

**ELECTRONIC STRUCTURE ANALYSIS AND DENSITY FUNCTIONAL
STUDY OF AN ALTERNATING DONOR/ACCEPTOR POLYMER**

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June 2001

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ABSTRACT

ELECTRONIC STRUCTURE ANALYSIS AND DENSITY FUNCTIONAL STUDY OF AN ALTERNATING DONOR/ACCEPTOR POLYMER

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Conducting polymers have attracted great attention for the last two decades because of their potential applications in many fields. One of the major goals for the scientists who are studying in this field is to synthesize conducting polymers with extremely low band gap. Such polymers would be intrinsically conducting, and thus eliminating the need for doping. Several powerful approaches are proposed to synthesize low band gap polymers. One of them is the donor/acceptor concept, which was proposed by Havinga and his co-workers. In their model, they attached regularly alternating electron withdrawing and electron donating groups to the carbon backbone. By connecting these groups, they aimed to decrease the lowest unoccupied molecular orbital (LUMO) level, and to increase the highest occupied molecular orbital (HOMO) level of the polymer respectively. By this way they claimed that one could obtain very low band gap conducting polymers by introducing the alternating donor/acceptor groups, where the electronegativity difference between these groups is highest.

Huang and Pickup synthesized donor/acceptor copolymers of 3,4-ethylenedioxythiophene (EDOT) which is considered as electron donating group and 4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene (CDM) as electron withdrawing group. By changing the monomer ratio in the copolymers, they decreased the band gap to less than 0.16 eV, however, the intrinsic conductivity was about 10^{-3} S/cm. Although a very low band gap was achieved, the conductivities of copolymers were still low. To understand this behaviour and also to check the validity of donor/acceptor concept, we performed theoretical studies for these systems.

Monomer through hexamer of EDOT, oligomers for 1:1 copolymer of EDOT and CDM were optimized using density functional theory. Ionization potentials, electron affinities, energy gaps, and band widths of the polymers were obtained by extrapolation. The lowest band gaps are calculated for copolymer poly-CDM-EDOT and poly-CDM. Band gaps of the polymers are found to agree well with the experimental values.

When we combine two monomers (EDOT: electron-rich, CDM: electron-deficient) in one to one ratio and in different ratios in order to form co-oligomers, the highest occupied molecular orbitals of co-oligomers are averaged between the HOMO levels of parent homo-oligomers. Lowest unoccupied molecular orbitals of co-oligomers are also averaged between the LUMO levels of parent homo-oligomers; however, averaged LUMO levels of co-oligomers are more close in energy to the LUMO level of CDM oligomer. We also found that poly-CDM and poly-CDM-EDOT have very flat conduction bands. These narrow bands are attributed to the

localized states, which decrease the mobility of n-type carriers in these bands consistent with the experimental findings.

Overall, we concluded that donor/acceptor concept can be used to decrease the band gap while sacrificing the dispersion of valence and conduction bands. However, band broadening does not occur in alternating donor/acceptor polymers as donor/acceptor approach suggested.

Keywords Density Functional Theory, Low band gap polymers, Band Widths, Thiophene derivatives, Copolymers

ÖZET

SIRAYLA DEĞİŞEN ALICI/VERİCİ BİR POLİMERİN ELEKTRONİK YAPI ANALİZİ VE YOĞUNLUK FONKSİYONAL ÇALIŞMASI

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Birçok alanda potansiyel uygulamaları olan iletken polimerler son yirmi yılda büyük ilgi çekmiştir. Bu konuda çalışan bilim adamlarının başta gelen amaçlarından biri çok düşük bant aralıklı iletken polimerler sentezlemektir. Bu tür polimerler dop edilmeye ihtiyaç duyulmadan kendi halinde iletken olacaklardır. Düşük bant aralıklı polimer sentezlenebilmesi için birkaç önemli yaklaşım önerilmiştir. Bunlardan biri Havinga ve arkadaşları tarafından önerilen alıcı/verici kavramıdır. Modellerinde, karbon iskeletine düzenli olarak sırayla değişen elektron çeken ve elektron veren gruplar bağladılar. Bu grupları bağlayarak sırasıyla polimerin en düşük boş moleküler orbital (LUMO) düzeyini azaltmayı ve en yüksek dolu moleküler orbital (HOMO) düzeyini artırmayı amaçladılar. Böylece elektronegativite farkı en yüksek olan alıcı/verici grupları bağlayarak çok düşük bant aralıklı polimerler elde edilebileceğini öne sürdüler.

Huang ve Pickup 3,4-etilendioksitiyofeni (EDOT) elektron veren grup olarak ve 4-siyanometilen-4H-siklopenta[2,1-b:3,4-b']ditiyofeni (CDM) elektron çeken grup

olarak alıcı/verici kopolimerler sentezlediler. Kopolimerdeki monomerlerin oranını değiştirerek bant aralığını 0.16 eV'tan daha aşağıya indirdiler, ama kopolimerin öz iletkenliği yaklaşık 10^{-3} S/cm idi. Çok düşük bant aralığı sağlanmış olmasına rağmen bu kopolimerlerin iletkenlikleri hala düşüktü. Bu davranışı anlamak ve alıcı/verici konseptinin geçerliliğini kontrol etmek için bu sistemler üzerine teorik çalışmalar yaptık.

Yoğunluk Fonksiyonel teori kullanılarak EDOT'un monomerinden hegzamerine kadar olan oligomerleri ve CDM-EDOT'un kopolimerlerinin oligomerlerinin optimizasyonları yapıldı. Polimerlerin iyonizasyon potansiyelleri, elektron severlilikleri, enerji boşluğu ve bant genişlikleri dışdeğerbiçim metoduyla elde edildi. En düşük bant boşluğu kopolimer poli-CDM-EDOT ve poli-CDM için hesaplandı. Polimerlerin bant aralıklarının deneysel değerlere uyduğunu bulduk.

Ko-oligomer oluşturmak için iki monomeri (EDOT: elektron yönünden zengin, CDM: elektron yönünden fakir) bire bir ve farklı oranlarda birleştirdiğimizde, ko-oligomerlerin en yüksek dolu moleküler orbitalleri ana homo-oligomerlerin HOMO düzeyleri arasında averaj bir değere sahip olurlar. Ko-oligomerlerin boş en düşük moleküler orbitalleri de ana homo-oligomerlerin LUMO düzeyleri arasında bir averaj değere sahipler, ancak ko-oligomerlerin LUMO değerleri CDM oligomerlerinin LUMO değerlerine daha yakındırlar. Ayrıca poli-CDM ve poli-CDM-EDOT'un çok dar iletken bantları olduğunu bulduk. Deneysel bulgularla örtüşen ve n-tipi taşıyıcıların mobilitelerini azaltan bu dar bantların lokalize olmuş düzeylerden kaynaklanıyor.

