



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Synthesis, Structure and Band Gap of Novel Thiophene Based Conductive Polymers

S. Radhakrishnan^a, V. Subramanian^a, N. Somanathan^a, K. S. V. Srinivasan^a & T. Ramasami^a

^a Central Leather Research Institute, Adyar, Chennai, 600020, India

Version of record first published: 18 Oct 2010

To cite this article: S. Radhakrishnan, V. Subramanian, N. Somanathan, K. S. V. Srinivasan & T. Ramasami (2002): Synthesis, Structure and Band Gap of Novel Thiophene Based Conductive Polymers, *Molecular Crystals and Liquid Crystals*, 390:1, 113-120

To link to this article: <http://dx.doi.org/10.1080/10587250216164>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable

for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SYNTHESIS, STRUCTURE AND BAND GAP OF NOVEL THIOPHENE BASED CONDUCTIVE POLYMERS

S. Radhakrishnan, V. Subramanian*, N. Somanathan*,
K. S. V. Srinivasan, and T. Ramasami
Central Leather Research Institute, Adyar,
Chennai 600020, India

A novel poly 3-(2-benzo thiazolyl) thiophene based conductive polymer have been synthesized and characterized using various experimental techniques. The structure and band gap (difference between Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital) for the above polymer have been calculated using oligomeric approach employing B3LYP/3-21G method and semi-empirical AM1 and ZINDO methods. The calculated band gap for monomer, dimmer and trimer has been plotted versus $1/N$ (where N is the number units). The value at $1/N=0$, is taken as the band gap of the polymer having long chain length. It is evident from the theoretical investigations, the band gap of poly 3-(2-benzothiazolyl) thiophene is 3.77 eV. It is possible to change the band gap by designed alteration in the thiophene framework.*

Keywords: polythiophene; band gap; LEDs; molecular orbital calculations

INTRODUCTION

Molecular electronic materials based on conjugated polymers have potential applications in various fields in recent years [1–3], wide spread efforts have been made to develop novel light emitting devices (LED). Poly thiophenes (PT), Poly phenylene vinylene (PPV) and Poly para phenylene (PPP) etc. are such conjugated polymers whose electroluminescence (EL) emission falls in the visible range. Among the above, PT are good candidates since they can be easily processible when compared to other systems. Other advantages are the environmental stability and versatility because of their tailorable properties. One of the disadvantages is its poor solubility that can be overcome by functionalisation at the 3- position of the thiophene ring.

*Corresponding author

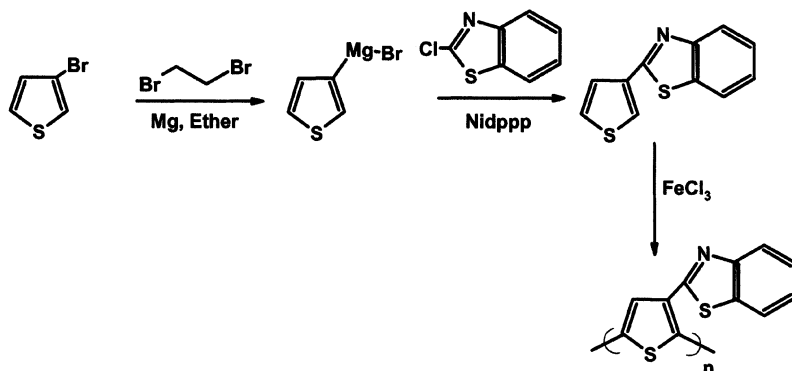
The principal requirements of polymeric light emitting devices are high efficiency and reliability [4]. PT based LEDs show low quantum yield due to the presence of sulfur. Hence in the case of PT based LEDs, the goal is to achieve maximum efficiency and brightness at minimum drive voltage. The present alternative method to improve efficiency in the case of PLEDs is to use multi layer technology using Electron conducting hole blocking (ECHB) low molecular materials [5]. The disadvantages of using these materials are the phase separation and crystallization at higher temperatures. The compatibility of these materials with the light emissive polymer layers is also affected. The Present study aims to incorporate the properties and functions of the above mentioned ECHB, by suitably substituting groups containing π -electron deficient hetero cyclics such as oxadiazole, triazoles, triazines, pyridines and extended benzo derivatives of the above. The proper structure and groups suitable for the above function viz. ECHB, was initially studied using molecular orbital calculations and subsequently synthesis of the modeled compounds have been made.

