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A DENSITY FUNCTIONAL THEORY STUDY OF SUBSTITUTED AND BRIDGED OLIGOTHIOPHENES FOR ELECTROCHEMICAL APPLICATIONS

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ABSTRACT : In this work the electronic and thermodynamic properties of both neutral and radical cationic oligothiophene chains with up to eight thiophene units, substituted and bridged oligothiophenes are investigated by performing hybrid DFT (BH and HLYP) and Hartree-Fock calculations using 6-31G* and 6-311G** basis sets. The thermodynamic property calculations show the radical cationic species are less stable than the corresponding neutral species. Oxidizing the oligomers decreases their band gap. The results obtained show that introducing side attachments like alkoxy and cyano substituents at 3-position lowers the band gap of the oligomers. Modifying the oligothiophene backbone by introducing bridge between two thiophene units also enhances the stability and lowers the band gap of the oligomers.

Key words/phrases: Bridged oligothiophenes, density functional theory, low band gap oligomers, thermodynamic properties

INTRODUCTION

Much attention has been given to the study of the structural and electronic properties of oligothiophenes because of the application of the thiophenes and substituted thiophene polymers in optical devices (De Paoli *et al*., 1999; Inganäs *et al*., 2001; Biallozor and Kupniewska, 2005), electrochromic materials (Ikeda and Higuchi, 2011; Nguyen *et al*., 2011), sensors (Onoda *et al*., 2004; Chen and Chzo, 2006) and electrocatalysis (Yoshino *et al*., 1997; Niklasson *et al*., 2004). The performance of the thin films is greatly dependent on the structural and electronic properties of the oligomers (Hirota *et al*., 1996; Andersson *et al*., 1999; Tan *et al*., 2007).

Understanding of the electronic structure and related properties of the basic repeating units is fundamental for the study of the more complex polymeric systems, since small variations in the chemical and structural properties can play a vital role in modifying the characteristics of the oligomers (Li *et al*., 2006; Choukri *et al*., 2007; Tan *et al*., 2007; Li and Zhang, 2008). The most promising application of conjugated polymers and oligomers are basically based on neutral systems. Currently, the polymers are being used for electronic devices, which need the movement of electrons in the conjugated systems. The electrical conductivity of the oligomers increases upon doping after oxidation or reduction (Kaya *et al*., 2009; Li and Zhang, 2008). From a theoretical viewpoint, polythiophene has become subject of considerable interest and has been considered as a model for the study of conducting conjugated polymers because of its high environmental stability in both its doped and undoped states. Different properties are observed when different substituents are introduced in the backbone of the oligomers (Yakovlev and Zolin, 1997; Kirschbaum *et al*., 1999; Ushula Mengesha and Teketel Yohannes, 2006; Chaieb *et al*., 2008; Shinar and Shinar, 2011).

The performance of most of the devices is directly related with the stability, nature, size and types of charge carriers in the monomers (Birgerson and Salaneck, 2001; Ushula Mengesha and Teketel Yohannes, 2006; Shinar and Shinar, 2011). Carefully selected monomers could have better performance with better stability. In our previous study on three newly synthesized alkoxy substituted phenyl-thiophenes, it is observed that alkoxy side attachments on the monomers increase the performance of the polymers in the devices (Taye Beyene *et al*., 2010). Bouzzine *et al.* (2009) reported the conformational analysis and optoelectronic properties of some bridged bithiophenes and showed that bridged bithiophenes, for example 3,4′-dicyano-2,2′-bithiophene, exhibited lower band gap than