Alıcı/verici konseptini bütünüyle ele aldığımızda şu sonuca vardık: alıcı/verici konsepti polimerlerin bant aralıklarını düşürmek için kullanılabilir, ama bu durumda valans ve iletken bantların genişliklerini feda etmemiz gerekecektir. Ayrıca, alıcı/verici konseptinin ileri sürdüğü gibi bant genişlemesi bu polimerlerde gerçekleşmemektedir.

Anahtar Kelimeler Yoğunluk Fonksiyonel Teori, Düşük bant boşluklu polimerler, Bant genişliği, Tiyofen türevleri, Kopolimerler

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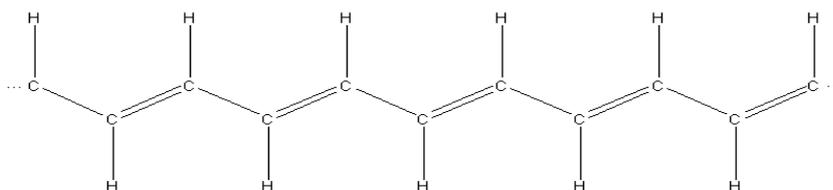
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1. INTRODUCTION

1.1 Conducting Polymers

Electronic and optical properties of linear π -conjugated systems have acquired a growing importance in many areas of modern chemistry and physics of condensed matter. The π -system in conjugated polymers gives rise to conductivity, electro- and thermochromic effects, electroluminescence, and non-linear optical properties [1]. The discovery that polysulfurnitride [2] is a metal in 1973, led the scientists to study the new class of chemical compounds, now known as conducting polymers. The simplest representative of conjugated organic polymers is polyacetylene (Scheme 1).

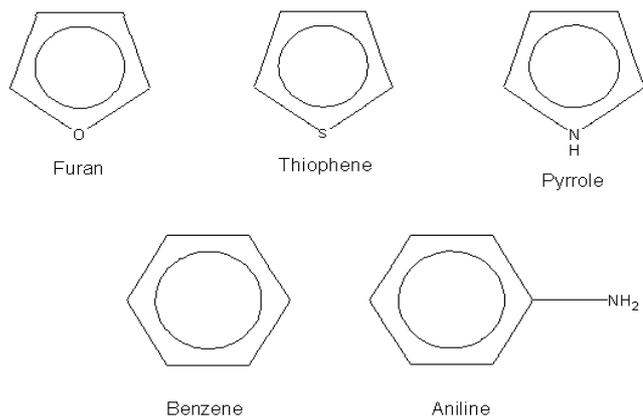


Scheme 1: *Polyacetylene.*

Undoped polyacetylene is a semiconductor with a band gap of 1.4 eV [3]. Interest in conjugated organic polymers accelerated in the late 1970s with the discovery of metallic electrical conductivity in oxidatively doped polyacetylene [4].

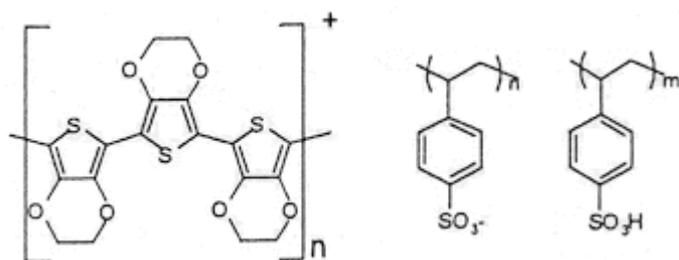
Conjugated organic polymers have been studied theoretically [5-21] and experimentally [22-62]. Investigations were devoted to (i) analysis of structure and properties using a whole arsenal of physical techniques, (ii) development of synthetic methods allowing better control of structure and electronic properties, (iii) synthesis of functionalized polymers in which the electronic properties of linear conjugated systems are modified by covalently attached groups, (iv) electronic structure analysis by using theoretical methods, and (v) applications, e.g. antistatic materials, electromagnetic shielding, anti-corrosion coatings, electrolytic capacitors, batteries, smart windows, light emitting diodes, photodiodes, solar cells, lasers, field effect transistors and sensors [1,63].

Applications of polyacetylene are limited because of poor thermal and environmental stability and also non-processability. Therefore, investigations were directed to the polymers, which would be processable and more promising for commercial applications [4]. Conjugated polymers based on aromatic precursors such as pyrrole, benzene, aniline or thiophene (Scheme 2) show improved environmental stability and can be synthesized electrochemically. Electrochemical synthesis of these polymers leads to conducting polymers in one step [1].



Scheme 2: Some aromatic precursors, which are used in the synthesis of low band gap conjugated conducting polymers.

Recently, it has been reported that some heterocyclic conjugated conducting polymers are being used in industrial applications [64]. Poly(3,4-ethylenedioxythiophene)/poly(styrene) sulfonic acid (poly-EDOT/PSS) is used by Bayer AG in the coating of photographic films (Scheme 3). More than 100 million square meters of photographic film are coated in this way every year. Poly-EDOT and its derivatives are also used as electrodes in solid electrolyte capacitors [64].

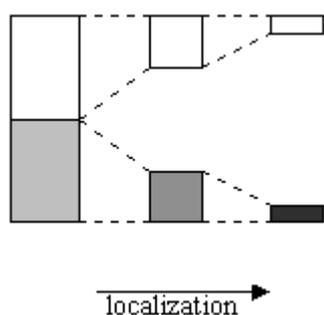


Scheme 3: Poly-EDOT/PSS [64]

1.2 Are Semiconducting Polymers Polymeric Semiconductors?

There are some similarities between semiconductors and semiconducting polymers, but also differences. Like inorganic semiconductors, polymeric semiconductors form energy bands. It is well known today that doping of π -conjugated polymer results in highly conducting states. Due to the one-dimensional character of the polymers, the effects of doping differ considerably from those observed in conventional inorganic semiconductors. In inorganic semiconductors, dopant species form energy levels close to the valence and the conduction bands which enable p-type and n-type conductivity. In polymeric semiconductors, electron-phonon coupling occurs, which tends to localize the charge. Depending on the type of the polymer, these defects are termed polarons, bipolarons or solitons [65].

