

**A DENSITY FUNCTIONAL STUDY ON NARROW
BAND GAP DONOR-ACCEPTOR TYPE CONDUCTING POLYMERS**

**A THESIS SUBMITTED TO
THE DEPARTMENT OF CHEMISTRY
AND THE INSTITUTE OF ENGINEERING AND SCIENCES OF
BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE**

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AUGUST 2004**

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ABSTRACT

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August 2004

The band gap is one of the most important factors for controlling the physical properties. The search for polymers having narrow band gaps is a current topic. Tuning of the band gap by structural modification is possible. There are some approaches used for designing narrow band gap polymers. One of the approaches used for designing low band gap polymers is the donor acceptor concept where it is thought that regularly alternating conjugated donor and acceptor like moieties in a conjugated chain will induce a small band gap and at the same time will lead to widening of the valence and conduction bands. Forcing the polymers to adopt unfavorable structures and decreasing the bond length alternation along the conjugated backbone are other two methods used for synthesizing narrow band gap polymers.

Yamashita et al. synthesized copolymers composed of benzobis(1,2,5-thiadiazole) and [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine units as acceptor and thiophene and pyrrole units as donors. These synthesized copolymers have very narrow band gaps. The success with designing these systems were attributed to the donor-acceptor concept.

We intended to understand the reasons for narrow band gaps and to determine whether donor acceptor concept is valid. Density functional theory (DFT)

calculations were performed for homo and co-oligomers (having 1:1 and 1:2 acceptor to donor ratios) of thiophene (Th), pyrrole (Py), benzo[1,2-c;3,4-c']bis[1,2,5]-thiadiazole (BBT) and [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine (TTP) We estimated the band gaps of polymers by extrapolating the HOMO-LUMO gaps of the oligomers, using second degree polynomial fit, at the B3P86-30% /CEP-31g* level of theory.

Theoretical analysis showed that the main reason for the band gap reduction is not the donor-acceptor concept and the prediction of the band width widening is not valid. Influence of the quinoid structures and reduce in the bond length alternation are the reasons for the band gap reduction.

Keywords: Density functional theory, conducting polymers, conjugated organic polymers, band gap, band width, donor-acceptor concept

ÖZET

DAR BANT ARALIKLI VERİCİ ALICI TİPTEKİ İLETKEN POLİMERLERİN YOĞUNLUK FONKSİYONEL TEORİSİ KULLANILARAK İNCELENMESİ

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Ağustos 2004

Fiziksel özelliklerin kontrol edilebilmesindeki önemli faktörlerden biri bant aralığıdır. Düşük bant aralıklı polimerlerin incelenmesi süregelen bir araştırma konusudur. Yapısal değişiklikle bant aralığı büyüklüğü ayarlanabilir. Dar bant aralıklı polimerlerin dizaynı için değişik yöntemler kullanılmaktadır. Verici alıcı konsepti düşük bant aralıklı polimer dizaynında kullanılan yöntemlerden biridir. Bu teoriye göre, bir konjuge zincirde düzenli olarak sıralanan verici alıcı tipteki gruplar dar bir bant aralığının ve aynı zamanda geniş iletken ve valans bantlarının oluşmasını sağlarlar. Dar bant aralıklı polimer sentezinde kullanılan diğer iki metod ise polimerlerin uygun olmayan yapılara zorlanması ve sıralı bağ uzunluğu değişim farkının azaltılmasıdır.

Yamashita ve grubu benzobis(1,2,5-thiadiazole) and [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine alıcı gruplarından, tiyofen ve pirol verici gruplarından oluşan polimerler sentezlediler. Bu sentezlenen polimerlerin bant aralıkları çok

düşüktür. Bu düşük bant aralıklı polimerlerin dizaynı da verici alıcı konseptine dayandırılmaktadır.

Biz de bu düşük bant aralıklarının nedenlerini bulmayı ve verici alıcı konseptinin geçerliliğini sınamayı amaçladık. Homo-oligomerler ve tiyofen (Th), pirol (Py), benzo[1,2-c;3,4-c']bis[1,2,5]-thiadiazole (BBT) ve [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine (TTP)'den oluşan, 1:1 ve 1:2 alıcı/verici oranına sahip olan ko-oligomerler yoğunluk fonksiyonel teorisi kullanılarak incelenmiştir. Polimerlerin bant aralıkları B3P86-30% /CEP-31g* teori seviyesinde HOMO-LUMO enerji farklarını ikinci dereceden polinom fit yapılarak tahmin edilmeye çalışılmıştır.

Teorik araştırma, bant aralığı düşüşündeki esas nedenin verici alıcı konsepti olmadığını ve bu konseptteki bant genişlemesi öngörüsünün de geçerli olmadığını göstermiştir. Bant aralığındaki daralmanın nedenleri kinoid geometri etkisi ve sıralı bağ uzunluğu değişim farkının azalmasıdır.

Anahtar Kelimeler: Yoğunluk fonksiyonel teori, iletken polimerler, sıralı organik polimerler, bant aralığı, bant genişliği, verici alıcı konsepti

ACKNOWLEDGEMENT

I am very grateful for the advice and support of my advisor, Assoc. Prof. Ulrike Salzner, for her feedback and for keeping me focussed in my research.

I would like to express my sincere gratitude to my family for their encouragement and support.

I would like to thank to my friends, Tuğrul Gazi Apa, Volkan Işıktan, Uğur Dayıođlu, Zübeyir Kılınç, Yavuz Küçükpetek, Ömer Dođan, Ahmet Örnek, İsmail Dođu Kılıç, Sabri Gürüzümcü, Ömer Faruk Emrah, Onur Kabul, Arif Varhan, Harun Yakar, Arif Doruk, Serkan Çayırılı, Uğur Mikyaz, Ali Alper Akgün, Kürşad Gölcük, Serdar Durdađı, İshak Uysal, Ahmet Günay, Harun Nezih Türkçü, Ferdi Karadaş, Cenk Tura, Faik Demirörs, İlknur Tunç Kaya, Banu Altıntaş, Ünal Şen, Ali Rıza Bozbulut, Kamer Kaya, Oğuz Atan, Onur Bakır for their friendship.

Finally, my deepest gratitude I must reserve for Sefa Nur for her love and endless support.

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CHAPTER 1 – Introduction

1.1 Conjugated Organic Polymers

Conjugated organic polymers are either insulators or semi-conductors having band gaps around 1-4 eV. They resemble inorganic semi-conductors with respect to their energy levels. They have electrons organized in bands rather than in discrete levels and have their ground state energy bands either completely filled or completely empty [1]. At first polymers were used as insulators. But, after the discovery that poly(sulfur nitride), $(\text{SN})_x$ exhibits metallic character in 1973 [2], and later that oxidizing (p-doping) increases the conductivity of polyacetylene (PA) (figure 1.1) in 1977 [3] a great deal of experimental and theoretical work has been done on searching for new conducting organic polymers.

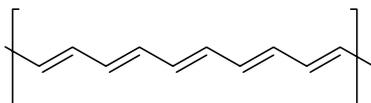


Figure 1.1 - trans polyacetylene

In saturated polymers all of the four valence electrons of carbon atoms are used in covalent bonds. However, in conjugated polymers, the chemical bonding leads to one unpaired electron, the π electron, per carbon atom. The π -bonding, where orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the polymer backbone. This delocalization provides the pathway for the charge mobility, and thus conductivity along the backbone of the polymer chain [4]. Films of p-doped polyacetylene have a conductivity of 10^5 S/cm [5]. Despite its high conductivity it has limited use because of its low environmental stability, insolubility in common solvents, and non-processability [6]. Therefore, investigations changed route to polymers, which would be promising for commercial ability. Conjugated organic polymers based on aromatic precursors such as benzene, thiophene, and pyrrole, which have

improved environmental stability have been developed. Illustrative conductivities of such polymers are: poly(p-phenylene) $15 \cdot 10^3$ S/cm, poly (3-methylthiophene) 2000 S/cm, and polypyrrole 1000 S/cm [7].

The band gap (E_g) of a system is defined as the difference between the lowest band energy in the conduction band and the highest band energy in the valence band [8]. Because a conjugated polymer is a semiconductor with a finite band gap, to transform it into a conductor requires introduction of charges. Doping of the conducting polymers can be done either by chemical or electrochemical methods [4]. Doping of the polymers is different from that of inorganic semi-conductors. Structural changes (figure 1.2) occur in a conjugated polymer upon oxidation (p-doping) or reduction (n-doping). These structural changes induce modifications in the band structure of the system [9].

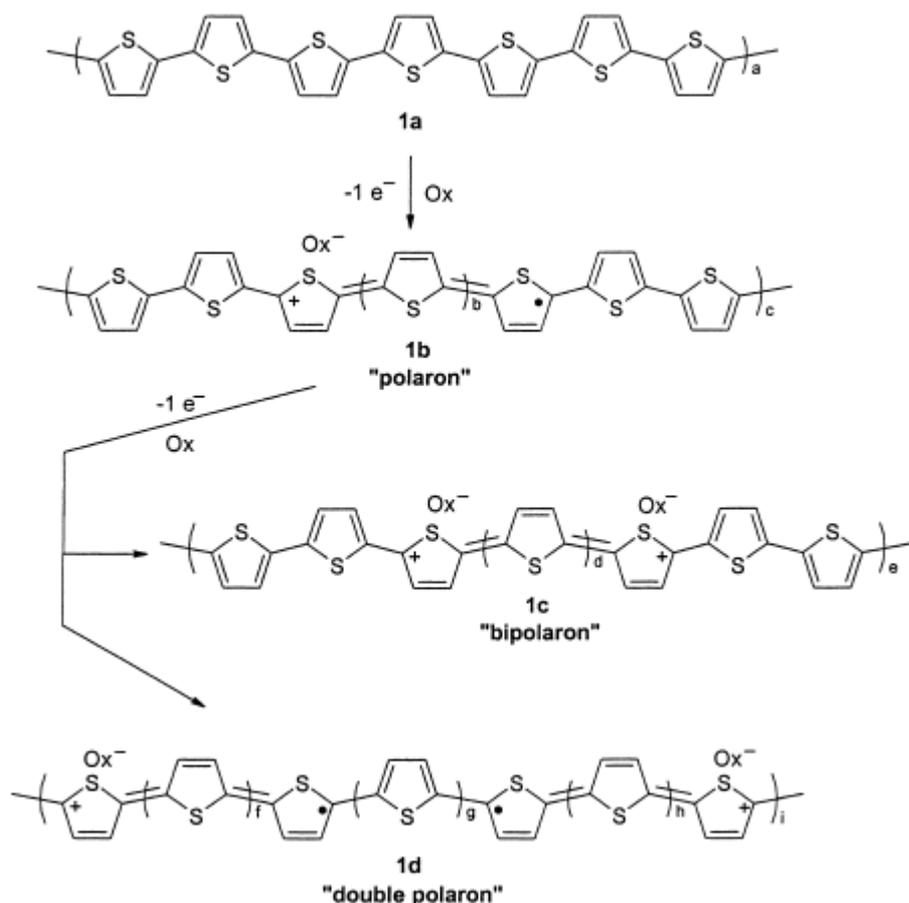


Figure 1.2- structural changes in polythiophene upon doping with an oxidant [1]

π - conjugated polymers that become conductive after doping, as described above, are classified as extrinsically conducting polymers. In contrast, intrinsically conducting polymers do not need additional doping and are characterized by electrically neutral conjugated systems in which some π electron bands are only partially filled [1]. Since intrinsic conductors like metals owe their conductivity to the partial filling of the valence band up to Fermi level, in order to have such a conductivity with a polymer, the band gap should be zero or close to zero.

1.2 Tuning the Band Gap in Linear π - Conjugated Systems

The band gap is one of the most important factors for controlling the physical properties. Because of this, in a high number of applications, control of the band gap of the conjugated organic polymer is essential. Especially the search for polymers having narrow band gaps is a current topic because such polymers are expected to be promising candidates for intrinsic organic conductor and non-linear optical devices [10]. They have potential application in photonic devices (e.g. LEDs [11]) and sensors. Tuning of the band gap by structural modification is possible. One has to understand the relationship between the chemical structure and band gap since with this information one is able to obtain the desired properties by a good molecular design. A large number of studies has been performed both experimentally and theoretically in search of small band gap polymers with the introduction of fused ring systems, ladder type polymers, substituents and so on. The band gap of linear conjugated systems is mainly affected by five contributions: magnitude of the bond length alternation $E^{\delta r}$, the aromatic resonance energy E^{Res} , the mean deviation from planarity E^{θ} , inductive and mesomeric effects of substituents E^{Sub} , and intermolecular or interchain coupling in the solid state [12]. Bond length alternation is the difference between the average lengths of single and double bonds. Peierls instability causes the presence of alternating single and double bonds in the conjugation path. For example, if polyacetylene had equal bond lengths instead of having alternating bond lengths, it would behave like a metal. Aromatic resonance energy, E^{Res} ,

plays a role when there are rings in the polymer backbone since there is a competition for the delocalization of the π -electrons within the rings or along the conjugated backbone [13]. When there is a deviation from planarity (E^0) orbital overlap between the repeat units decreases and this causes increase in the band gap. These five contributions can be used in different ways to construct small band gap polymers. For example, fusion of the benzene or thiophene rings (figure 1.3) leads to an increase in the quinoid character of the polythiophene backbone, to the detriment of its aromaticity which results into a reduction of band gap from 2.0- 2.2 eV to 1.1 eV [14].

