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Semi-Empirical (PM3) Study of Conformational Analysis and Electronic Properties of Functionalized Oligohexylthiophenes

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A semi empirical analysis of a series of 3-hexylthiophenes [3-XHT, where X = Br, NH_2, SH, CN, COOH, $CONC(CH_3)_2$ and $N(CH_3)_2$] having functional group attached to the hexyl substituent up to four monomeric units with head-tail-head-tail regioselectivity was carried out. The energy band gap obtained at PM3 level and the results showed that oligomers with 3-(N,N-dimethyl)aminohexylthiophene (3DAHT) present lowest energy band gap although larger that than 3-aminothiophene (3HT). 3DAHT and 3-aminothiophene (3AHT) both with electron donating substituents respond differently when the polymer was torsioned. The electronic donating ability of NH_2 through the hexyl carbon-carbon bonds was drastically reduced whereas that of $N(CH_3)_2$ was enhanced. The energy band gap changed with the functional group attached to hexyl substituents with some effects on the molecular properties related to electronic conductivity.

Key Words: Functionalized hexylthiophenes, Energy band gap, Semi empirical (PM3).

INTRODUCTION

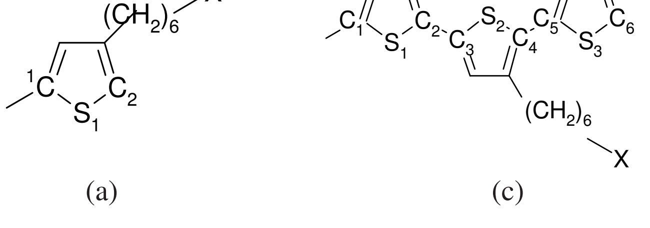
Regioregular polyalkylthiophenes are important building blocks for new electrical applications such as field effect transistors and nanoscale materials[1]. One way of adding complexity to the family of polythiophenes is side chain elaboration. The electronic and photonic properties of polythiophenes with functionalized side chains are known to be sensitive to chemical and electrochemical perturbations, chemical structure and ordering in solution[2,3]. These properties have made these series of polythiophenes interesting materials for chemosensors[4,5], through production of a variety of functionalized polymers with oxidized π-electrons with good conductivities and stability at oxygen atmosphere[6-10].

Recently theoretical quantum mechanical methods have been applied to the study of thiophene derivatives[11-16]. Oligomers up to six thiophene monomeric units have been considered with substituents like nitro[11], cyano[12] and phenyl[13] and the energy band gap was estimated (from LUMO-HOMO energy difference) using the configuration interaction (CI) approach. The head-tail-head-tail and head-head-tail-tail coupling of poly(3-alkylthiophenes) oligomers up to six monomeric units were also studied using Hartree Fock (HF) and density functional theory (DFT)[17,18]. Generally, the nature, length of alkyl side chains and bulkiness of side chains have been found to have great effect on performance and field-effect mobility of the polymers. The hexyl group at position 3 on the heterocyclic polymers has also been found to have better and long-term performance[19,20].

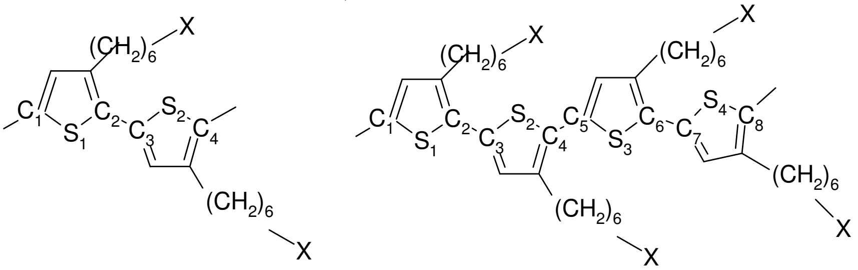
In this present work, we investigate the functionalized poly(3-hexylthiophenes, 3HT) oligomers of n monomeric units (n = 1, 2, 3 and 4) arranged in head-tail-head-tail fashion using semi empirical method at PM3 level of calculations. The functional groups chosen are electron donating [NH_2, SH and $N(CH_3)_2$], electron withdrawing (CN and COOH) and the intermediate between the two classes [Br and $CONC(CH_3)_2$] to study the effect of functional groups on electronic properties of hexylthiophenes. Structures and electronic properties are discussed as function of the number of monomeric units and functionalized hexyl substituent.