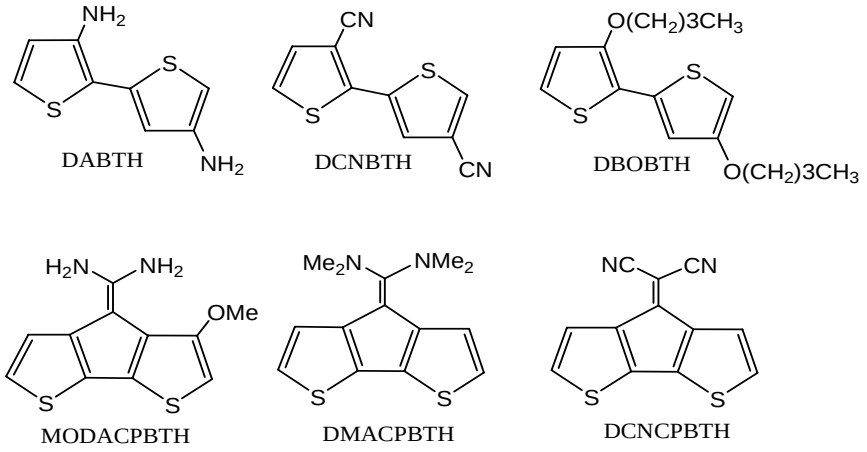
unbridged bithiophene. Bakhshi and Rattan (1998) and Subramanian and Lagowski (1998) also reported the study of dicyanomethylene-cyclopentabithiophene. The structural properties of different thiophene oligomers have been investigated and reported in different studies (Kuwabata *et al.*, 1987; McCullough *et al.*, 1993; Li *et al.*, 1995; Rubio *et al.*, 1996; Di Césare *et al.*, 1998). However, the theoretical investigations of the electronic and thermodynamic properties of the oligothiophenes and their derivatives using relatively appropriate methods are missing in the studies. On the other hand, polythiophene can be n-doped unlike its analogous polymers for example polypyrole and polyphosphole (Salzner *et al.*, 1998). Hence, systematic modification of the polythiophene backbone as well as introducing better side attachments could result in stable n- and p-dopable polymers.

Aiming the search of better oligothiophene derivative molecules with lower band gap and better stability at the oxidized state, we also considered different substituted and bridged oligothiophenes in addition to the unsubstituted oligothiophenes, namely 3,4′-diamino-2,2′-bithiophene(DABTH), 3,4′-dicyano-2,2′-bithiophene(DCNBTH), 3,4′-dibutyloxy-2,2′-bithiophene(DBOBTH), 3-methoxy-diaminomethylene-cyclopentabithiophene (MODACPBTH), dimethylaminomethylene-cyclopentabithiophene(DMACPBTH), and dicyanomethylene-cyclopentabithiophene (DCNCPBTH). Therefore, based on thermochemical properties the study shows and suggests new stable low band gap polymers. The structures of the substituted and bridged molecules considered are shown in Scheme 1.

METHODS

The structures of the reduced and radical cationic forms of the compounds studied were optimized using Becke's three parameter hybrid functional (Becke, 1993) for exchange combined with the correlation functional due to Lee, Yang, and Parr (Lee *et al.*, 1988), commonly called B3LYP and Hartree-Fock methods (Jensen, 2006) using 6–31G* (Krishnan *et al.*, 1980) and 6–311G** basis sets (Hehre *et al.*, 1972). The optimized geometries of the neutral forms were taken as starting geometries and an electron was removed during the optimization of the geometries of the radical cations. For the odd-ring number oligothiophenes C_{2v} symmetry is used and for the even-ring numbers C_{2h} symmetry is used for the unsubstituted oligomers throughout the calculations.

The changes in the thermodynamic properties were computed by subtracting the thermodynamic property of the reduced forms from the radical cationic forms. For all closed-shell calculations the restricted and for all open-shell calculations the unrestricted calculations were employed. The maximum absorption wavelengths of the reduced forms of the oligomers were calculated using time dependent density functional theory (TD-B3LYP) and 6–31G* and 6–311G** basis sets. The HOMO and LUMO energies were obtained from the energy calculations of both the neutral and radical cations of the compounds. All the optimizations were confirmed to be real minima without any imaginary frequency. All the calculations were performed at 298.15K and 1.00 atmosphere using Gaussian 03 program package (Frisch *et al.*, 2003).



Scheme 1. Structures of the substituted and bridged molecules.

RESULTS AND DISCUSSION

Band gaps

The calculated band gaps of the oligothiophenes for the neutral and radical cationic forms are listed in Table 1 and compared with some reported experimental and theoretical results in Table 2.