Molecular orbital calculation is a versatile tool in designing and predicting properties of new materials. Recent investigations [6,7] using molecular orbital calculations, exploits with the chain length of the geometric and electronic structure and optical properties of the various systems. The oligomeric approach of the polymers is used to establish relations between the chain length and physical properties and assumed to allow a more precise structure-activity relationship to be determined and also to allow extrapolation of these relationships towards those expected for polymers. Computing Highest Occupied Molecular Orbital- Lowest Unoccupied Molecular Orbital (HOMO-LUMO) energies with different substituents may be helpful in predicting the substituent effect on polymer band gap.

Based on the theoretical predictions, Benzo thiazole is used as a substituent attached to the 3- position of the thiophene (BTT) ring. In order to understand the influence of the substituent at the 4- position of the BTT, methyl (MBTT) and cyano (CBTT) groups substituted at the 4- position of the thiophene ring of BTT have also been studied by Density Functional and Semi- empirical calculations.

EXPERIMENTAL

The synthetic method used for the synthesis of BTT and its polymer is outlined in Scheme 1. In a three necked flask fitted with a condenser, a dropping funnel and nitrogen inlet, magnesium turnings and 3-bromo thiophene were introduced together with dry diethyl ether. The entrainer 1, 2-dibromo ethane in anhydrous diethyl ether is then added at ice-cold temperature for a period of 8 hrs. After the reaction begins, the solution



SCHEME 1

was brought to ambient temperature. The resulting Grignard compound was transferred to a second dropping funnel fitted to a second three necked flask containing 2-chloro benzothiazole and 1,3- bis (diphenyl phosphino propane) Nickel (II) chloride (Nidppp) in anhydrous diethyl ether. After cooling with an ice bath, the Grignard compound was added drop wise and the resulting adduct allowed to warm to ambient temperature before being stirred for 24 h. The mixture obtained is poured onto very dilute aqueous hydrochloric acid. The organic layer is washed with water, dried and concentrated. The crude product is purified on a silica gel column (eluting with Petroleum ether containing 10% ethyl acetate). NMR has confirmed the structure of the monomer. ^1H NMR (300 MHz, CDCl_3 , ppm): 8.02(t, 2H); 7.85(d,1H); 7.69(d,1H); 7.39(m,3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): 162.6; 153.8; 135.9; 134.6; 126.8; 126.5; 126.2; 126.0; 125.0; 123.0; 121.5.

Chemical Polymerisation

Polymer of (3-(2-benzothiazolyl)) thiophene was prepared by chemical oxidation of the monomer using Ferric chloride adopting a procedure similar to that of Sugimoto *et al.* [8]. In a three-necked flask, 0.012 M Ferric chloride was dissolved in chloroform under nitrogen to which a solution of 0.003 M of monomer in chloroform was added dropwise. The mixture was stirred for 24 h at room temperature under inert atmosphere and the solution was precipitated using methanol.

UV/visible spectra were recorded in chloroform solution using a Shimadzu-160 A spectrometer. The Photoluminescence of the polymers was studied in chloroform using Hitachi 650-40 fluorescence spectro-photometer.

DFT (B3LYP/3-21G*), AM1 and ZINDO calculation have been performed using the G 98 w suite of packages [9]. The starting geometries have been generated using model-building tools available in the Cerius² package from Molecular Simulation Inc (SanDiego, CA). The initial geometries have been optimized using AM1 Hamiltonian. All calculations have been made for AM1 optimized geometries. For comparison, the parent thiophene oligomers (T) also have been optimized. Excitation energies (HOMO-LUMO gap) calculated using B3LYP/3-21G*, AM1 and ZINDO methods and extrapolated to infinite chain length. The first excited state with significant oscillator strength has been used for calculating the excitation energies at the ZINDO.