COMPUTATIONAL DETAILS

Conformational analysis was carried out on the molecules sketched in Fig. 1 while the optimized structures of dimer, trimer and tetramer of 3-hexylthiophenes are presented in Fig. 2. Initial geometries were fully optimized using semi empirical method at PM3 level[21]. The vibrational frequency calculations were carried out to characterize the stationary points without any imposition of symmetry constraint. The derivatives of hexylthiophenes (3HT) considered are 3-bromohexylthiophene (3BHT), 3-(2(4,4-dimethylthyloxazolin-2-yl)-heptylthiophene (3DTHT), 3-heptanic acid thiophene (3HAT), 3-thiohexylthiophene (3THT), 3-cyanohexylthiophene (3CHT), 3-aminothiophene (3AHT) and 3-(N,N-dimethyl)-aminohexylthiophene (3DAHT) as represented in Figs. 1a-d. All calculations were performed using Spartan Essential 2.0.1 version[22] running on Pentium III 1.60 GHz computer.



(a) (c)



(b) (d)

Fig. 1. Head-tail-head-tail (HT-HT) structure of functionalized poly(3- hexylthiophenes) oligomers of n monomeric units (n = 1,2, 3 and 4) where, X = Br, NH_2, SH, CN, COOH, $CONC(CH_3)_2$ and $N(CH_3)_2$

RESULTS AND DISCUSSION

Geometries: The bond lengths and bond angles are listed in Tables 1-3. The bond lengths of S_1-C_1 for monomers are the same (1.723 Å) except 3DAHT that is shortened by 0.013 Å. The S_1-C_1 bond length for the monomers when compared to experimental value and B3LYP/CEP6-31G* deviated by 0.009 Å and 0.026 Å, respectively[17]. The bond lengths (except 3DAHT which slightly shortens) and C-S-C bond angles of all functionalized hexyl substituents considered are similar without appreciable differences as compared to 3HT. However, for tetramers the inter-ring bond lengths between rings 2 and 3 become longer (3DAHT is shortened), this means that the functional groups on the hexyl have little or no effect on geometry of 3HT and the structure remain untwisted at equilibrium geometry as the polymer chains grow. There is slight lengthening of S_1-C_2 and shortening of S_1-C_1 as 3XHT becomes larger, which indicates an increment in delocalization of π-electrons, hence increase in conductivity character[18] (Table-3).

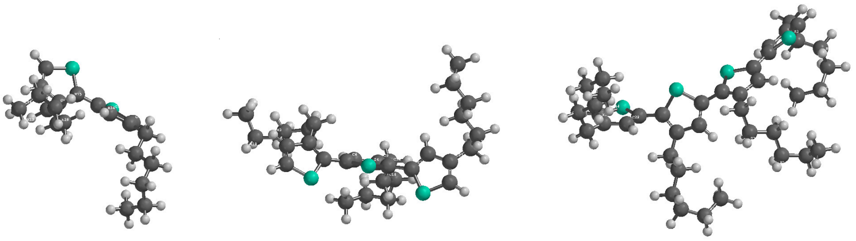


Fig. 2. Optimized structures of dimer, trimer and tetramer of 3-hexylthiophenes (3HT) at PM3

TABLE-1
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR OPTIMIZED STRUCTURE OF FUNCTIONALIZED POLY(HEXYLTHIOPHENES) OLIGOMERS AT PM3