The width of the bands depends on the strength of the interaction between the repeat units. Weak interaction leads to little delocalization, narrow bands, and poor mobility. Therefore, band widths give a clue about the mobility of the carriers (Scheme 4). Localization causes insulating states, which will be reflected as flat bands in the band picture of the systems in question [66].



Scheme 4: Composite picture for the half-filled band situation, showing generation of an insulating state by localization.

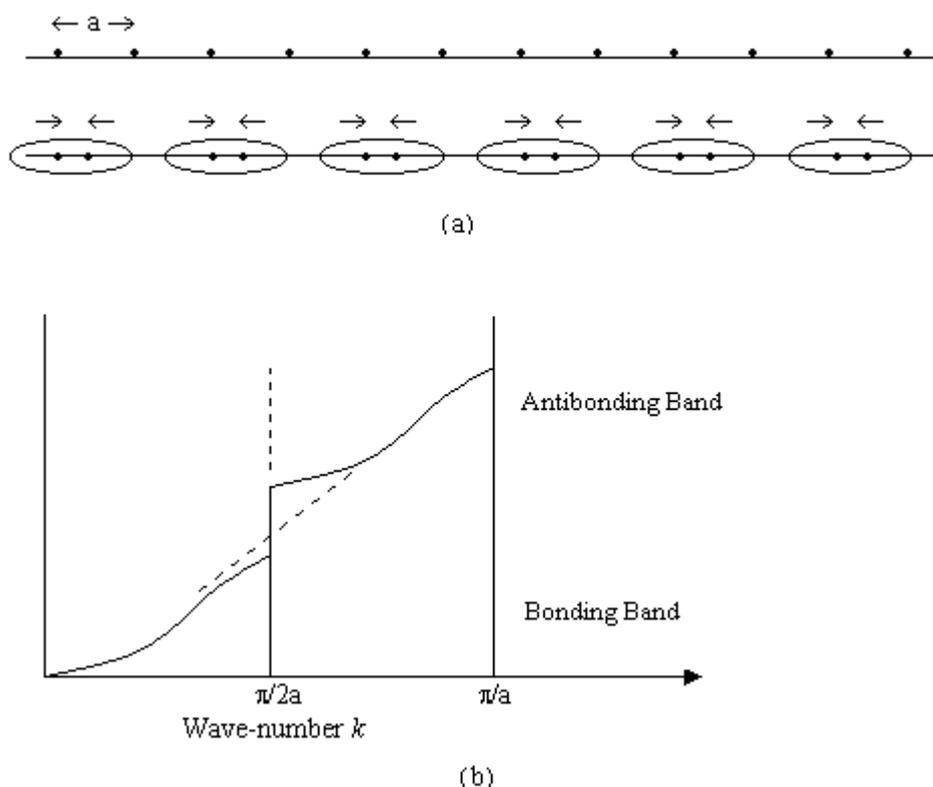
Numerous concepts have been developed to treat semiconducting polymers. The role of the electron-phonon interaction, one dimensionality, Coulomb repulsion, and disorder are much more marked than they are in three dimensional inorganic semiconductors such as silicon. Thus, although the band gap of the conducting polymers may be similar in magnitude to that of silicon, conductivity is usually much lower [4].

1.3 Band Gap Control in Linear π -Conjugated Systems

Electronic and optical properties of conducting polymers are, to some extent, related to the band gap, since the reduction of the band gap (E_g) will enhance the thermal population of the conduction band and create holes in the valence band. Thus, the smaller E_g , the larger the number of free charge carriers [67]. Lowering of E_{ox} or increasing of E_{red} increases stabilities of oxidized or reduced forms of conducting polymers. Therefore, it is essential to understand the evolution of band gaps of conjugated polymers in connection with their chemical structure. E_g values of linear conjugated systems are usually determined from the low-energy absorption edge of the electronic absorption spectrum. Band gaps can also be taken as the difference between oxidation (E_{ox}) and reduction (E_{red}) potentials.

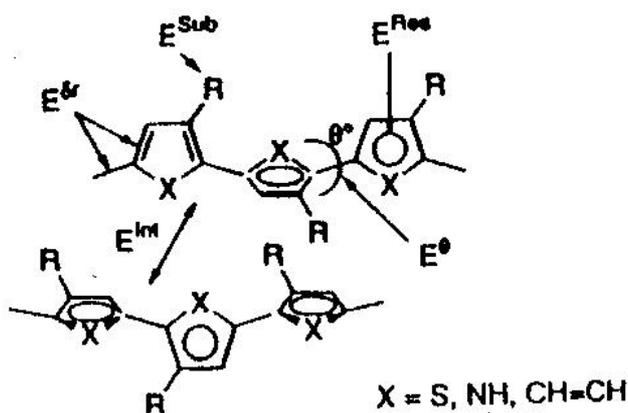
There are several factors that influence band gaps. As pointed out in many theoretical investigations, Peierls instability which causes the presence of alternating single and double bonds in the conjugated path represents one of the major contribution to the existence of a finite E_g value in linear conjugated systems (Scheme

5). A hypothetical polyacetylene with equal C-C bond distances would be a metal. The contribution of bond length alternation to E_g ($E^{\delta r}$) is related to the difference between single and double bond lengths.



Scheme 5: Peierls distortion in a half-filled band. (a) Distortion period of two lattice spacings gives an alternation of bond lengths, with electrons concentrating in the more bonding regions. (b) Band structure diagram, showing the splitting into a bonding and an antibonding band.

Apart from $E^{\delta r}$, several other factors play a determining role. The existence of single bonds allows the occurrence of inter-annular rotations (Scheme 6). Because orbital overlap between π -orbitals varies approximately with the cosine of the twist angle (θ), any departure from co-planarity will result in an increase in E_g [1].



Scheme 6: Parameters that affect the value of E_g in conjugated systems [1].

An important difference between $(CH)_x$ and aromatic conjugated systems lies in the resonance energy of the monomer unit (Scheme 6). Aromatic units are more stable than the non-aromatic systems due to π -electron delocalization around the inner ring. In conjugated chains, delocalization occurs also along the chain. There might therefore be a competition between π -electron confinement within the rings and delocalization along the conjugated backbone. Whereas this problem is still largely unsolved, it seems that the aromatic resonance energy of the cycle (E^{Res}) plays a role in this process and in the final value of E_g [1].