From the results it is observed that with increase in the number of thiophene units the band gap decreases for both the radical cations and reduced oligomers; for example bithiophene has a band gap of 4.23 eV while octathiophene has 2.43 eV in their neutral forms. For the shorter oligothiophenes the change in the band gap is larger (for example 1.89 eV between thiophene and bithiophene) whereas, for the longer ones the difference is small (for example 0.07 eV between heptathiophene and octathiophene). This shows that for the longer oligothiophenes the band gap seems to be consistent with increase in the thiophene units. The band gap energy versus number of thiophene rings for the oligothiophenes is plotted in Figure 1.

Table 1. Calculated band gaps obtained at the B3LYP/6-311G.**

Compounds	Neutral form			Radical cationic form		
	HOMO	LUMO	E_g (eV)	HOMO	LUMO	E_g (eV)
Thiophene	-6.61	-0.49	6.12	-13.41	-7.63	5.78
Bithiophene	-5.57	-1.34	4.23	-11.75	-8.87	2.88
Trithiophene	-5.15	-1.69	3.46	-10.16	-7.82	2.34
Tetrathiophene	-5.05	-1.91	3.14	-9.28	-7.46	1.82
Pentathiophene	-4.87	-2.08	2.79	-8.36	-6.90	1.46
Hexathiophene	-4.80	-2.18	2.62	-8.03	-6.83	1.20
Heptathiophene	-4.75	-2.25	2.50	-7.44	-6.45	0.99
Octathiophene	-4.74	-2.31	2.43	-7.32	-6.50	0.82

$E_g = (E_{LUMO}-E_{HOMO})$

Table 2. Comparison of the B3LYP calculated band gaps with experimental band gaps.

Compounds	E_g of neutral (eV)		E_g of radical cation (eV)		Experimental band gap of neutral forms
	6-31G*	6-311G**	6-31G*	6-311G**	
Thiophene	6.11	6.12	5.77	5.78	5.23[a]
Bithiophene	4.23	4.23	2.92	2.88	4.05[a]
Terthiophene	3.45	3.46	2.34	2.34	-
Tetrathiophene	3.13	3.14	1.83	1.83	-
Pentathiophene	2.78	2.79	1.46	1.46	-
Hexathiophene	2.62	2.62	1.19	1.20	2.40[b]
Heptathiophene	2.49	2.50	1.00	1.01	-
Octathiophene	2.41	2.43	0.83	0.82	(2.0-2.3) [a,c]

[a] Bantaculo *et al.* (2001), [b] Salzner *et al.* (1998), [c] the HOMO-LUMO gap of polythiophene

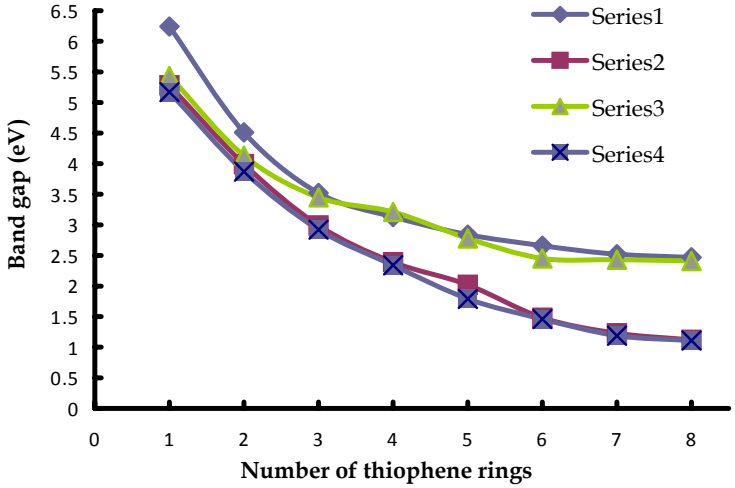


Fig. 1. Relation between band gaps (eV) of oligothiophenes versus number of thiophene rings. Series 1 and Series 2, band gap of neutral and radical cations calculated using B3LYP/6–31G*, respectively; Series 3 and Series 4, band gap of neutral and radical cations calculated using B3LYP/6–311G, respectively.**