RESULTS AND DISCUSSION

The calculated excitation energies for thiophene oligomers at the various levels of theory are shown in Table 1. The calculated excitation energies are slightly higher than experimental values obtained for polythiophene. This may be due to the fact that the theoretical values have been obtained in the gaseous phase, while the obtained experimental value is in solution phase,

TABLE 1 Calculated E_{exc} (eV) of the Different Thiophene Systems at the Various Computational Levels

	System	AM1	B3LYP/3-21G [*] (AM1 opt)	ZINDO (AM1 opt)
T	Monomer	9.79	6.52	4.86
	Dimer	8.02	4.50	3.74
	Trimer	7.29	3.71	3.13
	Polymer (T)	6.12	2.38	2.38
	Polymer (Exptl)		2.27	
BTT	Monomer	8.10	4.68	3.94
	Dimer	8.02	4.41	3.92
	Trimer	7.95	4.18	3.74
	Polymer (T)	7.87	4.00	3.72
	Exptl-monomer -polymer		3.99 3.77	
MBTT	Monomer	8.21	4.64	4.02
	Dimer	8.22	4.77	4.03
	Trimer	8.20	4.74	4.05
	Polymer (T)	8.19	4.82	4.05
CBTT	Monomer	8.08	4.61	3.99
	Dimer	8.02	4.62	3.99
	Trimer	7.92	4.55	4.03
	Polymer (T)	7.88	4.56	4.03

which may add some non-planarity to the system [7]. In addition to the environmental effects, the electron correlation would also influence to excitation energies obtained from MO calculations. The values obtained for poly thiophene using B3LYP/3-21G* and ZINDO method are in close agreement with each other.

Calculated excitation energies for BTT, MBTT and CBTT are plotted against the inverse number of monomer units [7] and extrapolated to an infinite number of units. The obtained band gap values are presented in Table 1. The band gap calculated using ZINDO and B3LYP/3-21G* is presented respectively in Figure 1a and 1b. The extrapolated band gap from ZINDO excitation energy using AM1 optimized geometries for BTT polymer is in agreement with the obtained experimental values, while B3LYP/3-21G* overestimates about 0.2 eV. In the case of BTT monomers, the theoretical values agree with the experimental values obtained in solution phase. The solution phase absorption spectrum of monomer and polymer of BTT is shown in Figure 2a–2b respectively. For BTT, as the conjugation length increases, the red shift is observed as expected. The extrapolated value is 3.72 eV, which agrees well with experimental value of 3.77 eV corresponds to an absorption maximum at 329 nm (in solution phase). In the experimental data, in addition to the peak at 329 nm (3.77 eV), a peak at 345 nm (3.59 eV) is also obtained. The overall studies suggest that the obtained 329 nm peak may be due to regio regular coupling while 345 nm may be due to mis coupling [10]. In contrast to BTT, in the case of MBTT and CBTT, as the chain length increases, blue shifting is observed in theoretical level. Due to the electron releasing effect of methyl group, blue shift is expected in the case of MBTT, when compared to BTT, whereas in the case of CBTT, due to electron withdrawing effect, red shift is expected when compared to BTT. Table 1 shows that, in both CBTT and MBTT, the obtained value does not show any characteristic change at ZINDO level, while a red shift (calculated using B3LYP/3-21G*) is obtained for CBTT when compared to MBTT. The blue shifting of CBTT and MBTT (compared to BTT) can be attributed to the overcoming steric effect produced by the methyl and cyano substituents at the 4 position of the thiophene ring, dominating over the electronic effect produced by the electron withdrawing and releasing natures of the substituents. In BTT monomer for an excitation of 299 nm, the emission is falls at 370–444 nm, while in the case of Poly BTT for an excitation at 345 nm the emission at 420 nm is observed which is shown in Figure 3.

Since the geometries are optimized at AM1, further optimizations at reasonable level of theory would also influence the results. But optimization at HF and/or DFT level would require more computational time for dimmer and trimmer. Hence calculation have been made at AM1 level to derive reasonable trend of excitation energies.