One of the most used methods to modify HOMO and LUMO levels of a π -electron system involves the grafting of electron releasing or withdrawing substituents that will, respectively, increase or decrease HOMO and LUMO levels. If HOMO and LUMO levels are influenced to a different extent, band gap reduction or increase results. Electron releasing or withdrawing substituents connected to the conjugated chain (Scheme 6) considerably contribute to the band gap (E^{Sub}).

The above four factors determine the magnitude of the HOMO-LUMO gap of single chain linear conjugated systems. In addition, interactions between individual polymer chains (Scheme 6) that are responsible for their organization into a condensed phase can represent an important contribution to the band gap (E^{Int}).

To summarize, the band gap of linear conjugated systems is determined by five contributions: the magnitude of bond length alternation $E^{\delta r}$, the mean deviation from planarity E^{θ} , the aromatic resonance energy E^{Res} , inductive and mesomeric electronic effects of substituents E^{Sub} , and intermolecular or interchain coupling in the solid state E^{Int} [1].

$$E_g = E^{\delta r} + E^{\theta} + E^{Res} + E^{Sub} + E^{Int}$$

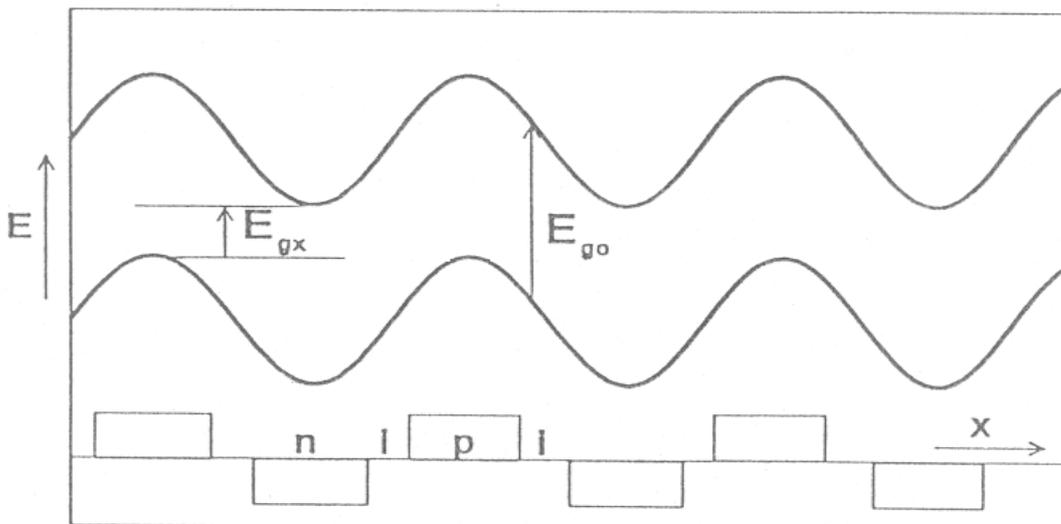
The above five factors can be used in various ways to lower band gaps. For instance, copolymerization of aromatic and *o*-quinoid units [22] has been employed to reduce bond length alternation. Another idea was put forward that aimed at directly influencing the HOMO and LUMO energy levels by employing two building blocks with different energy levels. This concept is subject of the next chapter.

1.4 Donor-Acceptor Concept

The donor/acceptor concept was proposed by Havinga and co-workers [23]. The principle behind this strategy is that conjugated polymers with alternate donor and acceptor moieties in the main chain are expected to have the lowest band gap for a combination in which the electronegativity difference between donor and acceptor

moieties is the highest. In this approach, donor moieties are intended to increase the valence band edge of the polymer by donation of electron density to the conjugated backbone; acceptor moieties are used to lower the conduction band edge of the polymer by withdrawing electron density from the conjugated backbone.

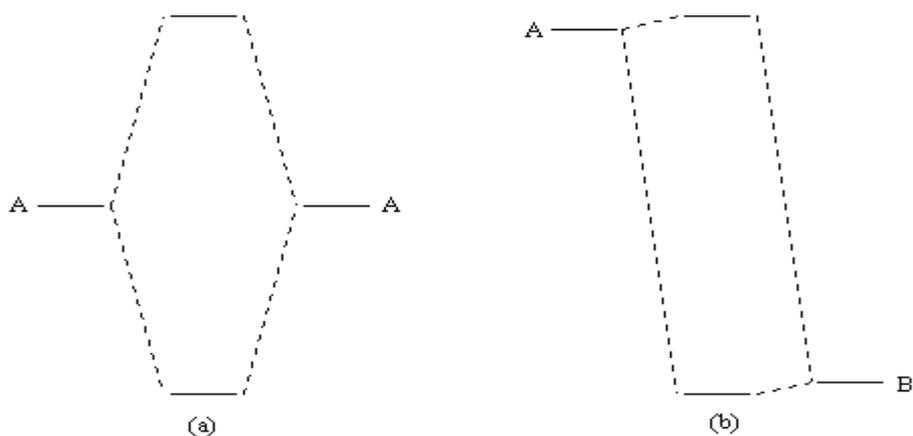
Scheme 7 shows the principle stated by Havinga and his co-workers. In scheme 7, n represents the acceptor-like moiety, p represents the donor-like moiety, and possibly these moieties are separated by neutral (i) parts. Extended donor and acceptor regions resemble a case similar to the inorganic n-i-p-i super lattice structures. Both, valence and conduction band are curved by space charge effects. The band gap, E_{go} , does not change at each repeat unit itself. However, a smaller band gap, E_{gx} , is found when the alternation of high and low energy levels is taken into account. In order to get very small E_{gx} values, strong donors and acceptors are needed. Havinga stated 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. It is likely 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.” For experimental verification of their hypothesis, they reported polysquaraines and polycroconaines as conjugated polymer semi-conductors which show band gaps down to 0.5 eV, and conductivities around 10^{-5} S/cm [23].



Scheme 7: Schematic band structure of an n-i-p-i quantum well structure [23].

By introducing these two different groups on the same conjugated system, it is claimed that it is possible to obtain low band gap systems. This approach has been investigated theoretically [7,13,68,69] and experimentally [14,24,36,38]. Even the band gap is small in a donor/acceptor system, the conductivity values are low.

Salzner has also theoretically investigated some donor/acceptor systems. In her studies she claimed that the donor/acceptor concept does not work in principle [68,69]. From a theoretical point of view, we have enough reasons for doubt concerning this approach. In general, the interaction between fragments with very different energies is small. Scheme 8 shows the schematic representation of two interacting molecules. In Scheme 8a, two 'A' molecules interact with each other, and the diatomic molecular orbitals are well separated. However, when two different molecules, which have relatively different molecular orbital energies interact with each other, the new diatomic molecular orbital energies will be close to the energies of parent interacting molecules (Scheme 8b).