For a neutral bithiophene molecule, the calculated band gap is 4.23 eV using B3LYP/6–311G** level whereas the experimental value reported is 4.05 eV (Bantaculo *et al.*, 2001). For hexathiophene, the experimental band gap is 2.40 eV (Salzner *et al.*, 1998) while the calculated value obtained in this work is 2.62 eV. The band gap of neutral octathiophene calculated in this work is 2.43 eV and the experimental value reported is 2.30 eV (Bantaculo *et al.*, 2001). The experimental band gap of neutral polythiophenes is within the range of 2.0–2.3 eV. Based on these results it is possible to consider octathiophene as a model molecule for theoretical investigation of polythiophenes and substituted polythiophenes.

Absorption wavelengths and excitation energies

In Table 3 the calculated absorption λ_{max} for the thiophene oligomers are depicted and compared with experimental values. From the results it is observed that the thiophene monomer is absorbing at a shorter wavelength, while with increase in the number of thiophene units the absorption wavelength increases and shifts to the visible range. The maximum absorption wavelength increases with the chain length of the oligothiophenes. Conversely, with increase in the chain length, the excitation energy decreases, implying ease of removing electrons upon polymerization.

The calculated absorption wavelength results obtained at both the B3LYP/6–31G* and B3LYP/6–311G** levels are plotted with the experimental results (Salzner *et al*. 1998) in Figure 2. A linear relationship between the calculated and the experimental results is obtained for the oligothiophenes. The agreement between the experimental and the theoretical results is excellent. The following linear equation is proposed to estimate either the experimental or theoretical values of longer oligothiophenes: $\lambda_{exp} = 114.65 + 0.64 \times \lambda_{cal}$. This result is also in fair agreement with the results obtained by Colditz *et al*. (1995). Using the proposed equation the expected experimental maximum absorption wave lengths for heptathiophene and octathiophene are 467.6 nm and 484.92 nm respectively.

Table 3. Experimental and calculated absorption wavelengths of the oligothiophenes.

Compounds	TD-B3LYP/6–31G*	TD-B3LYP/ 6–311G**	Experimental λ_{max} (nm)[a]
	λ_{max} /nm/ (E_{exc}/eV)	λ_{max} /nm/ (E_{exc}/eV)	
Thiophene	206.69 (6.00)	209.59 (5.92)	243.00
Bithiophene	307.65 (4.03)	309.56 (4.02)	302.00
Terthiophene	379.37 (3.27)	380.56 (3.26)	355.00
Tetrathiophene	436.90 (2.84)	440.48 (2.82)	390.00
Pentathiophene	482.36 (2.57)	483.34 (2.57)	416.00
Hexathiophene	520.22 (2.38)	523.69 (2.37)	432.00
Heptathiophene	551.51 (2.25)	553.78 (2.24)	Not available
Octathiophene	578.54 (2.14)	578.79 (2.14)	Not available

[a]Kuwabata *et al.* (1987), excitation energies in brackets

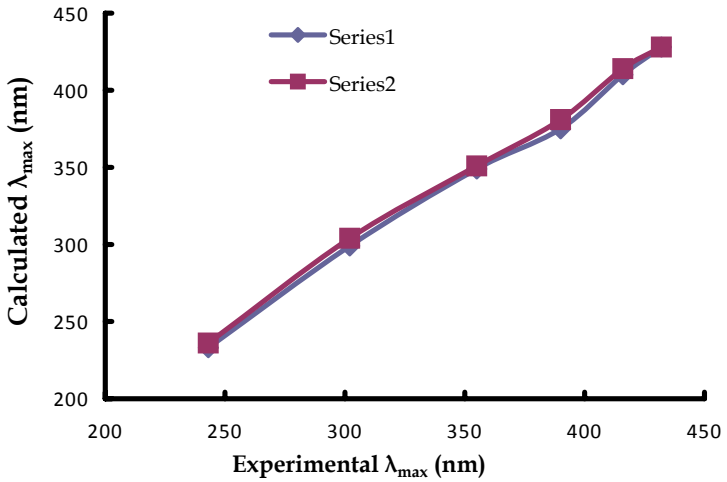


Fig. 2. Relation between experimental and calculated absorption wave lengths (λmax): Series 1, calculated using B3LYP/6–31G*, and Series 2, calculated using 6–311G levels.**