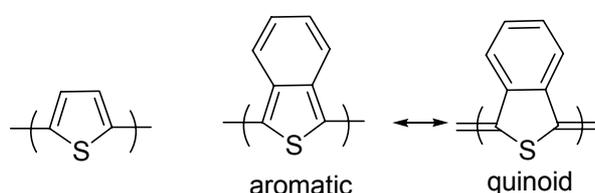


Figure 1.3 – Addition of benzene on to thiophene

Also, co-polymerization of aromatic-donor and o-quinoid-acceptor units [15] has been employed to reduce the bond length alternation. Another approach is grafting of electron releasing or withdrawing substituents, which will, respectively, increase or decrease the HOMO and LUMO levels. Rigidification of the π -conjugated system [16] in order to increase the coplanarity and reduce the bond length alternation is also another method that is used. Roncali et.al. showed experimentally and theoretically that the observed narrowing of the HOMO - LUMO gap results from a reduction of bond length alternation of the new substituted bridged dithienylene (DTE), induced by the rigidification of the (DTE) molecule (figure 1.4) [16].

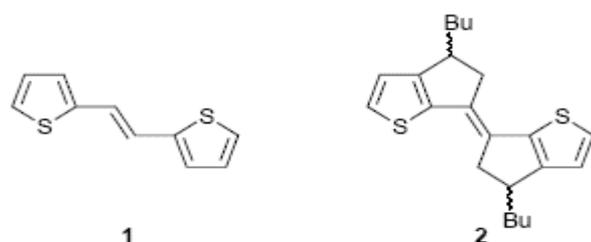


Figure 1.4- 1 dithienyl-ene -2

Also influence of quinoid structures can be another reason for the small band gaps. COPs tend to adopt the structure with the larger band gap that is more stable isomer. If there is a possibility for a polymer to be either quinoid or aromatic, it turns out that the more stable form is always the one with the larger band gap. Meaning that, for example polymers that would have close to no band gap in the quinoid form may have substantial band gaps in the aromatic form.

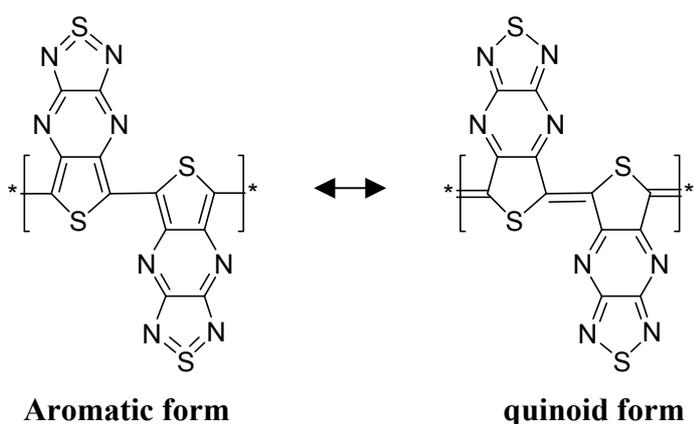


Figure 1.5- aromatic and quinoid forms of bi-TTP

1.3 Donor-Acceptor Concept

One of the approaches used for designing low band gap polymers is the donor acceptor concept, which was proposed by Havinga et al. in 1993[17]. They suggested that regularly alternating conjugated donor and acceptor like moieties in a conjugated chain will induce a small band gap and at the same time will lead to widening of the valence and conduction bands. The conjugated main chain of these polymers represents the one-dimensional analogue of a so-called n-i-p-i semiconductor structure, that is, they have donor and acceptor units separated by neutral parts. The mechanism that causes the band curving was expected to work equally well in this case. In order to get strong curvature of the bands strong donors and acceptors are needed such that already in the ground state of the system appreciable charge transfer from donor to acceptor occurs Havinga et al. were aware of the fact that if the extension of the donor and acceptor regions is

decreased, the curved band structure will not remain stable and a reshuffling of the bands will take place. They expected, however, that at least some of the broadening of the energy bands will survive and that the new valence and conduction bands will be broader than in the neutral case leading to a smaller band gap (figure 1.6). Basically by connecting these groups they aimed to decrease the level of lowest unoccupied molecular orbital (LUMO) and increase the highest occupied molecular orbital (HOMO) for reduction of the band gap compared to homopolymers.

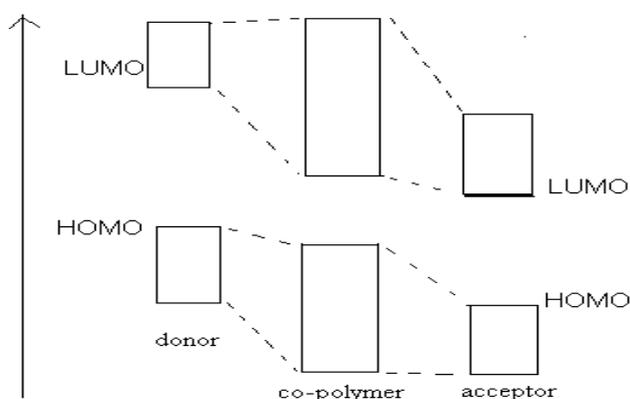


Figure 1.6- Representation for the hypothetical interaction between polymers according to donor acceptor model

Havinga et al. have used squaric acid and croconic acid as acceptors and heteroring systems containing nitrogen and sulfur atoms as donors for testing the idea [17]. The smallest band gap they have measured was 0.5 eV, leading to an intrinsic conductivity of 10^{-5} S/cm. Upon doping they reached a conductivity of 1 S/cm. This is not a very promising value considering that homopolymers like polythiophene have conductivities of around 10^3 S/cm.

Various types of donor-acceptor conjugated polymers were synthesized after Havinga's proposal. Mainly, thiophene, pyrrole, and their different substituted forms are used as electron donors since they are electron-rich moieties. However, for the electron acceptor part different kinds of moieties are used. Mullekom et al. carries out systematic investigations on donor-acceptor type

polymers by using different kinds of acceptor moieties [18]. The electron acceptor parts used for the donor-acceptor systems can mainly be divided into 5 groups [18]: acceptors based on squaraine unit (figure 1.7 copolymers 1-3), as used by Havinga, cyano or nitro substituted acceptors, acceptor units with the electron deficient atoms close to the conjugated backbone, electron acceptors with multiply fused pyrazine and thiadiazole rings.

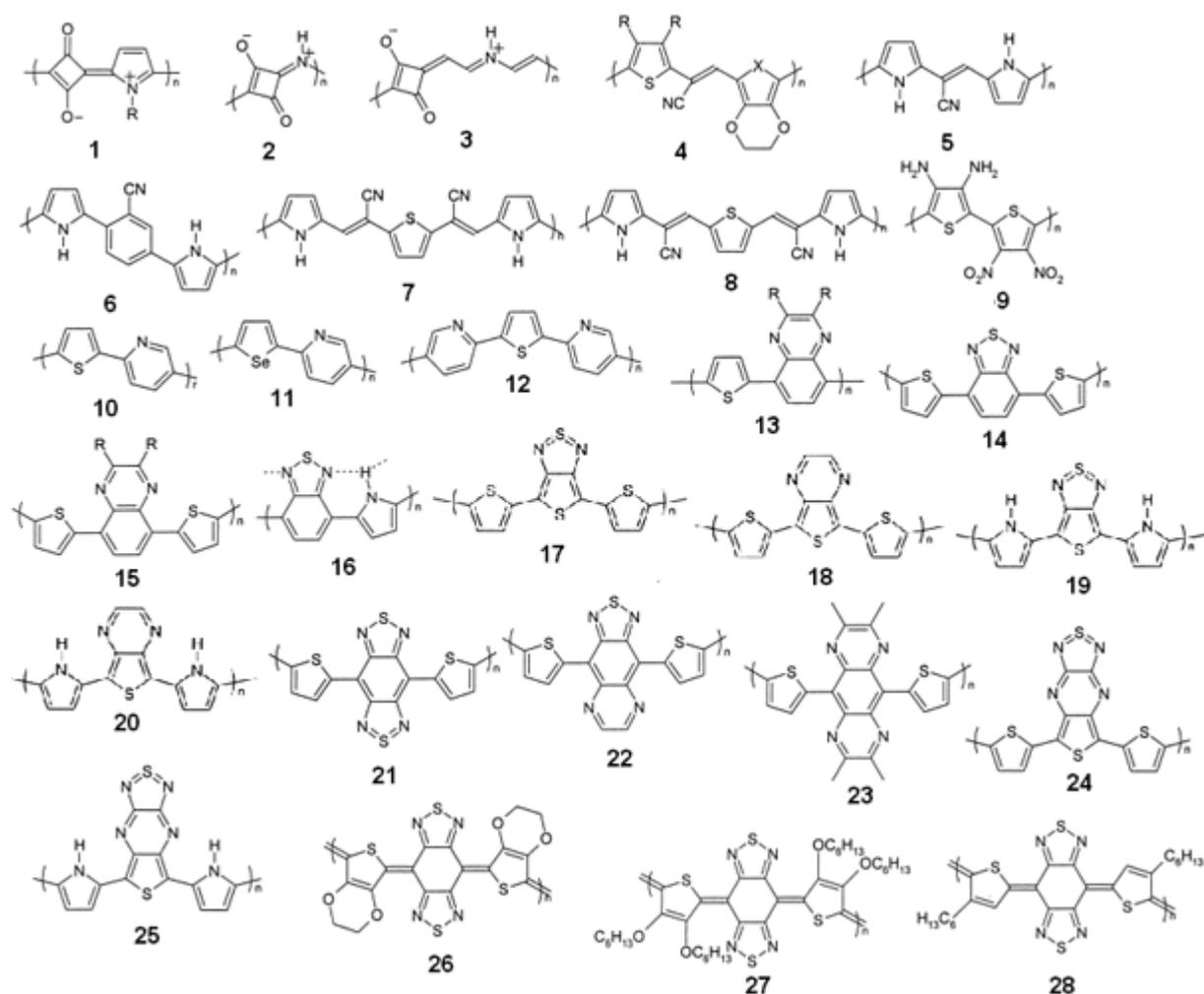


Figure 1.7 – different kinds of donor-acceptor type polymers

Since cyano- or nitro- groups are strong electron withdrawing groups, aryl units substituted with these groups are used as electron acceptors like in copolymers 4-9 in figure 1.7 cyano- substituted aryls with pyrrole containing polymers 4-8 have band gaps of 2.2, 2.7, 1.6, 2.0 eV, respectively [19-21]. An example of a copolymer containing an electron-accepting group differing from cyano-substituted aryl units is the polymer 9 in figure 1.7 which has the solution

and solid state optical band gaps are 1.4 and 1.1 eV, respectively [22]. If one looks at the band gaps, they are all higher than 1 eV although strong donors and acceptors are used. These high band gap values are explained by i) steric hindrance for polymer 6 and ii) the small size of atomic orbital coefficients at the coupling positions for the other polymers [18].

In order to improve the size of small atomic orbital (AO) coefficients, pyridine, which has large AO coefficients on the coupling positions is used as the electron acceptor moiety in copolymers 10-12 [23-25]. These polymers are also not very encouraging in terms of low band gap because polymers 10-11 have λ_{\max} centered around 490 nm (2.52 eV) and λ_{\max} of 12 it is around 440 nm (2.82 eV). These large band gaps are interpreted as result of weak electron accepting power of pyridine.

For a better performance electron acceptor units in which pyrazine or thiadiazole unit fused onto thiophene ring (polymers 17-20) were used. However, only the band gap of polymer 17 was determined: 0.9 eV [26]. Comparison of the absorption maxima of the monomers 18-20 (529, 712, 616 nm respectively) with that of monomer 17 (618 nm) suggests that, those are also promising small band gap materials. Here it is important to note that the highest value of the absorption maximum is found for the monomer precursor of the polymer containing pyrrole and thienodiazole moieties.