Scheme 8: *Schematic representation for*
 (a) *Homonuclear interaction between two interacting 'A' molecule.*
 (b) *Heteronuclear interaction between A and B molecules with very different energies [70].*

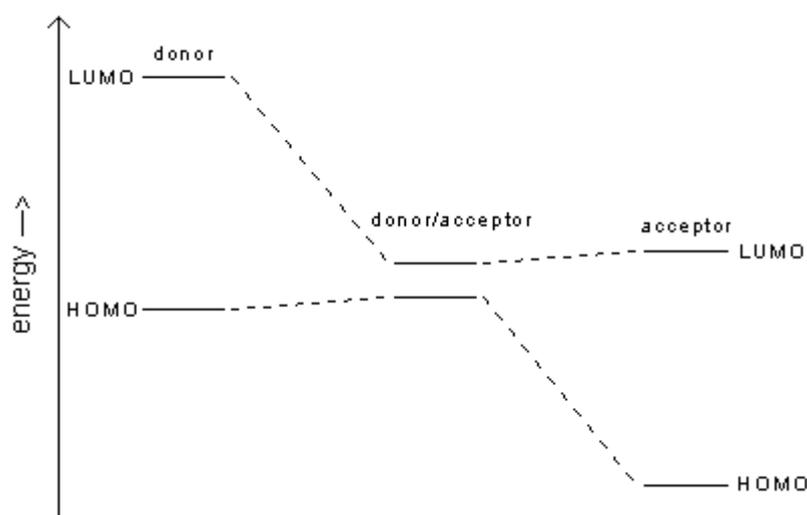
The donor/acceptor concept is a method that uses two different molecules as repeating units to form copolymers. For instance, if we take 'A' as acceptor molecule and 'D' as donor molecule, the copolymer will have the following chain structure:



Each acceptor (A) is interacting with two donor (D) molecules, or vice versa. That is, each molecule in the chain interacts with the neighbouring molecules, which have very different energies.

If we apply the general theoretical approach to donor/acceptor systems, we obtain a situation, which is shown in Scheme 9. Frontier orbitals of donor molecule are higher in energy compared to those of acceptor molecule. When donor and acceptor levels interact, they form donor/acceptor frontier orbitals. These orbitals are close to each other in energy and they form the frontier orbitals of 'AD' repeat unit. When copolymer is formed, these orbitals will lead to localized states, hence narrow

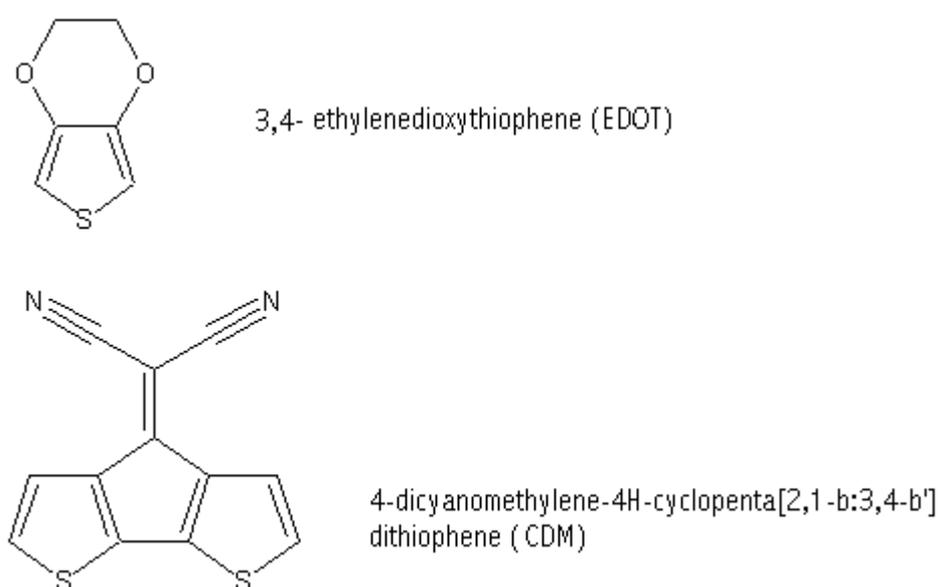
bands. Although band gap is decreased in this situation, very flat valence and conduction bands are formed. This is because the interaction between each repeating unit will be weak which will cause small dispersion of bands. At this point, it is important to emphasize that all our explanations are very crude interpretations for why donor/acceptor systems do not work theoretically. In our explanations, we only used frontier orbital energy levels to demonstrate the situation, however, symmetry constraints could considerably limit the interactions between units. And also, we only considered HOMO-HOMO or LUMO-LUMO interactions between donor and acceptor units. In fact, HOMO-LUMO interactions or some other interactions between different levels might occur depending on the symmetry properties of the system in question [71].



Scheme 9: Schematic representation for the interaction between the frontier orbitals of donor and acceptor molecules.

1.5 Previous Studies on EDOT and CDM

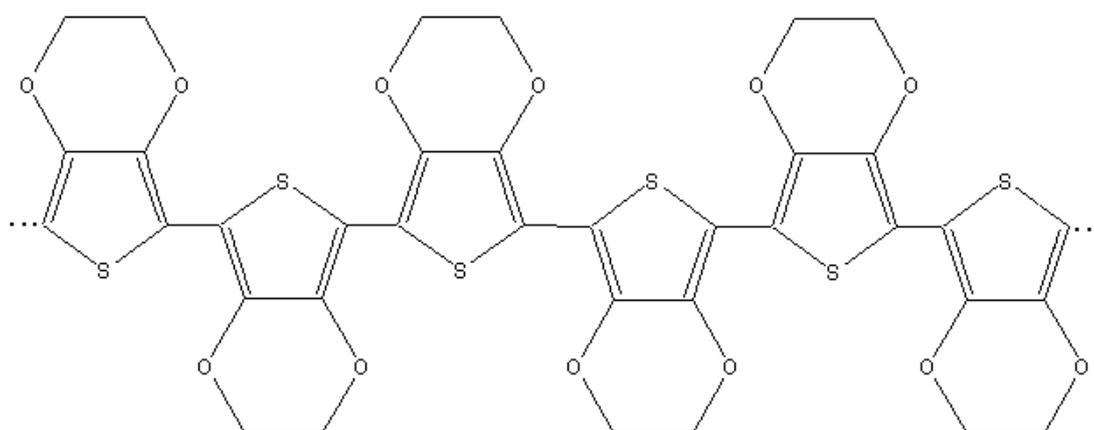
Scheme 10 shows the structures and IUPAC names of the monomers, which we studied during our research period. We will simply abbreviate 3,4-ethylenedioxythiophene as EDOT, and 4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene as CDM.