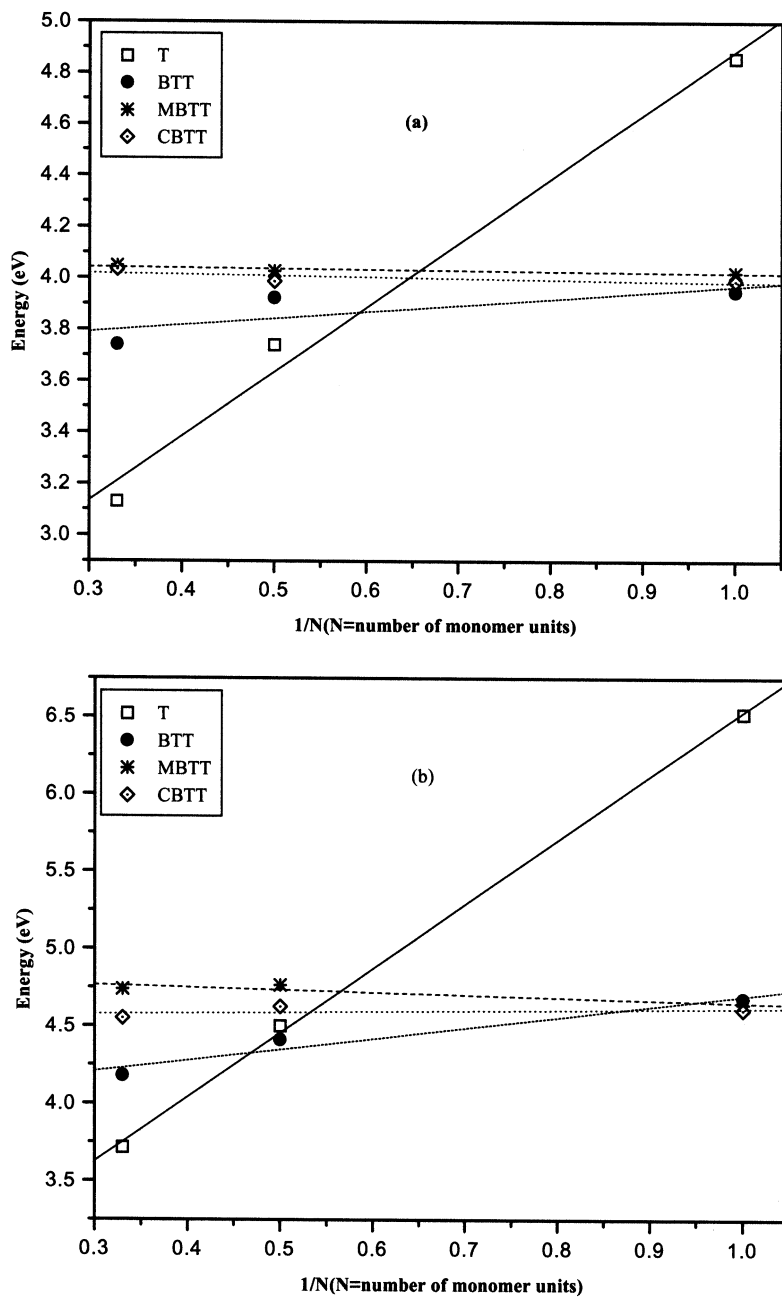


FIGURE 1 Band gaps extrapolated from plots of E_{exc} versus the inverse number of monomer units for different thiophenes: (a) ZINDO and (b) B3LYP/3-21G*.

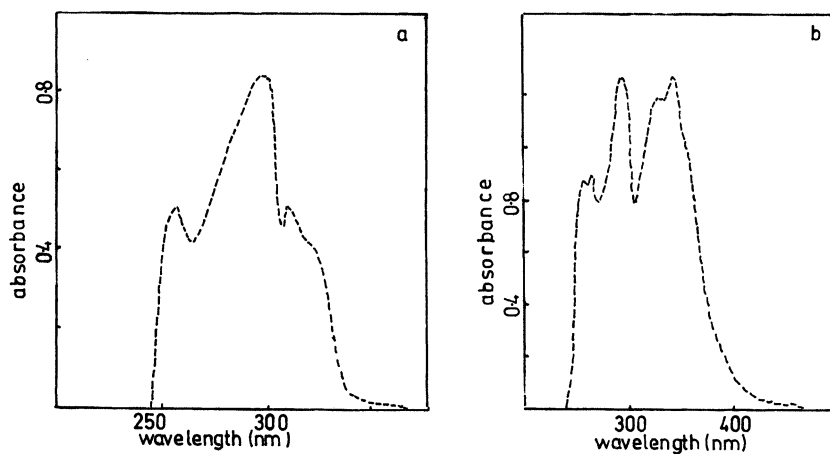


FIGURE 2 Absorption spectrum of (a) BTT and (b) Poly BTT.