In order to increase the electron withdrawing power of quinoxaline or 2,1,3-benzothiadiazole, another pyrazine or thiadiazole ring was fused onto the vacant sites, resulting in a different type of acceptor unit series. Pyrazinoquinoxaline (figure 1.8) thiadiazoloquinoxaline and benzobisthiadiazole were used as electron acceptor units.

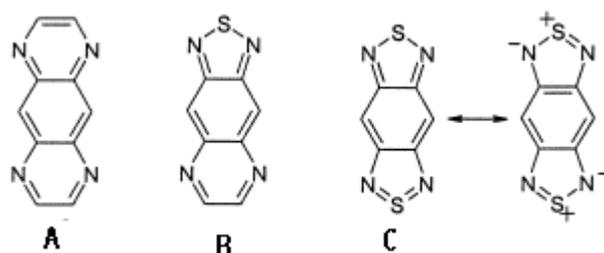


Figure 1.8-Pyrazinoquinoxaline A, thiadiazoloquinoxaline B, and benzobisthiadiazole C

Polymers 21, 22, 23 have band gaps of 0.5, 0.7, 0.9 eV respectively [27-29]. Polymer 21 enters the band gap region of below 0.5 eV, which is considered to be needed for intrinsic conductivity. N-methyl pyrrole analogue of polymer 21 was prepared to check whether it gives a lower band gap, since N-methyl pyrrole is a stronger donor than thiophene [12]. However, the band gap found was 0.6 eV and the larger band gap was attributed to the steric hindrance of the methyl groups [30]. 3,4-ethylenedioxy thiophene, which is a stronger donor than thiophene, is used as donor in the analogue polymer 26. It showed a band of 0.3 eV and its films showed a conductivity of the order of 1 S/cm after doping [18]. Soon after, copolymers containing thiadiazolo-thienopyrazine as electron acceptor units were synthesized [31]. Polymer 24 has a band gap of 0.3 eV that is smaller than all the band gaps reported before. Since pyrrole analogues of this kind of copolymers give lower band gap values compared to that of thiophene analogues, polymer 25 was prepared with the expectation of having $E_g \sim 0$ eV. The absorption maximum of the monomer found at 1345 nm (0.92eV) [32] is a low value for a monomeric unit, but electrochemical determination of the band gap of the polymer was not possible and no optical data for the polymer were presented to support the expectation.

In summary some donor acceptor systems have small band gaps, others do not. Conductivities are generally lower than those of homopolymers. Because of this the experimental data are not enough to make a clear decision about the validity of the donor/acceptor concept. What we think is that donor acceptor substitution cannot lead at the same time to low band gaps and wide bandwidths. Therefore we do not think that they will have a very improved conductivity. From a theoretical point of view this seems plausible. As mentioned before, high electronegativity difference is required according to this concept. When there is high electronegativity difference what we obtain is an ionic bond with the bonding orbital localized at the donor and the anti bonding localized at electronegative acceptor unit. The width of the bands depends on the strength of the interaction between the repeat units. When there is weak interaction, we have little

delocalization, which leads to narrow bands and poor mobility. Therefore, bandwidths can give a clue about the mobility of the carriers. Since the conductivity is a product of charge, charge carrier density and mobility, conductivity decreases when mobility decreases. If the donor/acceptor character (large energy difference) is conserved during polymerization, narrower bandwidths for copolymers than the homopolymers are predicted by the perturbation theory. This is in contradiction with the donor acceptor concept. But if the donor/acceptor character is not conserved in polymers conjugation would increase the band widths due to delocalization and charge transfer. This, however, would increase the band gaps as well. Also other factors rather than donor-acceptor concept may be responsible for the small band gaps of the polymers studied. For example, decrease in the bond length alternation upon polymerization or change in the ground state aromatic form to quinoid form may be the cause of the small band gaps. In this work, we aimed to understand the electronic and structural properties of some donor-acceptor type polymers. With this information we intended to understand the reasons for small band gaps and to determine whether donor acceptor concept is valid.

1.4 Previous studies on benzo[1,2-c;3,4-c']bis[1,2,5]thiadiazole and [1,2,5]thiadiazolo [3,4-b]thieno [3,4-e] pyrazine containing polymers

1.4.1 Experimental Studies

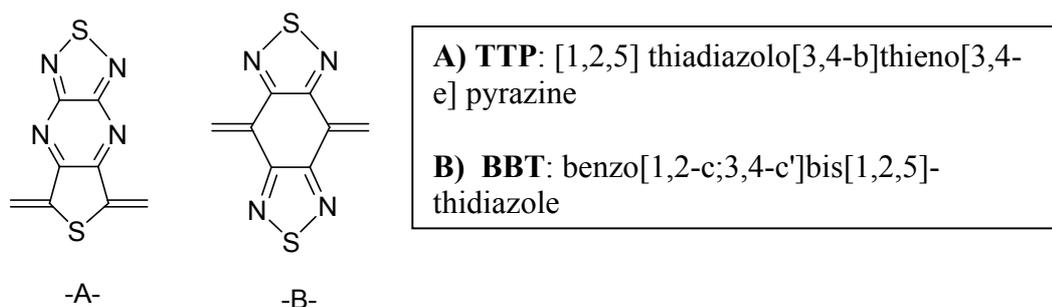


Figure 1.9- Acceptor units used in calculations

Polymers, having the trimeric fused ring systems as the repeat unit (figure 1.10), were first synthesized and characterized by Yamashita et al [32-33].

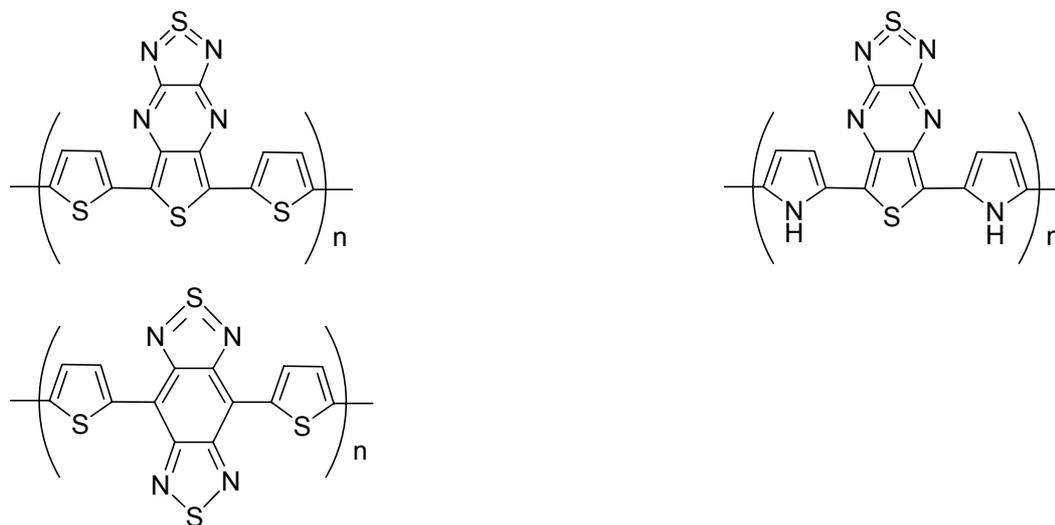


Figure 1.10- polymers synthesized by Yamashita et al.

First they synthesized the polymer containing thiophene as the aromatic donor and benzobis(1,2,5-thiadiazole) as the o-quinoid acceptor[33]. This polymer has almost coplanar structure. The optical band gap estimated from the absorption edge of the dedoped film is below 0.5 eV. The electrical conductivities of compressed pellets of dedoped and I₂ doped polymers were 5.0* 10⁻⁵ and 5.6*10⁻³ S/cm, respectively.

In 1997 Yamashita et al. reported the synthesis of [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine containing polymers [32]. They showed both experimentally and theoretically that these polymers have coplanar structures. For the thiophene-containing polymer the low energy absorption edge of the optical spectrum gave a band gap of below 0.5 eV and the electrochemical band gap was 0.3 eV. For the pyrrole-containing polymer, it is found that the potential gap between the p- type and n- type doping of this material vanishes in the cyclic voltammogram which means that electrochemical band gap is ≈ 0 eV. As it is seen the co-polymers have very small band gaps. The success with designing these systems were attributed to the donor-acceptor concept [18].

1.4.2 Theoretical Studies

Tachibana et al. made theoretical studies on, TTP, [1,2,5] thiadiazolo [3,4-b] thieno [3,4-e] pyrazine containing polymers [34]. They performed calculations on both homo-oligomers and co-oligomers (figure 1.11).

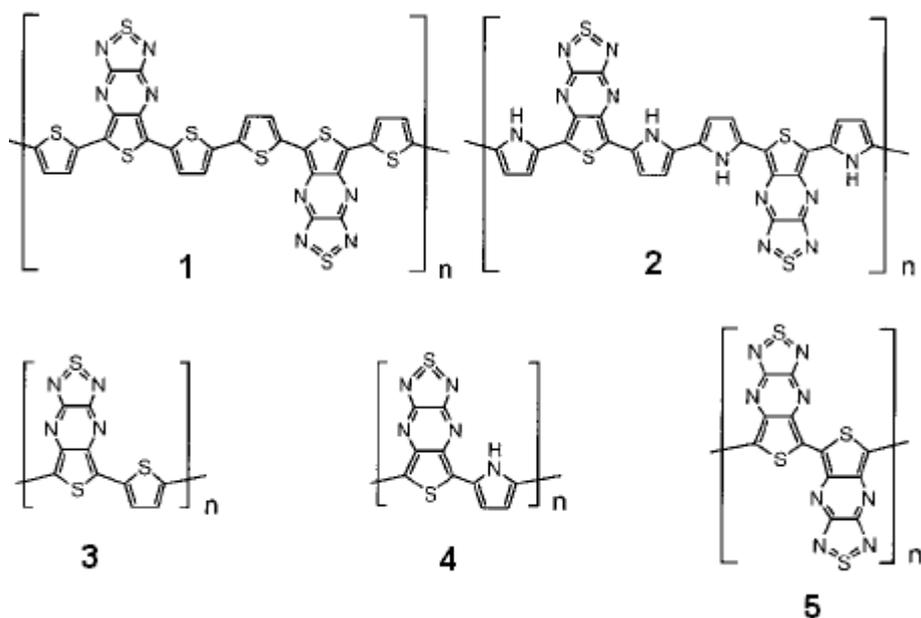


Figure 1.11- TTP containing polymers

They have calculated and analyzed the band gaps at extended Hückel level of theory and for the homo-oligomers they performed also calculations at B3LYP [35] / 6-31G* [36] level of theory. The calculated the band gaps of polymers 1-5 are 0.47, 0.33, 0.34, 0.22 and 0.10 eV respectively. For polymer 5 with B3LYP, which will be discussed later, they reported a band gap close to zero that is slightly negative. They attributed this negative band gap to the errors involved in the method that they have used. But this negative band gap has no physical meaning. It is probably because they have used oligomer models terminated with -H atoms throughout the work which forces the ends of the oligomers to have an aromatic structure. However these molecules have quinoid structures in their

ground states. Calculations of oligomers in the less favorable structure leads to very small band gaps.

1.5 Methods

1.5.1 Density Functional Theory (DFT)

Hohenberg, Kohn and Sham showed in 1964-65 that the energy of a quantum mechanical system is uniquely determined by its electron density. This quantity is more easily handled than the complicated wave function in the Schrödinger equation. Kohn also proved a method that made it possible to set up equations whose solutions give the system's electron density and energy. This method is called density functional theory (DFT), has become widely used in chemistry since, because of simplicity, it can be applied to fairly large molecules.

DFT is a way of simplifying the many body problem by working with the electronic charge density as fundamental variable rather than the wave function. It is a ground state theory that incorporates both exchange and correlation effects, and is more computationally efficient than Hartree-Fock methods.

Hohenberg-Kohn theorem does not tell the form of the functional dependence of energy on density, it confirms only that such a functional exists. Later, Kohn and Sham derived the set of one-electron equations from which in theory the electron density ρ could be obtained [37]. The Kohn-Sham (KS) orbitals are found by solving the Kohn-Sham equations. The significance of the KS orbitals is that they allow density ρ to be computed from equation $\rho(r) = \sum_{i=1}^n |\psi_i(r)|^2$.

The basic idea in KS formalism is splitting the kinetic energy term into two parts, one of which can be calculated exactly and a small correction term [38]. E_{xc} (exchange correlation energy) is the one that cannot be obtained exactly.