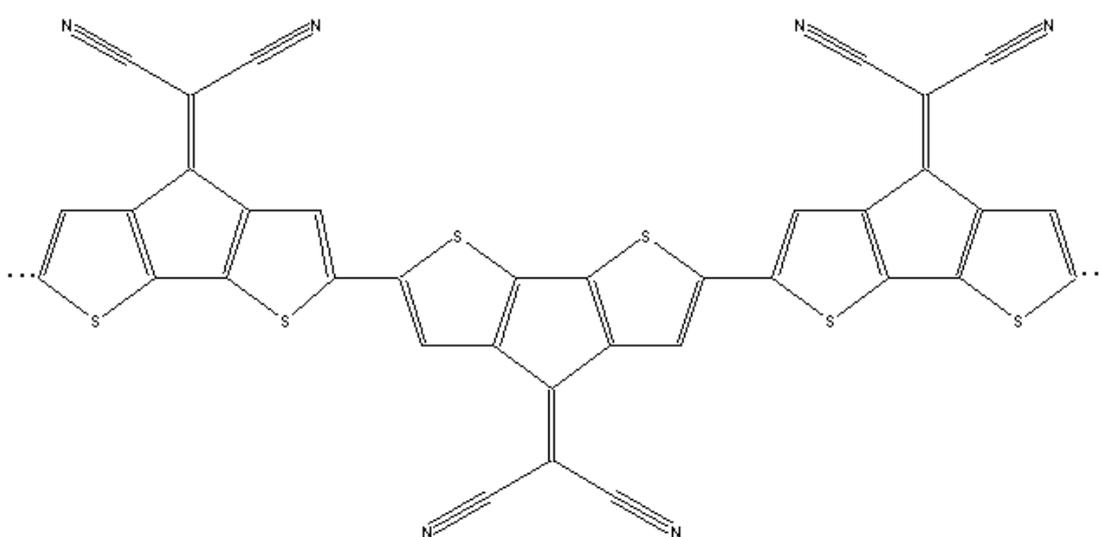
Scheme 10: Repeat units for conducting polymers, which are investigated in this study.

Poly-EDOT (Scheme 11a) has a very low ionization potential and is air stable in the p-doped form. It has high conductivity in combination with excellent stability in the conducting state, a relatively high transparency to visible light, and aqueous processability of the PSS-doped form. These features have allowed the material to become industrially useful [64]. To obtain low band gap n-dopable conjugated polymers, poly-CDM (Scheme 11b) was synthesized by introducing an electron-withdrawing group to 3,4' position of bithiophene unit. Thus, it is aimed to decrease the band gap with the accompanying decrease in the LUMO level. According to the

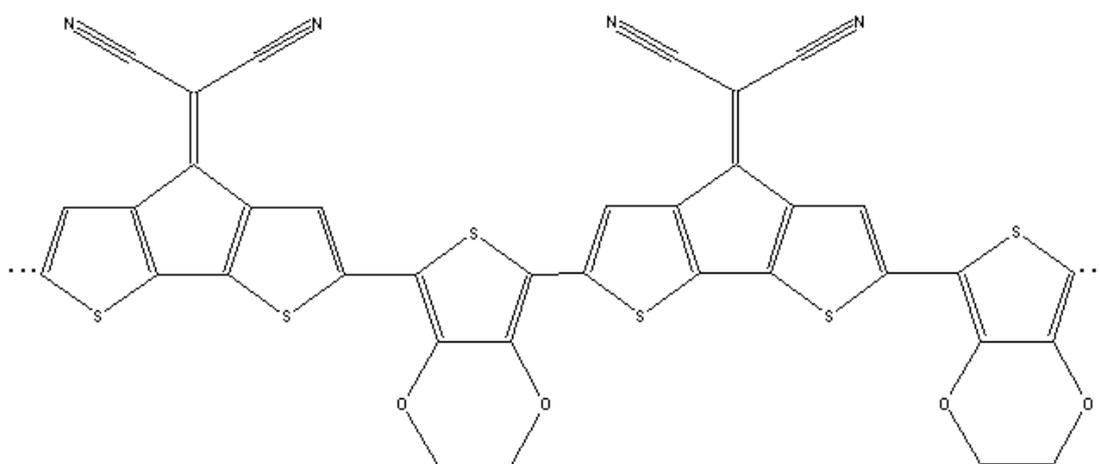
donor/acceptor concept [23] copolymerization of EDOT and CDM (Scheme 11c) should reduce the band gap with respect to the homopolymers. Such a low band gap system would be intrinsic conductor, eliminating the need for doping. Huang and Pickup carried out electrochemical studies on such copolymers [24]. The band gaps of these copolymers are reduced to less than 0.16 eV and the highest conductivity was measured to be 10^{-3} S/cm. However, such copolymers can not be used as intrinsic conductors because of their low conductivities. This is an increase of 5 orders of magnitude compared to poly-CDM but 9 orders of magnitude less than the conductivity of copper.



(a)



(b)



(c)

Scheme 11: (a) *Poly-EDOT*, (b) *Poly-CDM*, (c) *Poly-CDM-EDOT*

In this study we investigated electronic properties of EDOT, CDM and the copolymer of these two polymers in connection with the approach of donor-acceptor systems. Theoretically the monomers have heterocyclic aromatic rings, and both EDOT and CDM have a thiophene based conjugated backbone. Previous studies on EDOT gave a 1.2 eV electrochemical band gap and a conductivity of 10^{-12} S/cm [24]. CDM showed an electrochemical band gap of 0.75 eV and a conductivity of 10^{-8} S/cm [25]. A copolymer of EDOT and CDM gave an intrinsic conductivity 6.9×10^{-4} S/cm and a band gap of 0.19 eV [24]. Although the band gap of the copolymer is reduced significantly and its intrinsic conductivity is increased 4-8 orders of magnitude compared to those of homopolymers, conductivity values of this copolymer are far away from practical use. It is found that the conduction band of poly-CDM was flat and the mobility of n-type charge carriers was 40 times smaller than the mobility of p-type carriers [25]. The situation was not different for copolymers of CDM with EDOT. The ratio of the mobility of p-type carriers to the mobility of n-type carriers

was about 500 [24]. By playing with the monomer ratios in the copolymer, the band gap is reduced to <0.16 eV, however, conductivity is still low (10^{-3} S/cm) for the copolymers of EDOT and CDM. This experimental result led us to find out the reasons of this behaviour. Our aim is to determine whether donor/acceptor concept could really be used to enhance the electrical properties of conducting polymers.