Thermodynamic properties

The changes in thermodynamic properties results are listed in Table 4. The results obtained from HF/6–31G* are also included. The same trend is observed upon polymerization for all levels of calculations, *i.e.,* the monomer has the largest thermodynamic property than the dimer and trimer, *etc.* The decrease in the change in thermodynamic properties upon polymerization indicates that the radical cationic forms of the shorter oligomers are unstable when compared with the longer oligomers in which charge delocalization is the major stabilizing factor for the longer oligomers. The results obtained, for change in Gibbs free energy versus number of thiophene oligomers, are plotted in Figure 3. The figure shows that as the conjugation length increases the stability of the radical cationic species increases. This fact is favoured by the delocalization of the radical cation through the longer conjugated molecule that supports it to stay for a longer time at the radical cationic state. This can also be extrapolated to the polymers, in that; the highly conjugated polythiophenes are stable at the radical cationic state than the oligothiophenes.

Substituted oligothiophenes

Bakshi *et al*. (1998) reported the calculated band gap of 5.92 eV for DCNCBTH using semi-empirical AM1 method. In this work a band gap of 2.72eV is obtained for DCNCBTH using B3LYP/6–311G** level as listed in Table 5. DBOBTH has a better thermodynamic stability than the rest. DMACPBTH is the next in its stability at the oxidized state with lower band gap than DBOBTH. MODACPBTH has relatively lower band gap than DMACPBTH and its stability at the oxidized state is better compared to the parent bithiophene molecule, implying enhanced performance of the corresponding polymers in electrochemical applications

Table 4. Thermodynamic properties of the oligomers

	HF/6–31G*			B3LYP/6–31G*			B3LYP/6–311G**		
Compounds	ΔG^0/ kJ/mol	ΔH^0/ kJ/mol	ΔS^0/ J/mol.K	ΔG^0/ kJ/mol	ΔH^0/ kJ/mol	ΔS^0/ J/mol.K	ΔG^0/ kJ/mol	ΔH^0/ kJ/mol	ΔS^0/ J/mol.K
Thiophene	598.87	595.90	-9.96	829.52	832.57	10.23	835.72	836.87	3.85
Bithiophene	461.96	460.87	-3.66	692.62	700.11	25.12	732.32	739.25	23.25
Trithiophene	412.42	409.95	-8.28	633.98	640.36	21.40	634.38	654.43	67.25
Tetrathiophene	386.81	385.26	-5.21	596.26	608.14	39.85	598.25	620.06	73.18
Pentathiophene	378.51	376.02	-8.35	575.43	585.63	34.21	577.43	597.78	68.27
Hexathiophene	373.46	371.46	-6.71	560.32	569.78	31.73	557.80	584.89	90.88
Heptathiophene	366.18	363.55	-8.82	550.91	558.06	23.98	533.31	558.23	83.58
Octathiophene	361.54	358.15	-11.37	544.17	549.95	19.39	518.12	569.59	172.63