Number of units (n)	3-Hexylthiophene derivatives							
	3BHT	3AHT	3THT	3CHT	3HAHT	3DTHT	3DAHT	3HT
n = 1								
Bond length								
S_1-C_1	1.723	1.724	1.723	1.723	1.723	1.723	1.708	1.723
S_1-C_2	1.725	1.726	1.725	1.725	1.725	1.725	1.710	1.725
Bond angle								
$C_2S_1C_5$	91.46	91.42	91.44	91.45	91.49	91.44	91.43	91.45
n = 2								
Bond length								
S_1-C_1	1.721	1.721	1.720	1.721	1.721	1.721	1.704	1.720
S_1-C_2	1.746	1.747	1.746	1.746	1.746	1.746	1.716	1.748
C_2-C_3	1.444	1.444	1.444	1.444	1.444	1.444	1.440	1.442
S_2-C_3	1.746	1.747	1.746	1.746	1.746	1.746	1.711	1.747
S_2-C_4	1.721	1.721	1.721	1.721	1.721	1.721	1.709	1.721
Bond angle								
$C_1S_1C_2$	91.33	91.33	91.34	91.34	91.33	91.34	91.34	91.39
$C_3S_2C_4$	91.27	91.26	91.27	91.27	91.27	91.27	91.27	91.30
n = 3								
Bond length								
S_1-C_1	1.720	1.721	1.720	1.720	1.720	1.720	1.720	1.720
S_1-C_2	1.746	1.746	1.746	1.746	1.746	1.746	1.748	1.746
C_2-C_3	1.443	1.443	1.446	1.443	1.443	1.445	1.442	1.444
S_2-C_3	1.742	1.743	1.742	1.742	1.742	1.743	1.743	1.745
S_2-C_4	1.745	1.745	1.744	1.744	1.745	1.745	1.745	1.744
C_4-C_5	1.444	1.444	1.444	1.444	1.444	1.444	1.444	1.442
S_3-C_5	1.746	1.746	1.746	1.745	1.746	1.746	1.746	1.748
S_3-C_6	1.720	1.721	1.720	1.720	1.720	1.720	1.721	1.719
Bond angle								
$C_1S_1C_2$	91.37	91.38	91.36	91.37	91.36	91.30	91.41	91.27
$C_3S_2C_4$	91.26	91.25	91.24	91.26	91.28	91.14	91.27	91.27
$C_5S_2C_6$	91.27	91.26	91.29	91.28	91.29	91.29	91.27	91.42

Torsion potentials: The torsion potential curves of dimers for 3BHT, 3DTHT, 3HAHT, 3THT, 3CHT, 3AHT, 3DAHT and 3HT associated with the rotation of the two rings in different directions are displayed in Fig. 3. The energy barrier height is compared to the equilibrium energy of 3XHT dimers in the free state. Analysis of Fig. 3 shows that potential curves for 3XHT dimers are not flat but present shallow curves except 3HT which increase linearly (linear correlation is 0.98) in energy with increase in torsion

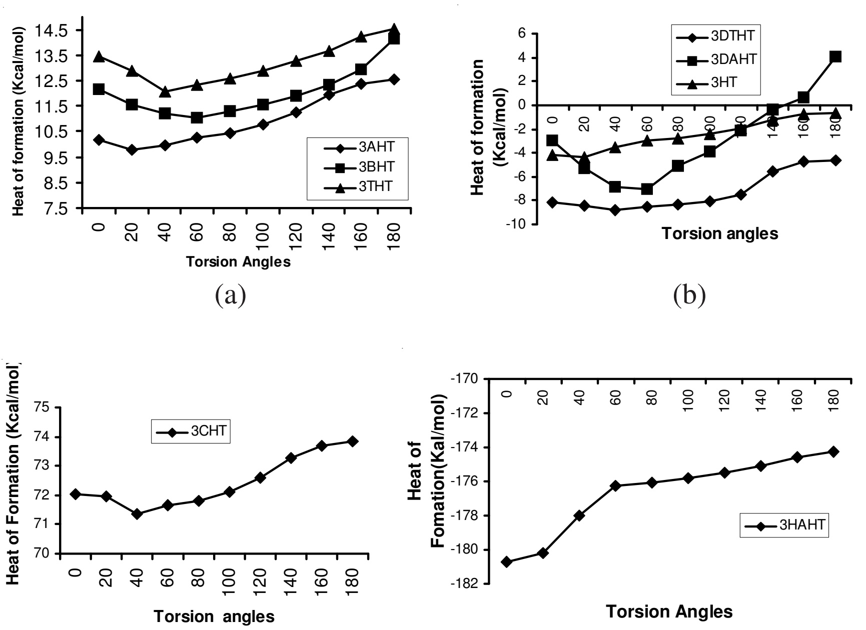
TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR OPTIMIZED STRUCTURE OF FUNCTIONALIZED POLY(HEXYLTHIOPHENES) OLIGOMERS AT PM3