The central goal of DFT was to find better approximations to exchange correlation energy and corresponding potential V_{xc} . Several different schemes have been developed for obtaining approximate forms for the exchange correlation energy.

One of the improvements was the local density approximation (LDA). The assumption is that the density can be treated locally as a uniform electron gas, or equivalently that the density is a slowly varying function [38]. Despite the simplicity of the fundamental assumptions the local density approximation often provides results with accuracy similar to that obtained by HF methods.

A way to improve the LDA is to make it depend not only on the local value of the density, but on the extent to which the density is locally changing, i.e, the gradient of the density [39]. Generalized gradient approximation (GGA) or gradient corrected methods (non-local methods) consider a non-uniform electron gas. The most popular gradient corrected functional is that developed by Becke 1988 (B88). Perdew 1986 (P86), Perdew and Wang 1991 (PW91), LYP (Lee, Yang, Parr 1988) are popular correlation functionals. Usually combinations of the GGA methods are used while performing the calculations like BP86, BLYP. For example a BLYP calculation combines Becke's GGA exchange with the correlational functional of Lee, Yang and Parr.

The use of hybrid methods gave great improvement over LDA, GGA and HF methods. The basic concept behind the hybrid functionals is to mix exchange energies calculated in an exact (Hartree-Fock-like) manner with those obtained from DFT methods in order to improve performance.

1.5.2 Problems with DFT, Advantages and Disadvantages

Until recently it was thought mostly that KS orbitals have no physical significance and that their only connection to the physical world is that the sum of their squares add up to the exact density. However, lately some authors reported the use of KS in interpreting qualitative molecular orbital schemes. They are accepted to be legitimate tools in qualitative MO considerations [40]. In fact HF orbitals can be seen in a sense much farther away from the real system since they do not reflect the correlation effects and do not give the exact density. However, the eigenvalues ϵ_i connected to the KS orbitals do not have a strict physical meaning like the HF eigenvalues. ϵ_i^{HF} are, according to the Koopmans' theorem, approximate ionization energies. But only ϵ_i^{KS} of the highest occupied orbital is an

approximation to the first ionization energy [41]. Although it seems controversial as shown in the above discussion, the DFT orbital energies obtained by using hybrid functionals give good results. They are in good agreement with λ_{\max} from UV spectroscopy [9].

Hartree-Fock approach is in principle straightforward to study also excited states, whereas the DFT theory is a pure ground state approach [41].

Another difference between HF approach and DFT methods is the use of basis sets. In the HF approach any improvement in the basis set in principle will lead to better results that are closer to HF limit. However, in DFT small basis sets can be enough for achieving results close to exact values.

The advantage of DFT over ab initio method stems in its computational expedience and its reliability in most cases compared with the experimental results.

1.5.3 Methods Used in This Study

All calculations were done with Gaussian 98 [42]. Orbital plots were drawn by Molekel program [43]. Origin 7.0 was used for sketching the graphs and performing the polynomial fits [44]. Structures were drawn using ChemDraw Ultra 7.0 [45]. We estimated the band gaps of polymers by extrapolating the HOMO-LUMO gaps of the oligomers, using second degree polynomial fit, at the B3P86-30% /CEP-31g* level of theory. The abbreviation B3P86-30% stands for Becke's three parameter hybrid functional[46] modified to include 30 % Hartree-Fock exchange, and combined with Perdew's 1986 correlation functional[47] . This functional provides the HOMO and LUMO gaps in close agreement with λ_{\max} values from the UV spectroscopy [9]. The theoretical value gives the vertical λ_{\max} value of an isolated chain in the gas phase. The electrochemical band gap is the onset of absorption and does not have to be vertical. Optical band gaps and experimental λ_{\max} values differ usually about 0.5 eV. The electrochemical band gaps are about 0.5-1.0 eV lower than the experimental λ_{\max} values [9]. The excitation energies can be calculated by subtracting EA ($-E_{\text{LUMO}}$)

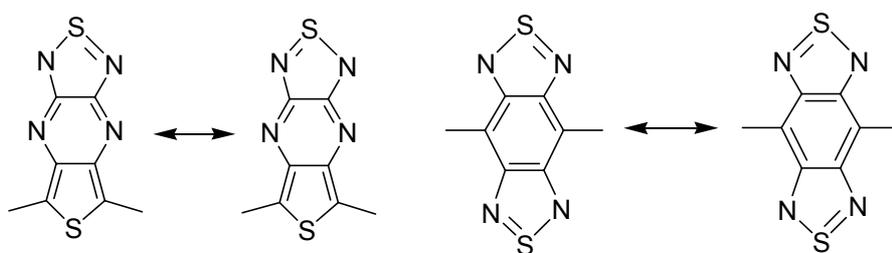
from IP ($-E_{\text{HOMO}}$) if we consider the electronic excitation as removal of one electron from HOMO and addition of one electron to LUMO.

CHAPTER 2 – Band Structure Calculations

2.1 Results

2.1.1- Moieties used in Calculations

Acceptor Units:



TTP: [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine **BBT**: benzo[1,2-c;3,4-c']bis[1,2,5]-thiazole

Figure 2.1- Structures of the acceptors

Donor Units:

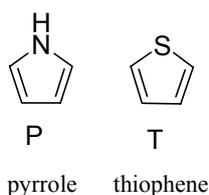


Figure 2.2- structures of the donors

2.1.2 Do the Moieties Show Donor-Acceptor Type Character?

We investigated the energy levels of the monomers to see whether they are right the choice for making donor-acceptor type systems. In table 2.1, HOMO and LUMO energy levels of the monomers and their energy gaps are given.

Table 2.1- HOMO and LUMO energies and HOMO-LUMO gaps of monomers

Moieties	HOMO (eV)	LUMO (eV)	E _{gap} (eV)
Thiophene	-7.04	-1.10	5.94
Pyrrole	-6.22	0.39	6.61
BBT	-7.34	-4.11	3.23
TTP	-7.32	-4.31	3.01

From figure 2.3, it is easily seen that donors, thiophene and pyrrole, have higher lying HOMO energies compared to BBT and TTP. Also the LUMO energies of TTP and BBT are very low lying compared to thiophene and pyrrole. Both indicate that copolymers will have D-A character. Also it is seen that pyrrole is a stronger donor than thiophene and TTP is a stronger acceptor than BBT. Copolymers consisting of these moieties should have smaller band gaps relative to thiophene and BBT containing ones according to the donor-acceptor concept. But one should recognize that LUMOs show a stronger donor-acceptor character than HOMOs because the energy difference between the LUMOs of donors and acceptors is larger compared to that involving HOMOs. Therefore investigation of the conduction bands would give more valuable information about donor-acceptor systems.

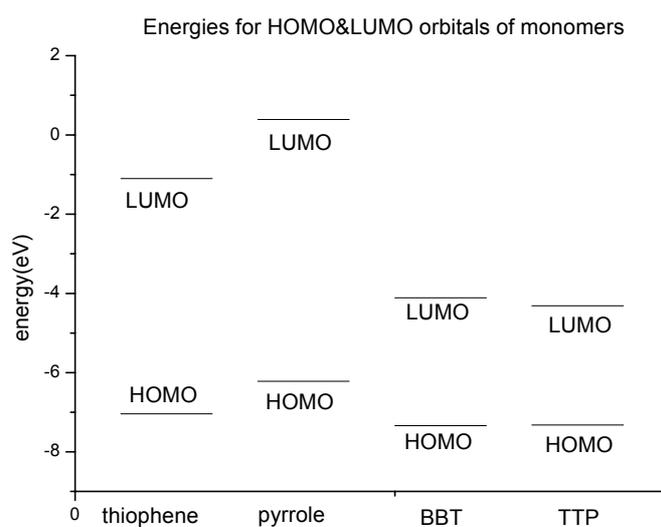


Figure 2.3 Energy levels of monomers

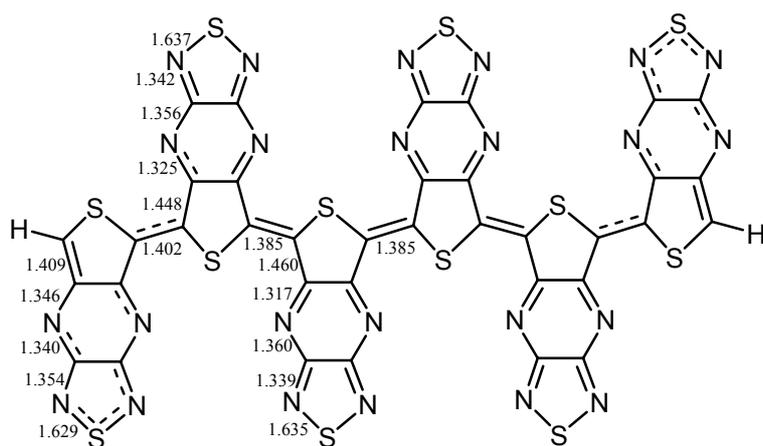


Figure 2.5- Change in the bond lengths from outer rings to inner rings in hexa-TTP

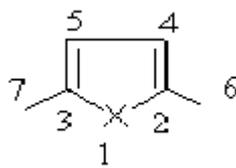
To determine which model (-H capped or -CH₂ capped) should be used for the calculations, we compared the energies of the inner two rings. The more stable form of the oligomer can be determined by calculating the energetic difference between the aromatic and quinoid structure alternatives. The energies of two different model oligomers, one -H capped and the other -CH₂ capped, cannot be compared directly because of the different end groups. The calculation is performed by subtracting the energies of oligomers that differ in size by two rings so that the end group effects are removed. For example, to determine the geometric preference for TTP oligomers, the energies of dimers are subtracted from those of the tetramers for both -H capped and -CH₂ capped models. The energy difference between the tetramer and dimer of -CH₂ capped model is -190.379 a.u., which gives crudely the energy for the inner two rings for a tetramer removing the effect of the end groups. The same is done for the -H capped oligomers. It is seen that there is a difference of $(\Delta(\Delta E_{4-2}))$ 0.025 a.u. (15.7 kcal/mol) between two models. This comparison shows that the quinoid structure is ~8 kcal/mol per ring more stable than the aromatic structure for TTP oligomers. In the ground states homo-oligomers and co-oligomers are more stable in the quinoid form. Because of this -CH₂ capped models are used for the calculations.

Table 2.2 HF energies of TTP oligomer

	Terminal group -CH ₂	Terminal group -H
E _{n=2} a.u.	-204.345	-191.570
E _{n=4} a.u.	-394.725	-381.924
ΔE ₄₋₂ a.u.	-190.379	-190.354

Using the correct models for the oligomers is very important because calculation of oligomers in the less favorable structure leads to very small band gaps, as reported in Tachibana's paper [34].

2.1.3.1 Thiophene and Pyrrole Oligomers

Table 2.3-bond distances in polythiophene and polypyrrole


	C2-X	C2=C4	C4-C5	C2-C6
PPy	1.380	1.402	1.429	1.457
PTh	1.752	1.396	1.427	1.459

Both thiophene and pyrrole oligomers are in the aromatic form in their ground states [49]. The values for polythiophene and polypyrrole are taken from an early work of Salzner [49]. pTh has a band gap of 2.3 eV and pPy has a band gap 3.2 eV. However, when we use the quinoid form (-CH₂ capped) instead of aromatic the extrapolation of the HOMO and LUMO energies gives a band gap value of 0.15 eV for PTh. This shows that using the incorrect model for the oligomers leads to very small band gaps. This is a striking example of how the band gap changes upon the change of ground state structure from aromatic to quinoid. The bond length alternation, bond length difference between C4-C2 bond and C2-C6 bond, in pTh is $\delta_1 = 0.063 \text{ \AA}$. The bond length alternation in pPy is $\delta_1 = 0.055 \text{ \AA}$. Also the conduction and valence band widths of polybithiophene are 2.2 eV and 1.9 eV and those of polybipyrrole are 2.4 eV and 1.5 eV.

2.1.3.2 [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine (TTP)

Oligomers of monomer to hexamer and octamer were investigated using both -CH₂ and -H capped models. As was mentioned before, the quinoid form is found to be 8 kcal/mol per ring more stable. The sharp changes in the inter-ring bond lengths upon chain length increase while using the -H capped models but little change in the -CH₂ capped models also confirms the preference for the quinoid form. From figure 2.6, it is seen that the 1.384 Å inter-ring bond lengths are double bonds, which is an indication of the quinoid structure. The oligomer structures have C_{2v} and C_{2h} symmetries. Frequency calculations confirmed that the planar structures of the oligomers are minima.