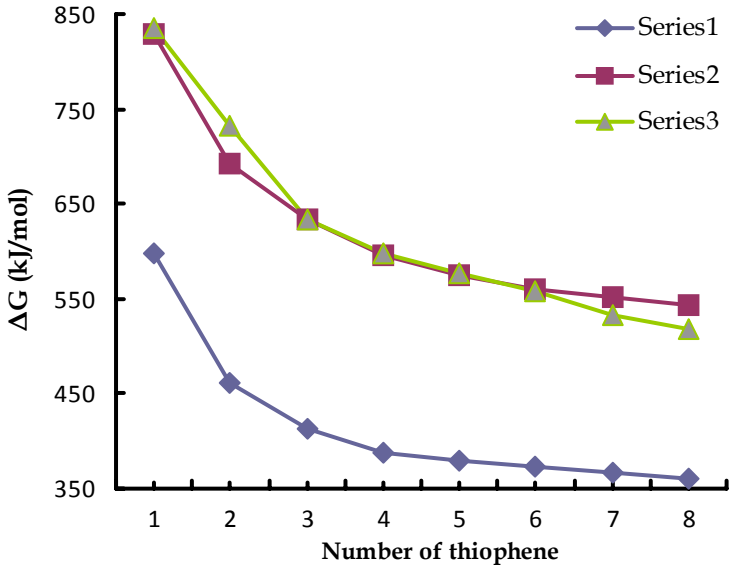


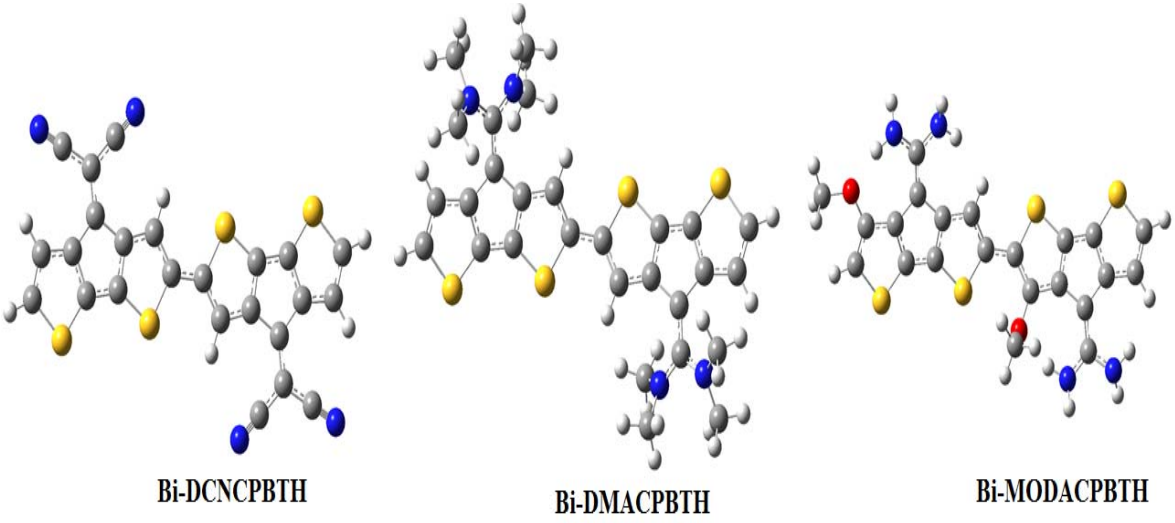
Fig. 3. Change in Gibbs free energy of oligothiophenes as a function of number of thiophene rings. Series 1 is using HF/6-31G*; Series 2 is using B3LYP/6-31G* and Series 3 is using B3LYP/6–311G level of calculation.**

Table 5. Change in Gibbs free energy, absorption wavelength, excitation energy, and band gap of the substituted and bridged molecules obtained at B3LYP/6–311G level of calculation.**