Number of units (n)	3-Hexylthiophene derivatives							
	3BHT	3AHT	3THT	3CHT	3HAHT	3DTHT	3DAHT	3HT
n = 4								
Bond length								
S_1-C_1	1.720	1.720	1.720	1.720	1.720	1.720	1.704	1.720
S_1-C_2	1.746	1.747	1.746	1.746	1.746	1.746	1.715	1.746
C_2-C_3	1.444	1.444	1.444	1.444	1.444	1.444	1.439	1.443
S_2-C_3	1.743	1.744	1.743	1.743	1.743	1.743	1.709	1.745
S_2-C_4	1.741	1.740	1.740	1.740	1.740	1.741	1.709	1.743
C_4-C_5	1.445	1.445	1.445	1.445	1.445	1.445	1.436	1.442
S_3-C_5	1.742	1.742	1.742	1.742	1.742	1.743	1.704	1.746
S_3-C_6	1.745	1.744	1.744	1.744	1.744	1.746	1.714	1.743
C_6-C_7	1.444	1.444	1.444	1.444	1.444	1.443	1.439	1.441
S_4-C_7	1.743	1.743	1.743	1.742	1.743	1.744	1.709	1.749
S_4-C_8	1.721	1.722	1.721	1.720	1.721	1.724	1.710	1.721
Bond angle								
$C_1S_1C_2$	91.34	91.34	91.35	91.35	91.34	91.34	91.40	91.28
$C_3S_2C_4$	91.10	91.10	91.14	91.14	91.14	91.08	91.26	91.28
$C_5S_3C_6$	91.08	91.03	91.13	91.14	91.13	91.01	91.36	91.39
$C_7S_4C_8$	91.27	91.20	91.23	91.26	91.24	91.20	91.40	91.32

TABLE-3
DIHEDRAL ANGLES (°) OF FUNCTIONALIZED POLY(3-HEXYLFURANS) OLIGOMERS (n = 2, 3 and 4) at PM3

Thiophene	n = 2	n = 3		Dihedral angle		
	$S_1C_2C_3S_2$	$S_1C_2C_3S_2$	$S_2C_4C_5S_3$	$S_1C_2C_3S_2$	$S_2C_4C_5S_3$	$S_3C_6C_7S_4$
3BHT	-91.87	61.48	-48.80	61.73	-46.77	62.14
3AHT	-92.33	59.28	-44.24	61.15	-49.50	149.28
3THT	-85.77	58.88	-45.50	59.19	-45.70	88.70
3CHT	-51.93	62.67	-46.12	57.51	-55.62	142.72
3HAHT	-79.53	61.42	-74.66	62.37	-50.79	123.48
3DTHT	-58.66	59.16	-55.06	66.07	-64.67	125.85
3DAHT	-53.61	62.64	-74.76	62.48	-85.55	117.81
3HT	-52.24	61.97	-47.99	60.58	-47.16	149.75

angles. The energy barrier towards 0° and 90° conformations are 0.08 and 1.64 Kcal/mol, respectively and that towards 180° conformation is 3.62 Kcal/mol, therefore the polymer could adopt 0°-90° conformation when closely packed. The energy barriers height towards 0° conformation for 3AHT, 3BHT, 3DAHT and 3THT are 1.05, 1.39, 0.51 and 1.63 Kcal/mol and that towards 180° conformation are 1.36, 3.37, 6.51 and 2.68 Kcal/mol, respectively and they are less than 1.0 Kcal/mol for perpendicular conformation in exception of 3DAHT (2.0 Kcal/mol). The equilibrium torsion angles for 3AHT, 3BHT, 3DAHT and 3THT are 60°, 80°, 60° and 20°, respectively, meanwhile the torsional potential in the region between 20°-80° for 3BHT, 0°-60° for 3AHT and 40°-60° are quite flat. These segments would be flexible in the free state and may be driven to more coplanar conformations by the packing force[23].