Bond lengths can be compared with those of polythiophene, which is calculated at the same level of theory. It was mentioned in table 2.3 that conjugated single bonds in polythiophene are around 1.46 Å and conjugated double bonds are about 1.39-1.40 Å.

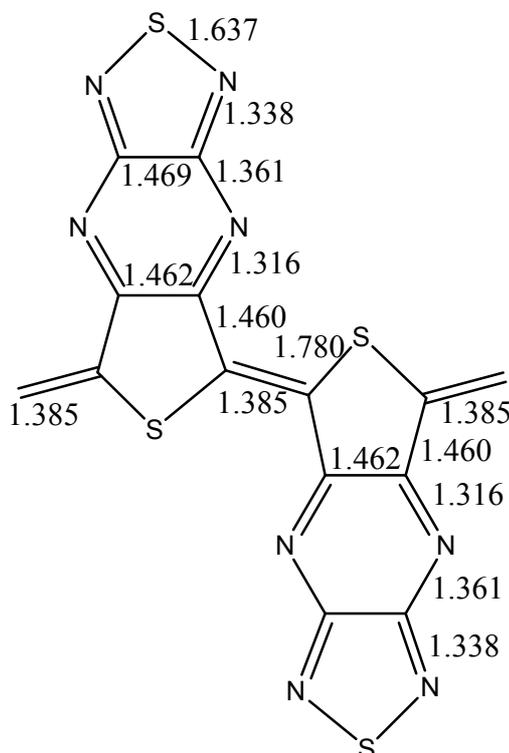


Figure 2.6 - The inter-ring bond lengths found in octa-TTP (-CH₂ capped model)

Figure 2.6 shows the bond lengths in the inner rings of octa-TTP. After pentamer bond lengths do not change any further, which indicates that bond lengths are

converged to polymer values. This means that we can use the octamer bond lengths as the polymer values. The short inter-ring bonds of 1.385 Å in octamer are clearly C=C double bonds. The thiophene polymer backbone contains no C-C double bonds since all bonds are around 1.460 Å. The structure is probably appearing due to the resistance of thiadiazole group, the upper group in the tricyclic unit, to adopt a non-classical structure. This can be seen easily if one looks at the structure of thieno [3,4-b] pyrazine [50] (figure 2.7), the structure of the pyrazine ring, middle part in the tricyclic unit, changes upon addition of thiadiazole.

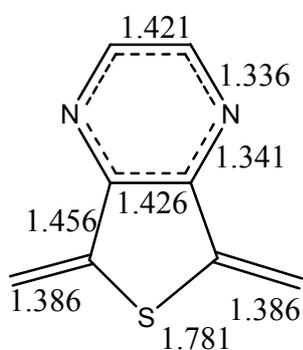


Figure 2.7 – Bond lengths in poly-thieno [3,4-b] pyrazine

The bond length alternation, the difference between the double inter-ring bond and neighbouring single bond, in poly-TTP is 0.075 Å. Later, this value will be compared with the copolymer values to see whether there is a decrease or an increase in BLA upon copolymerization and how this affects the size of the band gap.

Ionization potentials ($-E_{\text{HOMO}}$), electron affinities ($-E_{\text{LUMO}}$) and energy gaps (IP-EA) of TTP oligomers are given in table 2.4. The polymer values are found by extrapolation of the oligomer data with respect to $1/n$ (n is the number of repeat units) using second order polynomial fit. The general procedure done is using the linear fit but here it is clearly seen that data are not linearly correlated. Second order polynomial fit is a better choice for the extrapolation.

Table 2.4 IPs, EAs and Egaps of TTP oligomers and poly-TTP

n	IP (eV)	EA (eV)	E _{gap} (eV)
1	7.19	3.90	3.30
2	6.81	4.22	2.59
3	6.64	4.23	2.41
4	6.56	4.25	2.31
5	6.51	4.26	2.26
6	6.49	4.27	2.22
8	6.46	4.29	2.18

∞	6.37	4.32	2.05
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The band gap of poly-TTP is 2.05 eV. It is smaller than those of both poly-thiophene and poly-pyrrole. The decrease in IP and the increase in EA upon polymerization are 0.82 and 0.42 eV. These values are even higher in poly-thiophene and poly-pyrrole. Starting with a monomer having small band gap for polymerization is important but how the levels change upon polymerization is also very crucial in designing small band gap polymers. We will compare these values with those of co-polymers to see whether co-polymerization of donor acceptor moieties, which have large IP and EA energy differences compared to each other, is useful for synthesizing small band gap polymers.

Bandwidths of valence and conduction bands of poly-biTTP are 1.60 and 0.06 eV respectively. We used the biTTP as the repeating unit for the band widths in order to compare with the co-polymers. Although it has a relatively wide valence band, the homo-polymer poly-biTTP has negligible conduction band dispersion. This is because a node goes through the α -carbon atoms, which is shown in figure 2.8. Also formation of the valence and conduction bands from oligomers is shown in figure 2.9.

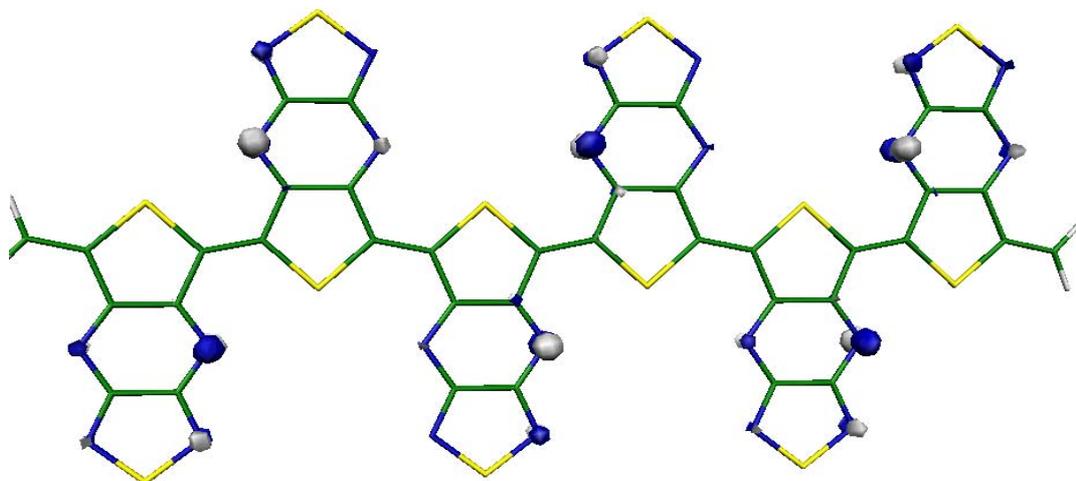


Figure 2.8 – orbital plot of LUMO of hexa-TTP

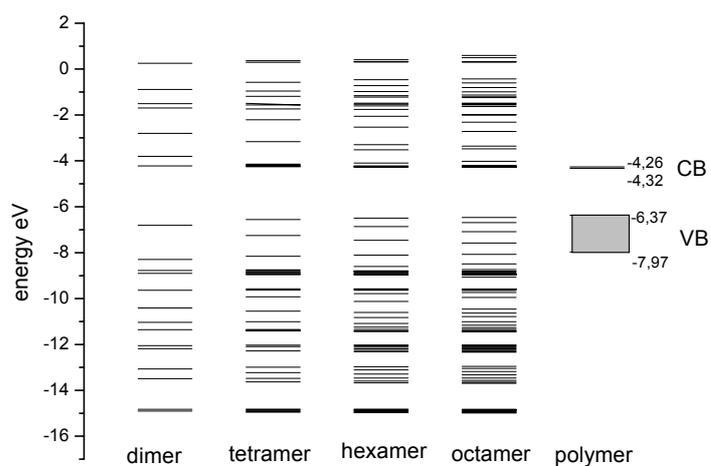


Figure 2.9 Formation of the valence and conduction bands of poly-biTTP from its oligomers

2.1.3.3 benzo [1,2-c; 3,4-c'] bis [1,2,5]-thidiazole (BBT)

Oligomers of monomer to hexamer were investigated using both $-CH_2$ and $-H$ capped models. It is found that the quinoid form is favoured over the aromatic form. The frequency calculations showed that these oligomers are not planar like the other homopolymer and copolymers which will be mentioned later. This is probably caused by the steric repulsion of the nitrogen lone pairs. Because of this

we also performed calculations on non-planar oligomers. Comparison of the oligomer structures shows that the non-planar oligomers adopt quinoid form more easily than planar ones because of reduced repulsion of the lone pairs. From figure 2.10, shortening of the inter-ring bonds of the dimer can easily be seen.

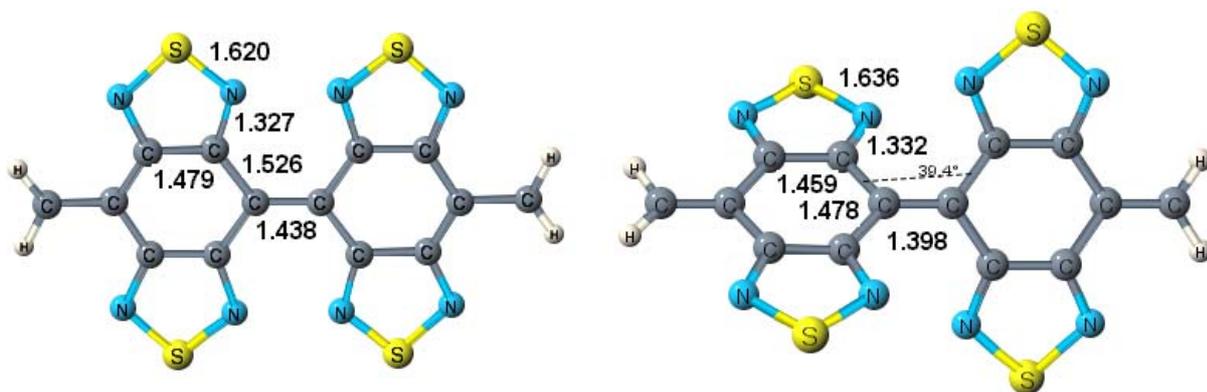


Figure 2.10 – bond lengths in BBT dimers – planar and nonplanar

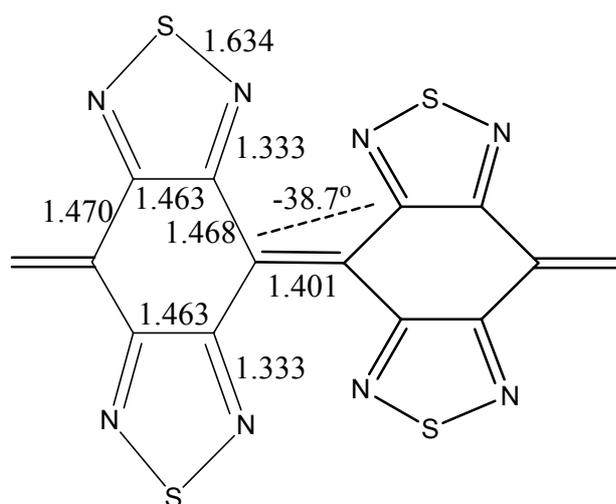


Figure 2.11 Optimized structure of the repeating unit of poly-BBT

There is a 38.7° dihedral angle between the repeat units. Because of the reduced repulsion of the nitrogen lone pairs the inter-ring bond is now clearly a double bond. The structure of the repeating unit is determined by the strong preference of the thiadiazole part not to adopt a non-classical geometry. The nitrogens in the thiadiazole group make double bonds with carbon atoms, which cause the benzene ring to relieve the double bonds. It is seen from figure 2.11 that all the bonds in the benzene ring are single bonds. Although the oligomers are non-planar, there is strong conjugation in the system. This can be seen from the smaller band gap of

the non-planar polymer compared to planar polymer and change in IP and EA upon polymerization. The band gap of the non-planar homopolymer is found to be 1.2 eV and that of planar is 2.1 eV.

Table 2.5 IPs, EAs, and Egaps of BBT oligomers- nonplanar

n	IP (eV)	EA (eV)	E _{gap} (eV)
1	7.45	3.04	4.41
2	6.81	3.90	2.91
3	6.57	4.10	2.47
4	6.43	4.23	2.20
∞	5.9	4.7	1.2

Table 2.6 IPs, EAs, and Egaps of BBT oligomers-planar

n	IP (eV)	EA (eV)	E _{gap} (eV)
1	7.45	3.04	4.41
2	7.06	3.50	3.56
3	6.88	3.74	3.13
4	6.74	3.88	2.87
5	6.70	3.95	2.75
∞	6.4	4.3	2.1

The conduction band width of the non-planar homopolymer is 2.6 eV and valence band width is 1.9 eV.