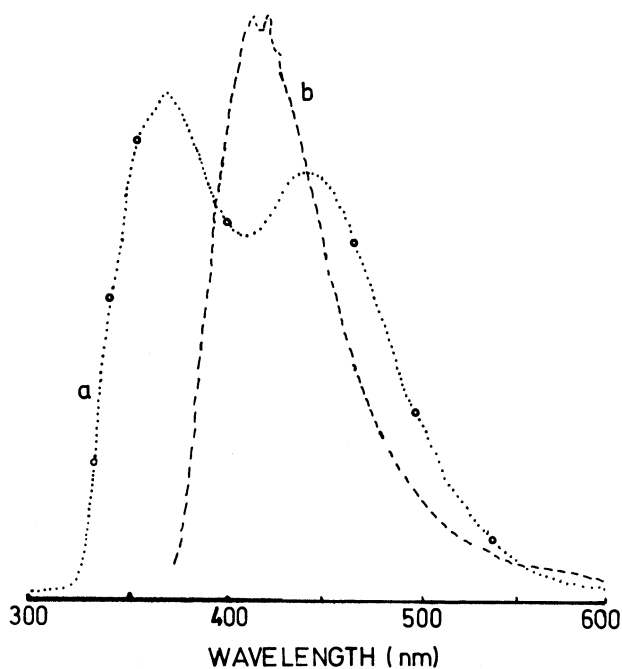


FIGURE 3 Emission spectrum of (a) BTT and (b) PolyBTT.

The over all studies show that the computational methods help to predict the properties and the band gap obtained from experimental results of BTT polymers, coincides well with the theoretical one. The photoemission of the BTT polymer falls in the blue light range with high intensity, which will be useful for the development of white light.

REFERENCES

- [1] Kraft, A., Grimsdale, A. C., & Holmes, A. B. (1998). *Angew. Chem. Int. Ed.*, **37**, 402–428.
- [2] Heeger, A. J. (1998). *Solid State commun.*, **107**, 673–679.
- [3] Skotheim, T. A., Elsenbaumer, R. L., & Reynolds, J. R. (ed) (1998). *Handbook of conducting Polymers*, Marcel Dekker: NY, II Ed.
- [4] Sheats, J. R., Antoniadis, H., Hueschen, M., Leonard, W., Miller, J., Moon, R., Roitman, D., & Stocking, A. (1996). *Science*, **273**, 884–888.
- [5] Thelakkat, M. & Schmidt, H. W. (1998). *Polymer for Advanced Technologies*, **9**, 429–442.
- [6] Mullen, K. & Wegner, G. (ed.) (1998). *Electronic Materials: The Oligomeric Approach*, WILEY-VCH Verlag GmbH.
- [7] Ohyun Kwon & McKee, M. L. (2000). *J. Phys. Chem. A*, **104**, 7106–7112.
- [8] Sugimoto, K., Takeda, S., Gu, H. B., & Yoshimo, K. (1986). *Chem. Express*, **1**, 635.
- [9] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A., Stratmann, R. E., Brant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Patterson, G. A., Ayala, P. Y., Cui, Q., Morokuma, K., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Cioslowski, J., Ortiz, J. V., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P. M. W., Johnson, B. G., Chen, W., Wong, M. W., Andres, J. L., Head-Gordon, M., Replogle, E. S., & Pople, J. A. (1998). Gaussian 98W, Revision A.1; Gaussian, Inc.: Pittsburgh, PA.
- [10] Barbarella, G., Bongini, A., & Zambianchi, M. (1994). *Macromolecules*, **27**, 3039–3045.