(a) (b)

(c) (d)

Fig. 3. Torsion potential curves of the functionalized hexylthiophenes obtained with PM3 calculations

In the case of 3DTHT and 3CHT, the energies barriers towards 0° conformation are 4.78 and 2.88 Kcal/mol; for 180° conformation are 8.31 and 4.69 Kcal/mol and towards perpendicular conformation are 4.75 and 2.82 Kcal/mol, respectively. The energy barrier is sufficiently high especially for 3DTHT to inhibit a co-planar conformation[24]. The change in 3HAHT is not similar to others in the sense that the energy barrier towards co-planar is lower while that of perpendicular conformation is higher (Fig. 3). The change of the torsion curves for all the functionalized hexyl thiophenes (except 3HAHT) are similar with that of the dihexyl-substituted bithiophene

(DHBT)[23] and 3,3'-diehyl-bithiophene (DE33BT)[24]. Increase in energy barrier and change in torsion curves of the functionalized polymers (3XHT) as compared to hexyl polymer (3HT), indicates that addition of functional groups can be used to selectively control the electronic and molecular properties of the hexylpolymer.

Energy bands gaps: Spectroscopic data for organic π-systems are usually determined either in solution or in solid state (crystal or thin film). Since our calculations are for isolated molecules in the gas phase, we have attempted to compare our calculations to un-substituted thiophene oligomers and also with alkyl thiophene oligomers results performed at different levels of calculations.

The energy band gaps calculated for all functionalized polyhexylthiophene oligomers considered have lower energy band gaps as compared to those calculated using HF/6-31G*(d)[23]. This is not only due to overestimate of energy band gap because of the absence of correlation contribution[25], but also as a result of effect of functional group attached to the hexyl substituent (Table-4). Although, the energy gaps calculated are higher than the experimental results of un-substituted monomer[26] and dimer[27], this could be improved by using DFT and advance correlation methods. However, our interest is to study the effect of functional groups on electronic properties of hexylthiophenes (3HT). The analysis of the values HOMO-LUMO differences of the tetramers (Table-4) show that the energy band gaps obtained for hexylthiophenes could be arranged in decrease order as 3DTHT > 3BHT > 3HAHT ~ 3CHT > 3THT > 3DAHT > 3AHT > 3HT. It is interesting to note that decrease in energy band gap is observed as the oligomer chain becomes larger. Although the energy band gaps are larger than that of 3HT, the electron donating effect of $N(CH_3)_2$, NH_2 and SH through hexyl carbon-carbon bonds are noticed by presenting lower energy band gap as compared to other functional groups. The extrapolated energy band gaps of the infinity polymers were predicted as shown in Table-4 and Fig. 4. The

TABLE-4
HOMO-LUMO ENERGY BAND DIFFERENCE [ENERGY BAND GAP (Eg)] IN eV AT PM3 LEVEL OF SEMI EMPIRICAL CALCULATIONS

Thiophene unit	3BHT	3AHT	3THT	3CHT	3HAHT	3DTHT	3DAHT	3HT
Monomer	9.20	9.14	9.02	9.21	9.20	9.20	8.89	9.20
Dimer	8.57	8.89	8.45	8.59	8.57	8.58	8.40	8.38
Trimer	8.04	7.88	8.05	8.03	8.06	8.37	7.97	7.95
Tetramer	8.03	7.58	7.96	7.97	7.97	8.28	7.72	7.54
H*	7.62	7.66	7.63	7.58	7.59	7.97	7.48	7.19

H* = Energy band gap for the infinity polymers calculated considering a linear behaviour Eg with 1/n being number of monomeric units.

quality of the correlation used is exemplified for the HT-HT derivatives as shown in Figs. 1 and 2 and the results obtained in the present study show that the inclusion of functional groups to hexyl side chain in thiophene derivatives allows selective control of the molecular structure and energy band gaps that are sufficient to control macroscopic properties.