Direct comparison of the poly-BBT with the copolymers in the following sections will not be possible because of the non-planar structure.

2.1.4 Copolymers

2.1.4.1 Copolymers Having 1:1 Acceptor to Donor Ratio

2.1.4.1.1 Copolymers of TTP with Thiophene (Th) and Pyrrole (Py)

The repeating units contain thiophene or pyrrole (donor) and TTP (acceptor) in a 1:1 ratio. The geometry of the oligomers ($n=1-4$) having both H and CH_2 terminal groups are optimized and frequency calculations on the oligomers showed that they have planar structures. Calculations showed that both oligomers are in quinoid form in their ground states. Quinoid forms are 6.97 kcal/mol and 6.66 kcal/mol per repeat unit more stable for TTP-Th and TTP-Py respectively. The short inter-ring bonds also confirms the quinoid structures.

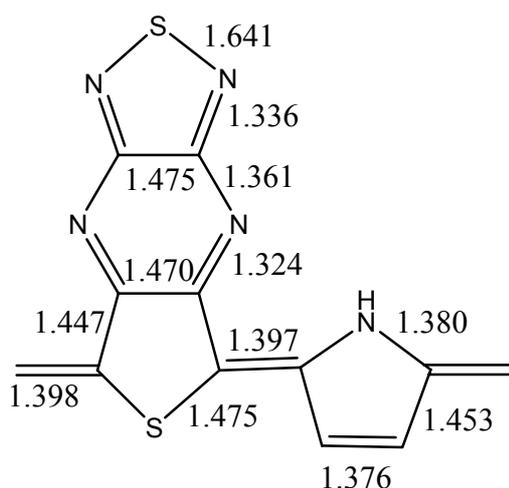


Figure 2.12 – optimized structure of the repeating unit of poly-TTP-Py

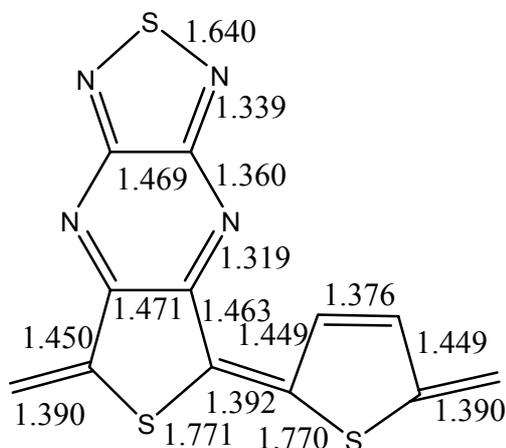


Figure 2.13 – optimized structure of the repeating unit of poly-TTP-Th

If one checks the structures in figures 2.11 and 2.12 the structure of the thiadiazolo pyrazine fragment doesn't change upon copolymerization compared to homopolymer. However, there is an absolute change in the structures of thiophene and pyrrole fragments. The thiophene and pyrrole rings changed their structures from aromatic to quinoid upon copolymerization. Thus, the tricyclic non-classical thiophenes successfully impose their quinoid structures on thiophene and pyrrole. In the copolymer of TTP and pyrrole the bond length alternation of TTP and pyrrole are 0.050 Å and 0.056 Å respectively. In the copolymer with thiophene these values are 0.060 Å and 0.057 Å. The BLA in the thiophene ring of TTP is decreased compared to the homopolymer. The BLA in thiophene and pyrrole are nearly same in copolymers and in homopolymers.

Table 2.7 IPs, EAs, and Egaps of TTP-Th co-oligomers

n	IP (eV)	EA (eV)	E _{gap} (eV)
1	6,39	3,76	2.63
2	6.12	4.19	1.93
3	6.04	4.27	1.77
4	6.01	4.31	1.70
∞	5.9	4.4	1.5

Table 2.8 IPs, EAs, and Egaps of TTP-Py co-oligomers

n	IP (eV)	EA (eV)	E _{gap} (eV)
1	6.16	3.64	2.52
2	5.76	3.98	1.78
3	5.62	3.99	1.63
4	5.56	4.00	1.56
∞	5.4	4.0	1.4

The band gaps of copolymers poly-TTP-Th and poly-TTP-Py are 1.5 eV and 1.4 eV respectively. This means that upon copolymerization the band gaps are reduced compared to homopolymers. The copolymer with pyrrole has a slightly

smaller band gap than that with thiophene. From table 2.1 it is seen that the donor strength of pyrrole is higher than thiophene. This situation agrees with donor acceptor concept in the way that is stronger donors and acceptors are used the band gap will be smaller.

Table 2. 9 Band widths for copoly-TTP-Py & Band widths for copolyTTP-Th

Valance Band (eV)		Conduction Band (eV)		Valance Band (eV)		Conduction Band (eV)	
Edge	HOMO	LUMO	Edge	Edge	HOMO	LUMO	Edge
-7.5	-5.4	-4.0	-3.2	-7.9	-6.0	-4.4	-3.6
2.1		0.8		1.9		0.8	

The valence and conduction band widths are 2.1 eV and 0.8 eV for poly-TTP-Py, 1.9 eV and 0.8 eV for poly-TTP-Th. Both have wide valence bands but relatively narrow conduction bands probably caused because of the high energy difference between the LUMO of TTP and those of thiophene or pyrrole. The large difference between the LUMO energies should have caused band width increase of the conduction bands according to the donor acceptor concept. This is not borne out in the above results.

2.1.4.1.2 Copolymers of BBT with Thiophene (Th) and Pyrrole (Py)

Co-oligomers, from monomer to tetramer, of BBT with thiophene and pyrrole were optimized by using both -H capped and -CH₂ capped models. Although oligomers of BBT are non-planar, both co-oligomers have planar structures, which is verified by frequency calculations. Since the distance between the two BBT units increases upon polymerization, repulsion of the nitrogen lone pairs decreases and probably because of this the co-oligomers are planar. Hydrogen bond formation in the pyrrole containing co-oligomers helps planarization as well. The co-oligomers have quinoid structures. The quinoid form is preferred over the aromatic form 6.0 kcal/mol and 6.5 kcal/mol per repeating unit for thiophene and pyrrole containing co-polymers, respectively.

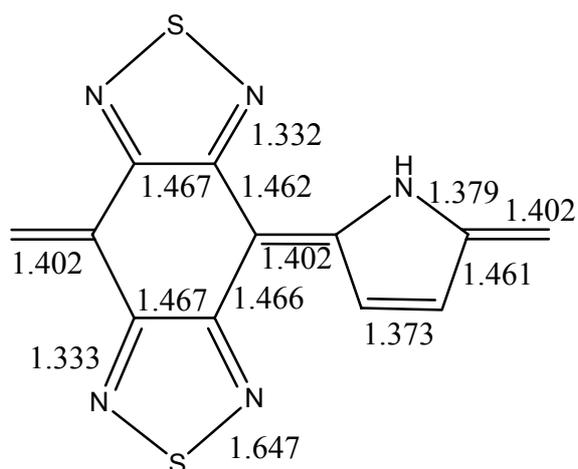


Figure 2.14 Structure of the repeating unit of poly-BBT-Py

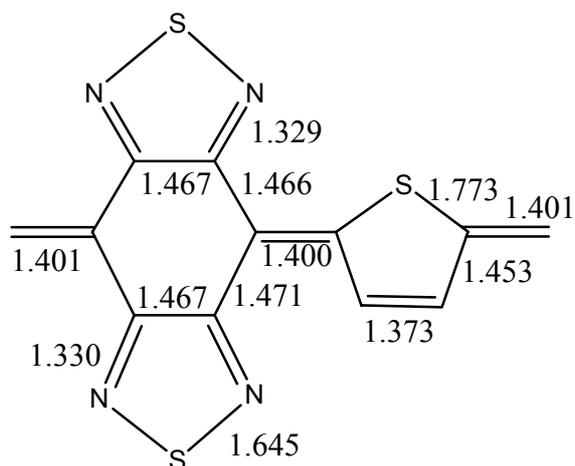


Figure 2.15 Structure of the repeating unit of poly-BBT-Th

Upon polymerization both the structure of thiophene and pyrrole changes. The donor units, thiophene and pyrrole, adopts the unfavorable quinoid forms. Bond length alternations in thiophene and pyrrole rings are 0.052 Å and 0.059 Å, respectively. The bond length alternation in pyrrole is increased and in thiophene it is decreased compared to homopolymers, but the changes are small. The structure of BBT is not much changed upon co-polymerization. The structure of the repeat unit in the non-planar homopolymer is nearly same compared to copolymer, since the thiophene units separates the BBT units, lone pair repulsion is reduced like in the non-planar homopolymer.

Table 2.10 Table 2. IPs, EAs, and Egaps of BBT-Th co-oligomers

n	IP (eV)	EA (eV)	Egap (eV)
1	6.51	3.19	3.32
2	6.19	3.77	3.41
3	6.07	3.91	2.16
4	6.02	3.99	2.03
∞	5.9	4.2	1.7

Table 2.11 IPs, EAs, and Egaps of BBT-Py co-oligomers

n	IP (eV)	EA (eV)	Egap (eV)
1	6.29	3.02	3.27
2	5.93	3.61	2.32
3	5.81	3.73	2.08
4	5.76	3.80	1.96
∞	5.6	4.0	1.6

Ionization potentials, electron affinities and energy gaps of co-oligomers are given in tables 2.11 and 2.12 copolymers poly-(BBT-Th) and poly-(BBT-Py) have band gaps of 1.7 eV and 1.6 eV. Once more in these, the copolymer with the stronger donor unit, pyrrole, has a smaller band gap.

Table 2.12 Band widths for copolyBBT-Th & Band widths for copolyBBT-Py

Valance Band (eV)		Conduction Band (eV)	
Edge	HOMO	LUMO	Edge
-7.7	-5.9	-4.2	-3.3
1.8		0.9	

Valance Band (eV)		Conduction Band (eV)	
Edge	HOMO	LUMO	Edge
-7.5	-5.6	-4.0	-3.1
1.9		0.9	

The valence and conduction band widths of poly-(BBT-Th) are 1.8 eV and 0.9 eV, respectively. In poly-(BBT-Py), they are 1.9 eV and 0.9 eV. In both copolymers the conduction band is narrower than the valence band, as it is in the copolymers containing TTP. This is not surprising since the energies LUMOs of the moieties differ considerably, showing a good donor-acceptor type character, which do not interact very well.

2.1.4.2 Copolymers Having 1:2 Acceptor to Donor Ratio

We have also done calculations on cooligomers having 1:2 acceptor to donor ratio. These copolymers are experimentally studied as indicated in the introduction.

2.1.4.2.1 Copolymers of TTP with Two Thiophenes (Th) and Two Pyrroles (Py)

Experimentally synthesized copolymers have quinoid type structures and the electrochemical band gaps for thiophene and pyrrole containing copolymers are 0.3 eV and ~0 eV, respectively.

The geometries of monomer to tetramer are optimized using both $-CH_2$ and $-H$ capped models. The calculations showed that cooligomers prefer to be quinoid in the ground state, in line with the experimental results. However, when we compare the energies, we see that the preference for quinoid forms decreases as the ratio of the aromatic donor unit increases. The quinoid form is preferred over the aromatic form 3.64 kcal/mol and 3.85 kcal/mol per repeating unit for thiophene and pyrrole containing co-polymers respectively. In fact this is a likely situation since the donors, thiophene and pyrrole, prefer to be aromatic and if the ratio in the repeating unit increases the quinoidal preference of the cooligomers should decrease. The optimized structure of the repeating units, double inter-ring bonds and quinoid structures of donors, also supports the results of calculations on the geometry.