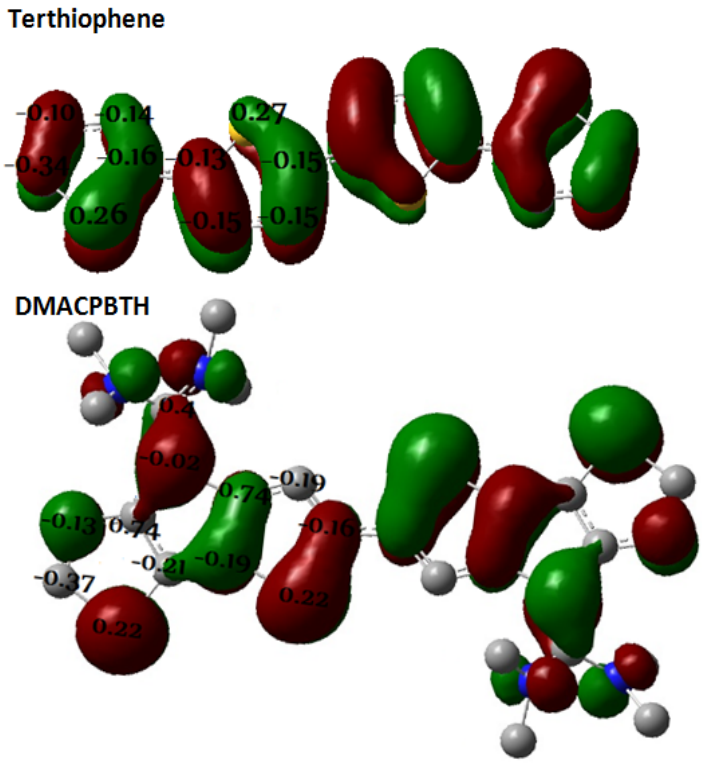
Compounds	ΔG (kJ/mol)	λ_{max} (nm)	E_{exc} (eV)	E_g (eV), reduced
Bithiophene	818.47	309.56	4.02	4.23
Tetrathiophene	598.25	440.48	2.82	3.14
DCNBTH	778.64	271.88	4.56	4.08
DABTH	652.75	302.35	4.10	4.29
DBOBTH	599.36	323.63	3.83	4.03
DCNCPBTH	875.92	637.91	1.64	2.72
DMACPBTH	620.96	354.66	3.49	3.94
MODACPBTH	632.04	382.82	3.24	3.79
Bi-DCNCPBTH	716.41	870.24	1.43	1.99
Bi-DMACPBTH	491.93	492.21	2.52	2.84
Bi-MODACPBTH	502.29	470.42	2.64	2.92
Octa-DCNCPBTH	639.23	942.11	1.32	1.45
Octa-DMACPBTH	410.52	582.36	2.13	2.16
Octa-MODACPBTH	426.69	567.52	2.18	2.24

DCNCPBTH has the lowest band gap than all the rest molecules but less stable at the oxidized state than DMACPBTH and MODACPBTH. The thermodynamic and electronic properties of the tetramers and octamers of the bridged (bithiophenes) are also listed in Table 5. The optimized geometries of the dimers of the three bridged-bithiophenes are given in Scheme 2.

The octamer of DCNCPBTH has smaller band gap and excitation energy, see Table 5, but is less stable compared to the other two bridged oligomers which is basically because of the electron withdrawing nature of the -C=C(CN)$_2$ group in the bridge. On the other hand, the dimethyl amine and diamino groups on the bridge highly stabilized the oligomer by donating more electrons to the thiophene backbone that could support the radical cation to stay at the oxidized state for longer time compared to the octamer of DCNCPBTH and octathiophene. This evidence is shown in Scheme 3, in which the carbon atoms next to sulfur, the polymerization sites, get more negative charge compared to the terthiophene backbone. The HOMO plot in the Scheme also shows the difference in electron distribution between the modified and unmodified terthiophene backbone. Therefore, if modifications are made on the polythiophene backbone, especially bridge between two thiophene units, the stability of the oligomers increases at the oxidized state and decreases their band gap, which are the most important criteria for the performance of the polymers in opto-electronic materials.



Scheme 2. Optimized geometries of the dimers of the bridged-bithiophenes



Scheme 3. Mulliken charges of the atoms and HOMO plot of terthiophene and DMACPBTH. Hydrogen atoms are removed for clarity.

CONCLUSION

In this study the thermodynamic properties of oligothiophenes starting from the monomer up to the octamer have been studied. The stability of the oligothiophenes at the radical cationic state increases with increase in the number of thiophene rings. The band gap estimations also showed increase in the number of thiophene rings, decreases the band gap and improves the conductivity. Therefore, based on the stability and band gap factors observed in this work, the 3-alkoxy thiophenes are better for the application of conducting polythiophenes in different electronic devices. On the other hand, if the bridged bithiophene units are modified by introducing side attachments, a better stable and low band gap polymer can be obtained. It is also observed that alkoxy side attachments increase the performance of the polymers by having lower band gap and better stability. The bridged-bithiophenes have more conjugation compared to the unmodified oligothiophenes and the donor groups attached to the backbone enhanced the stability and decreased the band gaps of the oligomers which could also enhance the electrochemical activity of the polymers.

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