2. METHODS

2.1 Electronic Structure Methods

Before going into details of density functional theory, I will give a brief overview of electronic structure methods. Electronic structure methods use the laws of quantum mechanics rather than classical physics. Quantum mechanics states that the energy of a molecule may be obtained by solving the Schrödinger equation:

$$\mathbf{H} \psi = E \psi$$

For any but the smallest systems, however, exact solutions to the Schrödinger equation are not possible, and accurate numerical solutions are not 'computationally practical'. The most complex part of quantum mechanical calculations is the treatment of electronic interactions. Due to their negative charge electrons repel each

other, due to the Pauli principle electrons with the same spin can not be at the same point in space. Thus the movement of the electrons is correlated. Electronic structure methods are characterized by various mathematical approximations to the treatment of electronic interactions. There are three major classes of electronic structure methods:

2.1.1 Semi-Empirical Methods

Austin Model 1 (AM1), Modified Intermediate Neglect of Differential Overlap-version 3 (MINDO/3) and Modified Neglect of Diatomic Orbital-Parametric Method Number 3 (PM3), which are implemented in programs like MOPAC, AMPAC, HyperChem, and Gaussian, neglect large parts of the electronic interactions and use parameters derived from experimental data to correct the results. Success depends on having appropriate parameters from experiments for the type of chemical system under investigation. Semi-empirical calculations are relatively inexpensive. They provide reasonable qualitative descriptions of molecular systems and fairly accurate quantitative predictions of energies and structures for systems where good parameter sets exist [72].

2.1.2 Ab Initio Methods

Semi-empirical and ab initio methods differ in the trade-off made between computational cost and accuracy of the result. The term *ab initio* means ‘from scratch’ and indicates that *ab initio* methods do not use experimental parameters. The computations are based on the laws of quantum mechanics and on a small number of physical constants. The Hartree-Fock method is a classical example of an ab initio

method. In Hartree-Fock theory electron-electron interactions are approximated. As a result Pauli repulsion or exchange terms are treated exactly, but Coulomb correlation is completely neglected.

2.1.3 Density Functional Methods

Recently, a third class of electronic structure methods has come into wide use: *density functional methods*. (A function is a prescription for producing a number from a set of variables. A functional similarly is a prescription for producing a number from a function, which in turn depends on variables.) DFT methods are attractive because they include the effects of exchange and Coulomb correlation and require about the same or even less amount of computation time than Hartree-Fock calculations, the least expensive ab initio method.

2.1.3.1 The History of Density Functional Theory

In 1927, Thomas and Fermi suggested a very attractive approximation to quantum mechanics, now known as Thomas-Fermi (TF) approximation. Instead of considering the wave-function, they tried to work with the much simpler electron density, $\rho(r)$, and to express the energy E as a function of ρ alone, symbolically written as $E[\rho]$. The TF approximation is a quantum statistical model for the kinetic energy of the electrons. Nuclear-electron and electron-electron contributions to the energy are treated classically, exchange and correlation effects are neglected. The TF model turned out to be of little use for chemical applications. In fact, there exists rigorous proof that within the TF model no molecular system is stable with respect to

its fragments. The failure is due to the crude approximation of E_{kin} . Dirac suggested an idea in order to solve HF equations by using some expressions depending on the density only. The result is similar to the TF model but includes quantum mechanical exchange effects. This attempt did not work for chemical applications. In 1964, Hohenberg and Kohn proved two very important theorems, which provide the theoretical foundation for the DFT approach in quantum mechanics. Briefly, they proved the existence of a functional $E[\rho]$, which gives the exact ground state energy for the exact ground state density. One year later, Kohn and Sham suggested how the existing but yet unknown functional could be approximated. The key to Kohn-Sham theory is the calculation of a better approximation for the kinetic energy. Since orbital based methods like HF theory perform well, the concept of a non-interacting reference system built from orbitals was introduced. In reality electrons are interacting, and Kohn-Sham approach doesn't provide the total kinetic energy. However, just as HF provides ~99% of the correct answer, the difference between the exact kinetic energy and that calculated by assuming non-interacting orbitals is small. The remaining kinetic energy is absorbed into a so-called exchange-correlation term (E_{xc}). The exchange-correlation term collects everything that can not be handled exactly, such as the non-classical portion of the electron-electron interaction, a correction term for the so-called self-interaction, and the correction to the kinetic energy. Like the correlation energy in the HF theory, exchange-correlation energy is the problematic part of solving the KS equations [73].

Since, the exact form of the functional is not known, the success of DFT depends on the quality of the approximation to E_{xc} . Kohn and his co-workers took the homogenous electron gas as a model for approximating E_{xc} . The homogenous

electron gas is a fairly good model for metals such as sodium, but less successful in applications to molecules, where the electron density is a rapidly varying function. The search for better functionals is an ongoing endeavour for large scale applications in chemistry.

Initially, local density methods were proposed. Local means that the exchange-correlation energy of a particle depends only on the electron density at the given point in space. In the local density approximation (LDA), it is assumed that the density can be treated as a uniform electron gas, or equivalently that the density is a slowly varying function. If the densities of spin-up and spin-down electrons are not equal, LDA takes the form of local spin density approximation (LSDA), which treats the densities of spin-up and spin-down electrons separately. Despite the simplicity of the fundamental assumptions, LSDA methods are often found to provide results with accuracy similar to that obtained by wave mechanics HF methods [74].