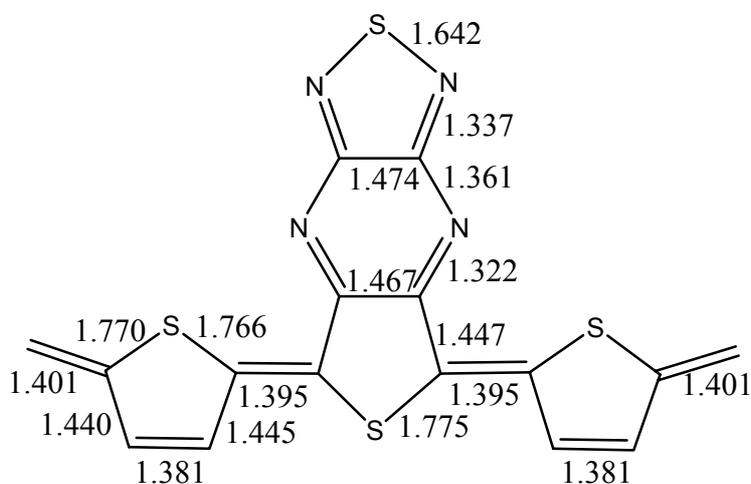


Figure 2. 16 Optimized structure of the repeating unit in poly(TTP-2Th)

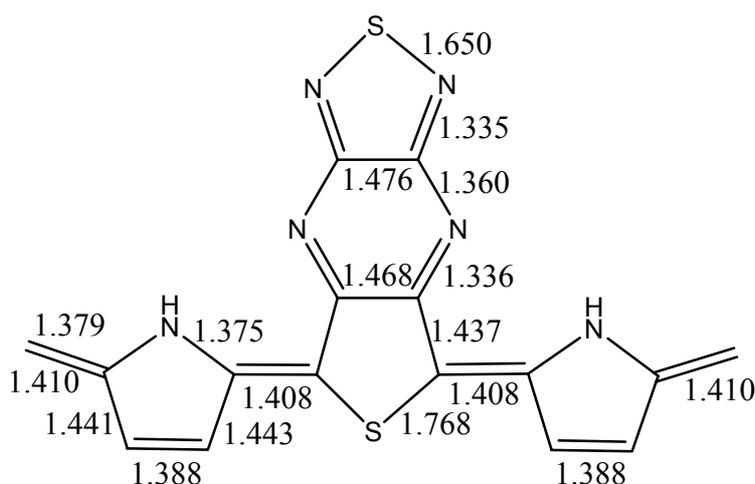


Figure 2.17 Optimized structure of the repeating unit in poly(TTP-2Py)

There are changes in the geometry upon increase of the donor ratio. The double inter-ring bonds and double bonds in the donor units elongate compared to 1:1 ratio copolymers. Also the single bonds in the conjugated path shorten. Together these two effects decrease the bond length alternation. The decrease in the bond length alternation can cause a decrease in the band gap. The bond length alternation in poly(TTP-2Th) is 0.050 Å near a TTP unit and 0.039 Å near an

other thiophene unit. In poly(TTP-2Py) it is 0.035 Å near a TTP unit and 0.030 Å near a pyrrole unit. Especially the bond length alternation is clearly decreased in the pyrrole containing copolymer compared to 1:1 ratio copolymers and homopolymers.

Table 2.13 IPs, EAs, and Egaps of TTP-2Th co-oligomers

N	IP (eV)	EA (eV)	Egap (eV)
1	6.03	3.66	2.37
2	5.73	4.15	1.58
3	5.66	4.20	1.46
4	5.63	4.23	1.40
∞	5.5	4.3	1.2

Table 2. 14 IPs, EAs, and Egaps of TTP-2Py co-oligomers

N	IP (eV)	EA (eV)	Egap (eV)
1	5,66	3,46	2.20
2	5,33	4,07	1.26
3	5,27	4,13	1.14
4	5,26	4,16	1.10
∞	5.2	4.2	1.0

The band gap of copolymer containing two thiophenes in the repeat unit is 1.2 eV and that of pyrrole containing is 1.0 eV. The copolymer with the pyrrole donor has a smaller band gap than the one with thiophene as it is in the other copolymers. Also the decrease in the band gap compared to 1:1 ratio copolymers is seen in these.

2.1.4.2.2 Copolymers of BBT with Two Thiophenes (Th) and Two Pyrroles (Py)

The copolymer of BBT with two thiophenes was also experimentally studied. This polymer has a band gap of 0.5 eV. The electrical conductivities of compressed pellets of dedoped and I₂ doped polymers were 5.0×10^{-5} and 5.6×10^{-3} S/cm, respectively [33]. Unfortunately there are no experimental data for the copolymer containing pyrrole.

For the thiophene containing copolymer the quinoid form is found to be 3.06 kcal/mol per repeat unit more stable than the aromatic form, which is in accordance with experiment. Again preference for the quinoid character is decreased compared to 1:1-ratio copolymer.

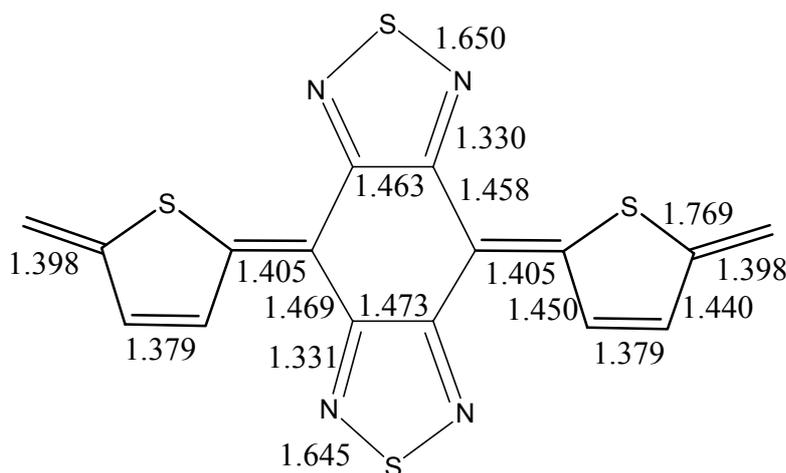


Figure 2.18 Optimized structure of the repeating unit in poly(BBT-2Th)

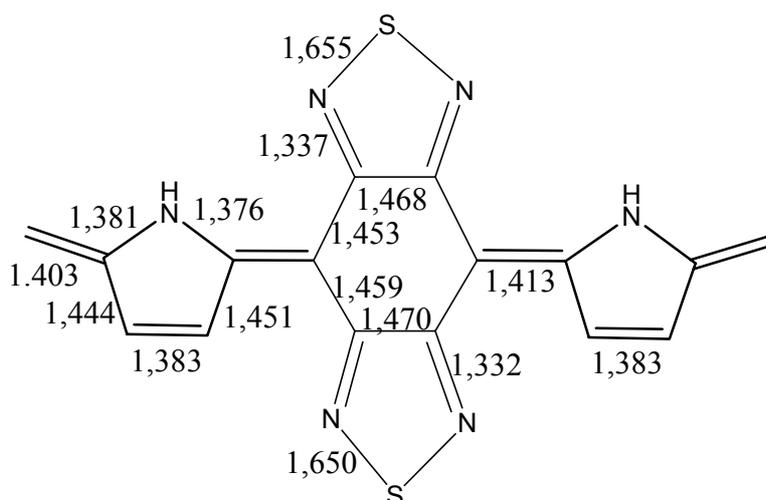


Figure 2. 19 Optimized structure of the repeating unit in poly(BBT-2Py)

From figures 2.18 and 2.19 it is seen that both donors have quinoid structures. There is increase in the double bonds compared to 1:1 ratio copolymers. The bond length alternation in poly(BBT-2Th) is 0.045 Å near a BBT unit and 0.042 Å an other thiophene. The bond length alternation in poly(BBT-2Py) is 0.038 Å near a BBT unit and 0.041 Å an other pyrrole. The bond length alternations in thiophene and pyrrole are decreased compared to thiophene and pyrrole in both homopolymers and copolymers.

Table 2.15 IPs, EAs, and Egaps of BBT-2Th co-oligomers

n	IP (eV)	EA (eV)	Egap (eV)
1	6.10	3.11	2.99
2	5.77	3.89	1.88
3	5.68	4.03	1.65
4	5.64	4.10	1.54
∞	5.5	4.2	1.3

Table 2.16 IPs, EAs, and Egaps of . BBT-2Py co-oligomers

n	IP (eV)	EA (eV)	Egap (eV)
1	5.75	2.91	2.81
2	5.38	3.71	1.67
3	5.27	3.84	1.43
∞	5.1	3.9	1.2

Band gap of poly(BBT-2Th) is 1.3 eV and that of poly(BBT-2Py) is 1.2 eV. Band gaps of the copolymers are decreased compared to both homopolymers and copolymers having 1:1 ratio.

2.2 Discussion

2.2.1 Geometries

The marked structural change upon polymerization is that in all copolymers the thiophene and pyrrole moieties have changed their structure from aromatic to quinoid. That is the acceptor units BBT and TTP successfully imposed their quinoid characters on to thiophene and pyrrole. There is not much change on the structure of the acceptor units upon copolymerization. Although the homopolymer poly(BBT) is non-planar, copolymers containing BBT have planar structures. The thiadiazole units play the important role in determining the geometries. Because this unit does not want to adopt a non-classical structure, it forces the BBT and TTP moieties to prefer the quinoid form in their ground states.

Bond length alternation on thiophene and pyrrole do not differ much between the homopolymers and copolymers having 1:1 acceptor to donor ratio. However, bond length alternation is reduced in copolymers having 1:2 acceptor to donor ratio. This is probably because addition of one more aromatic thiophene unit into the repeating unit decreases the quinoid character and increases the aromatic character of the polymer backbone. This is confirmed by the increase in the double bond lengths of the inter-ring bonds and double bonds of thiophene.

Comparing the preference energies of the repeating units also confirms the reduced preference for the quinoid form.

2.2.2 Band Gaps

Table 2.17 Band gaps of homopolymers

	polythiophene	polypyrrole	polyBBT	polyTTP
Eg (eV)	2.3	3.2	1.2	2.0

Table 2.18 Band gaps of copolymers 1:1 acceptor to donor ratio

	poly(BBT-Th)	poly(BBT-Py)	poly(TTP-Th)	poly(TTP-Py)
Eg (eV)	1.7	1.6	1.5	1.4

Table 2.19 Band gaps of copolymers 1:2 acceptor to donor ratio

	poly(BBT-2Th)	poly(BBT-2Py)	poly(TTP-2Th)	poly(TTP-2Py)
Eg(eV)	1.3	1.2	1.2	1.0

Band gaps of homopolymers and copolymers are given in tables 2.17-2.18. In the beginning I should mention that since the homopolymer poly(BBT) is non-planar direct comparison of it with other polymers is not an straight forward.

It is seen from the tables that all cooligomers have smaller band gaps than homopolymers. The reductions are between 0.5 and 1.0 eV compared to the homopolymer having the smaller band gap. Copolymers having 1:2 acceptor to donor ratio have smaller band gaps than the copolymer having 1:1 ratio. It was discussed in the introduction part that electrochemical band gaps lie 0.5-1 eV below the theoretical λ_{\max} values. This means that the our results are in accordance with the experimental data. Trends are also shown in our calculations like the polyTTP-2Py has the smallest band gap of all. In my systems, it is seen from the tables that the thiophene containing copolymers have larger band gaps than the pyrrole containing analogues. That is the stronger donor gives the smaller

band gap. The same applies on the acceptor part too. The copolymers containing stronger acceptor TTP have smaller band gaps than those contain BBT. The smallest band gap in my systems is found in the copolymer between the strongest acceptor TTP and strongest donor pyrrole. Up to here the predictions of the donor acceptor concept hold for my systems.

In order to determine whether small band gaps are a result of donor acceptor interaction or other things like the reduce in BLA and influence of the quinoid structure constraint on thiophenes, I made calculations on thiophene oligomers using fixed bond lengths. I have used the bond lengths of TTP-2Th co-oligomers in thiophene only analogues as shown in figure 2.20.