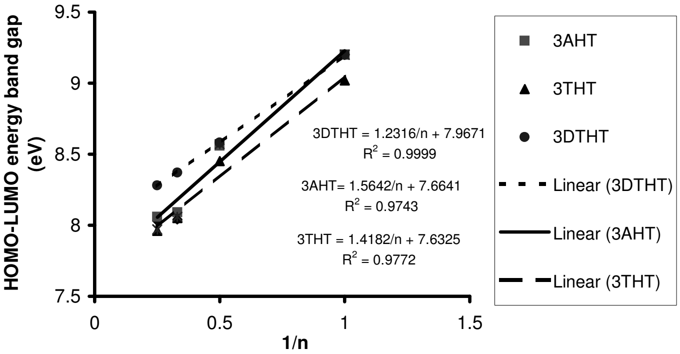


Fig. 4. Correlation of energy band gap (Eg) and reciprocal of the number of thiophenes (1/n), n being the number of monomeric units

Fig. 5 shows the evolution of the energy difference (ΔE) between the HOMO and the LUMO of 3BHT, 3DTHT, 3HAHT, 3THT, 3CHT, 3AHT, 3DAHT and 3HT dimers as function of torsion angles. As expected, the increment in interring torsion angles reduces the π-electrons delocalization and consequently increases the energy band gap (ΔE) between the HOMO and the LUMO. It is observed that the increment in ΔE becomes higher at the large torsion angles. This is important for the effect of the torsion angles in different torsion range, which means that the effect is less at the low torsion angle than at higher ones. All the curves except 3THT are more or less overlap in lower torsions and 3DTHT, 3HAHT, 3THT, 3CHT and 3HT overlap through out the torsion range indicating that the functional groups $CONC(CH_3)_2$, COOH, Br and CN have little or no electronic effect on the hexyl thiophene dimers especially when torsioned. On the other hand, the curves for 3THT and 3AHT lie above, indicating less electronic donating effect of the functional groups SH and NH_2 on the hexyl thiophene dimers. The curve for 3DAHT lies far below, indicating stronger electronic donating effect of functional group $N(CH_3)_2$. It is interesting to note that $N(CH_3)_2$ and NH_2 are both electron donating substituents but respond differently (opposition) when the polymer is torsioned, electronic donating ability of NH_2 through the hexyl carbon-carbon bonds is drastically reduced whereas that of $N(CH_3)_2$ is enhanced when the polymer is torsioned (Table-4 and Fig. 5). It could be argued that in molecular and electronic properties modulation of hexylthiophene using functional groups, polymer films preparation can affect regulating ability of the functional group attached to hexyl substituent as it is in torsional behaviours of $N(CH_3)_2$ and NH_2 functional groups. All curves are similar to those observed for bithiophene (BT) and dihexyl-substituted bithiophene (DHBT)[24], therefore the photoluminescence (PL) efficiency of the functionalized hexyl thiophenes considered are expected to decrease as the torsion angles increase[24].

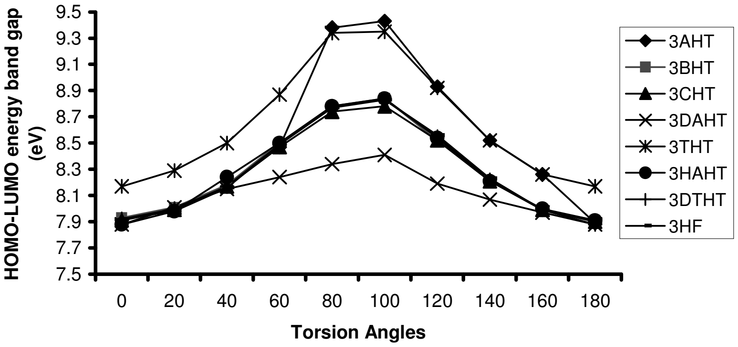


Fig. 5. Evolution of the energy difference between the HOMO and the LUMO as a function of the torsion angle between the rings at PM3 level of calculation

Conclusion

The structure and energy band gap are calculated for a series of functionalized poly(3-hexylthiophenes) oligomers using semi empirical methodology based on PM3 approaches.

The functionalized oligo(3-hexylthiophenes) energy band gaps calculated in the phase are found to be lowered for hexylthiophene carrying tertiary amine substituent (3DAHT), although higher than that of 3HT, indicating that tertiary amine has stronger electronic donation than all other functional groups considered. The electronic and molecular regulating abilities of the functional groups can be affected by polymer films preparation. The photoluminescence (PL) efficiency of the functionalized hexyl thiophenes considered are expected to decrease as the torsion angles increase. In general, the present results show that the energy band gap does change significantly with the functional group attached to hexyl substituents, which affect the molecular properties related to the electronic conductivity.

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