Bouachrine, (2007) *J. Mol. Struct*. (THEOCHEM), in press.
37. J-P, Lère-Porte, J.J.E Moreau and C. Torreilles, (1999) *Synt. Met.* **101**, 588.
38. E. Faulgnes, W. Wallufer, H. Kuzmany, (1989) *J. Chem. Phys*. **90**(12), 7585.
39. S.V. Meille, A. Farina, F. Bezziccheri and M.C. Gallazzi. (1994) *Adv. Mater*. 6**,** 848.
40. Philippe Leriche, Mathieu Turbiez, Vincent Monroche, Pierre Frère, Philippe Blanchard, Peter J. Skabara and Jean Roncali, (2003) *Tetrahedron Letters* **44**, 649.
41. J-F. Pan, S.L. Chua, W. Huang. (2002) *Chem. Phys. Lett*. **363**, 18.
42. JL. Bredas, R. Silbey, DS. Boudreaux, RR. Chance, (1983) *J. Chem. Soc.* **105**, 6555.
43. J. P. Hay, (2002) *J. Phy. Chem. A* **106**, 1634.
44. S. Hong, D. Y. Kim, C. Y. Kim, R. Hoffmann, (2001) *Macromolecules* **34**, 6474.
45. Li Yang, Ji-Kang Feng, Ai-Min Ren and Jia-Zhong Sun, (2006) *Polymer* **47**, 1397.
46. Songwut Suramitr, Supa Hannongbua and Peter Wolschann, (2007) *J. Mol. Struct*. (THEOCHEM) **807**, 109.
47. U. Salzner, J. B. Lagowski, P.G. Pickup, R.A. Poirier, (1998) *Synth. Met*. **96**, 177.
48. P. Puschning, C. Ambrosch-Draxl, G. Heimel, E. Zojer, R. Resel and G. Leising., (2001) *Synth. Met*. 116**,** 327.
49. Puschnig and C. Ambrosch-Draxl. (1999) *Phys. Rev. B* 60**,** 7891.