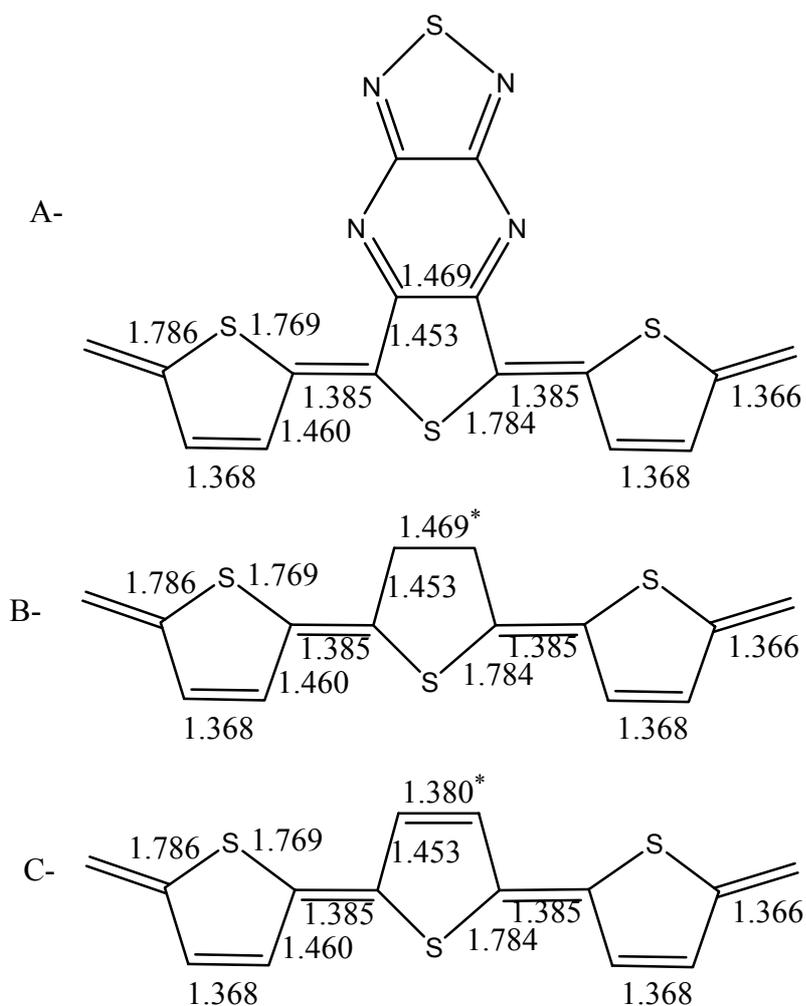


Figure 2.20 – bond lengths in monomers

In the B series of oligomers in figure 2.20, in all thiophenes I have used the same bond lengths as in the cooligomers , in the C series, I have included the optimized double bond length for the quinoid form.

Table 2.20 Band gaps of oligomers

n	E _{gap} (eV)		
	A	B	C
1	2.37	2.31	2.48
2	1.58	1.26	1.42
3	1.46	0.78	0.99

It is seen from the table 2.20 that the oligomers composed of thiophene only has smaller band gaps than the co-oligomers, except the C monomer. This means that the geometrical constraints on thiophenes have a clear effect on reducing the band gap. Data shows that the small band gaps are probably due to influence of the quinoid structures and decrease in bond length alternation instead of donor acceptor concept.

2.2.3 Band Widths

Table 2.21 Band widths of homopolymers

	p-biTh	p-biPy	p-BBT	p-biTTP
VB (eV)	2.2	2.4	2.6	1.6
CB (eV)	1.9	1.5	1.9	0.1

Table 2.2 Band widths of copolymers

	pBBT-Th	pBBT-Py	pTTP-Th	pTTP-Py
VB (eV)	1.8	1.9	1.9	2.1
CB (eV)	0.9	0.9	0.8	0.8

The valence band widths of copolymers are similar to those of homopolymers. The conduction band widths are decreased compared to homopolymers except poly-TTP. Poly(TTP) as discussed before has a very small dispersion in the

conduction band. Only in copolymer poly(TTP-Th) probably the valence band width is smaller than the reported value. These band widths are found by using the appropriate π orbital energies upon second order polynomial fit. For example, below the energies of orbitals starting from LUMO of tetra(TTP-Th) is plotted.

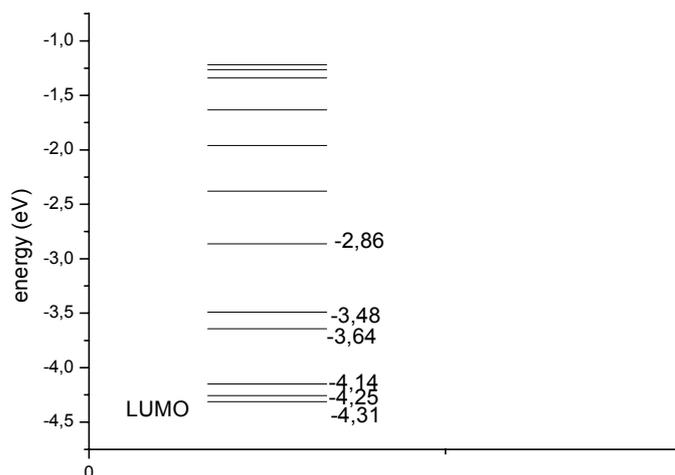


Figure 2.21 (LUMO + n) orbital energies in tetra(TTP-Th)

Normally the orbital having energy -3.64 eV is taken into account while calculating the band widths. However in this one there is a 0.5 gap between the LUMO+3 orbital and LUMO+2 orbitals. This gap is due to the different origins of the orbitals, which can be seen from figure 2.22. The first two, LUMO and LUMO+1, have same origins the third one is different but has a similar energy. Because of the big gap between the third and fourth orbitals we think that the conduction band should be smaller. We have the situation is same in poly(TTP-2Th) and poly (TTP-2Py) as it is seen from figure 2.22. They both will have narrow conduction band widths.

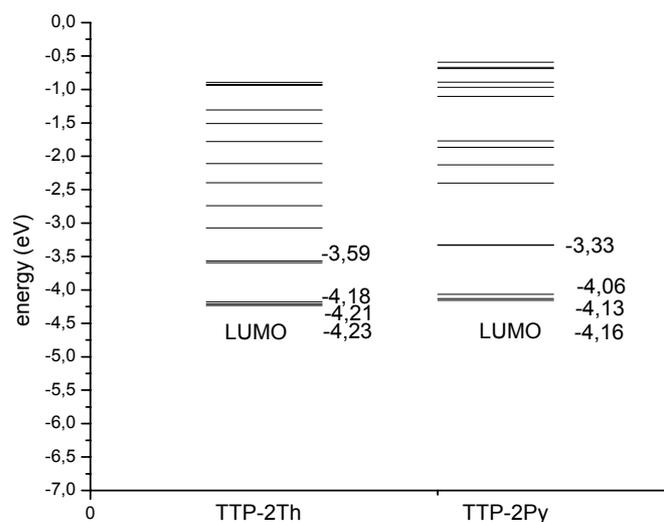


Figure 2.22 orbital energies in tetra(TTP-2Th) and (TTP-2Py)

Another important thing to notice is that LUMO and LUMO+1 orbitals have coefficients only on TTP acceptor, which is an expected result because of the high energy difference between the LUMO of thiophene and TTP. As mentioned in the introduction part when there is high electronegativity difference what we obtain is an ionic bond with the bonding orbital localized at the donor and the anti bonding localized at electronegative acceptor unit (figure 2.22). The width of the bands depends on the strength of the interaction between the repeat units. When there is weak interaction we have little delocalization, which leads to narrow bands and poor mobility. This is what we see in the conduction bands of the copolymers. So the prediction of wider band widths in the donor-acceptor concept is not valid. This explains the low conductivities of doped polymers. Unfortunately, n-type conductivities were not reported. The theoretical results suggests that the copolymers should be n-dopable because of the high EAs, but n-type conductivity should be low because of the small conduction band widths.

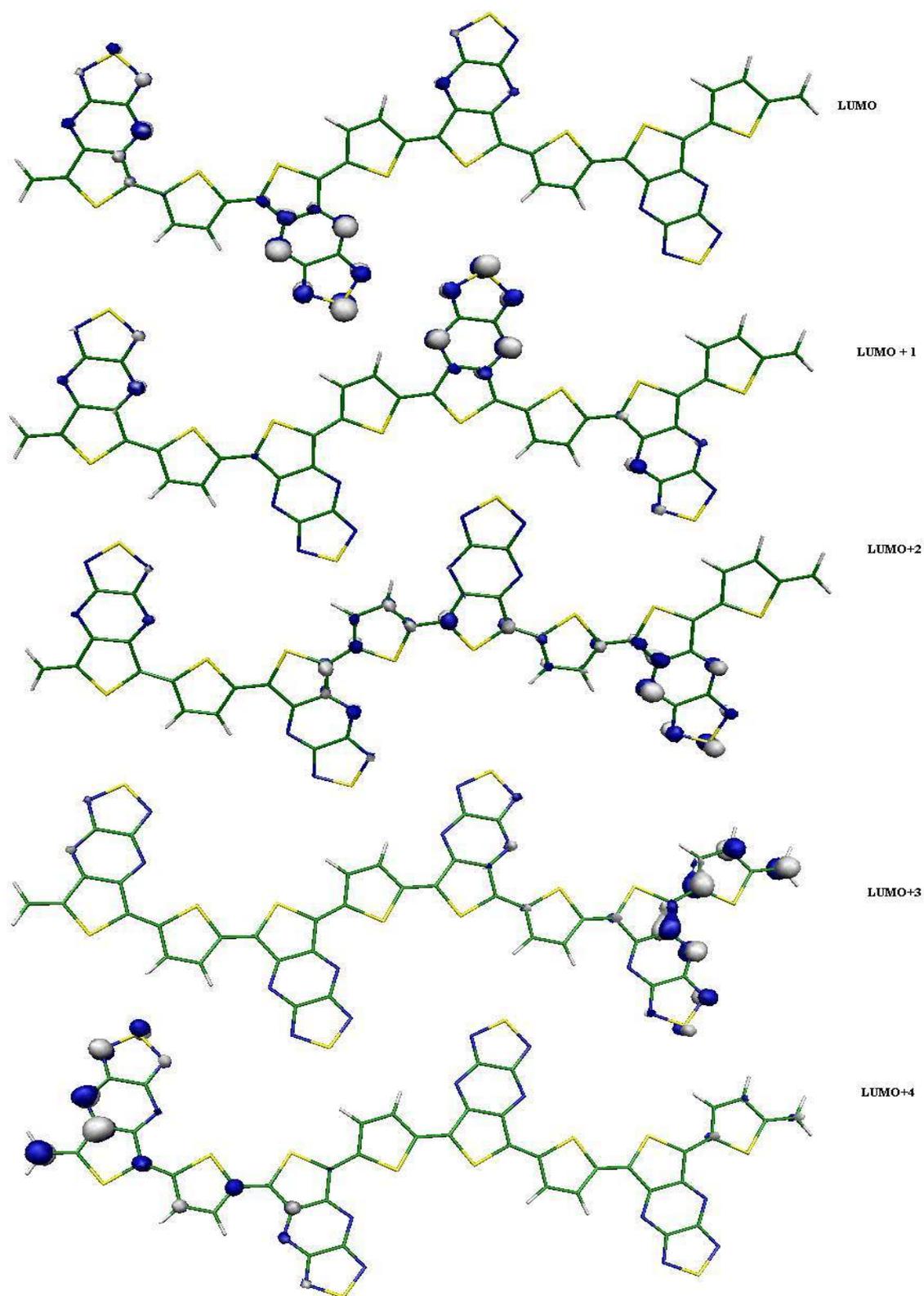


Figure 2.23 orbital plots of tetra(TTP-Th)

CHAPTER 3- Conclusion

Density functional theory (DFT) calculations were performed for homo and co-oligomers (having 1:1 and 1:2 acceptor to donor ratios) of thiophene (Th), pyrrole (Py), benzo[1,2-c;3,4-c']bis[1,2,5]-thiadiazole (BBT) and [1,2,5] thiadiazolo[3,4-b]thieno[3,4-e] pyrazine (TTP) to investigate the validity of the donor-acceptor concept.

Theoretical investigation showed that acceptor units BBT and TTP successfully imposed their quinoid characters on to thiophene and pyrrole. As the ratio of the donors increases in the copolymers, the preference for the quinoid structure decreases. All copolymers composed of pyrrole show stronger preference for quinoid structure than those composed of thiophene except copolymer polyTTP-Py. The BLA in homopolymers and copolymers having 1:1 acceptor to donor ratio is similar. However, BLA in 1:2 ratio copolymers is reduced compared to other polymers.

All copolymers have smaller band gaps than the homopolymers. Pyrrole containing copolymers have smaller band gaps than thiophene containing ones and copolymers that have TTP in their structure have smaller band gaps than those having BBT. Theoretical analysis showed that main reason for band gap reduction in copolymers in these systems is the geometrical constraint on thiophene units and pyrrole units polymers that adopt unfavourable structure, since the unstable isomer, aromatic or quinoid, possesses a smaller band gap than its counter part. The reduction in the BLA in 1:2 ratio copolymers can be the other reason for the further decrease in the band gap.

Conduction band widths of homopolymers and copolymers are similar. The valence band widths of the copolymers is narrower than that of the homopolymers except polyTTP. This situation does not agree with the donor-acceptor concept that predicts band widening upon copolymerization of moieties having large electronegativity differences.

The success with designing these small band gapsystems were attributed to the donor-acceptor concept [18], however it is found that the main reason for the band gap reduction is not the donor-acceptor concept and the prediction of the band

width widening is not valid. Influence of the quinoid structures and reduce in the bond length alternation are the reasons for the band gap reduction.

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