To improve over the LSDA approach a non-uniform electron distribution has to be considered. In connection with this idea, functionals are made dependent not only on the electron density, but also on derivatives of the density. Such methods are now known as *Gradient Corrected* or *Generalized Gradient Approximation* (GGA) methods. The use of gradient corrections has little influence on local properties such as bond lengths or vibrational frequencies, but leads usually to a significant improvement in binding energies [74]. GGA functionals usually split into an exchange and a correlation part, which are approximated individually. A popular gradient corrected functional is B88 (Becke's exchange which was developed in 1988), Becke 3 parameter functional, and either the LYP (developed by Lee, Yang

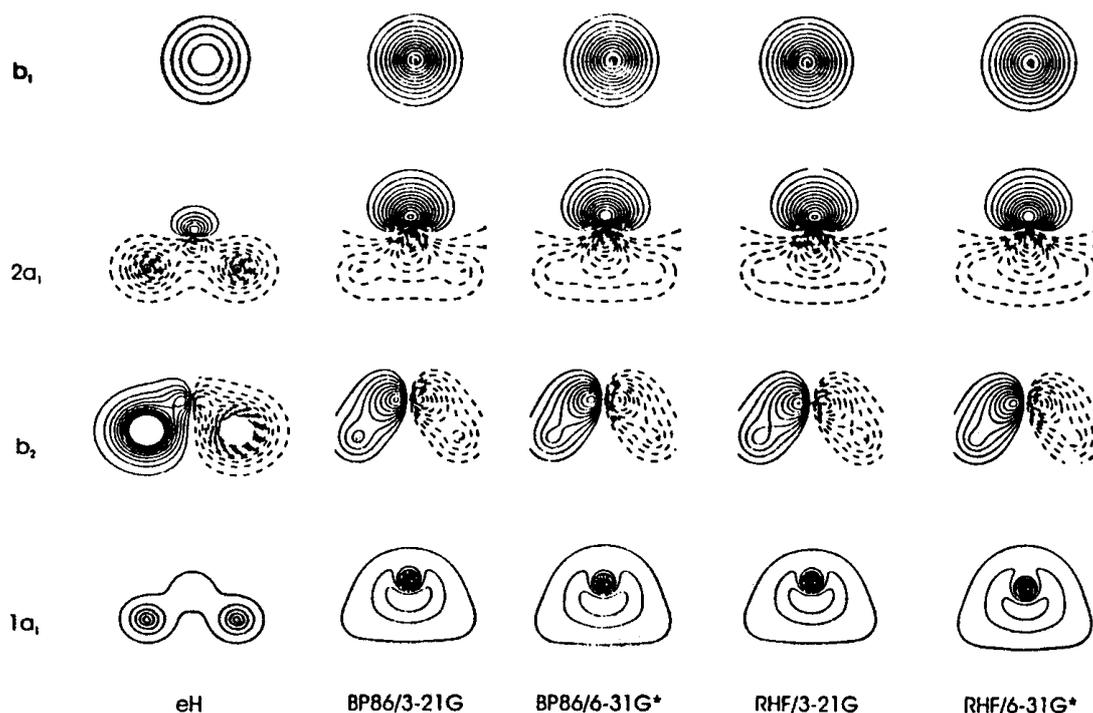
and Parr), P86 (developed by Perdew in 1986) or PW91 (developed by Perdew and Wang in 1991) correlation functionals. Associated acronyms are BLYP, BP86, and BPW91 [74].

Finally, hybrid methods became popular. Hybrid methods use a mixture of Hartree-Fock and DFT exchange. The basic idea is to achieve a correction to E_{xc} with the help of the exact exchange calculated at the HF level. The best ratio is determined by a parametric fit. The computational cost of hybrid methods is higher than that of LSDA or GGA since a HF calculation has to be performed as well. Modern implementation achieves about the same efficiency as a pure HF calculation. However, the quality of the results is far superior to HF. Hybrid methods give substantial improvement over LSDA and GGA methods [74]. Adiabatic Connection Model and B3 are examples of such hybrid models. Today, DFT is one of the most frequently used methods in quantum chemistry [74].

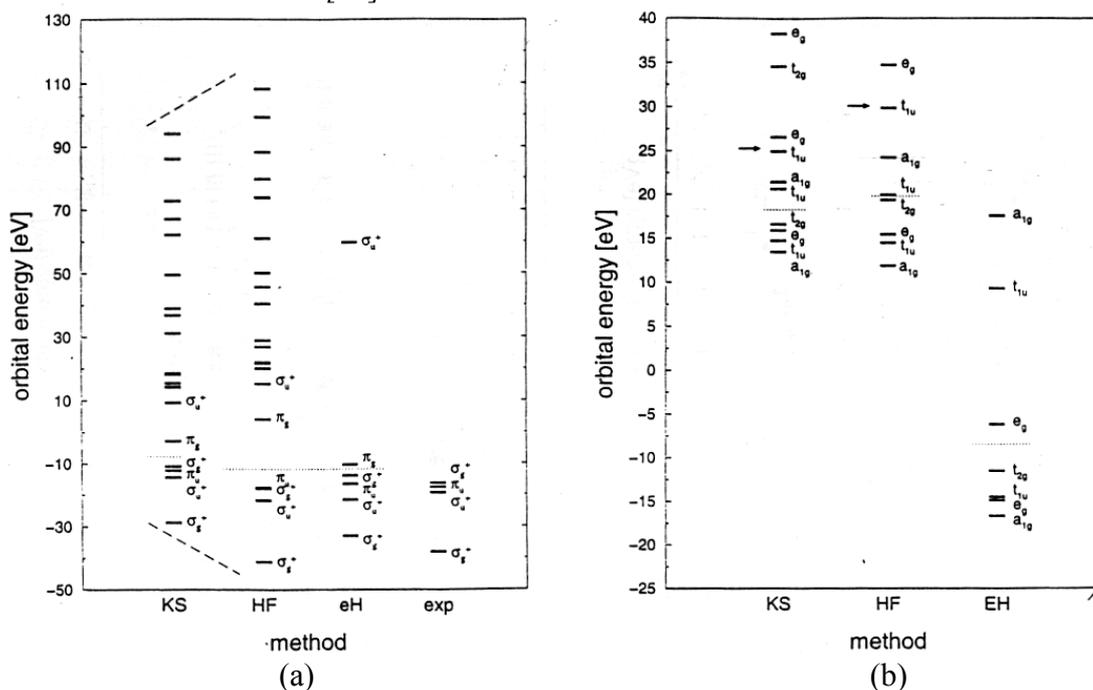
2.1.3.2 The Meaning of Kohn-Sham Orbitals and DFT Eigenvalues

Initially referred to as Kohn-Sham method, density functional theory is now used by many scientists. However, it is important to emphasize that the physical meaning of Kohn-Sham orbitals and eigenvalues is a controversial subject [75]. Initially, Kohn-Sham orbitals were not considered to have physical meaning, apart from the fact that the sum of their squares renders the total electron density. However, since Kohn-Sham orbitals are associated with the exact ground state electron density, they are closer to the real system than are HF orbitals which have physical meaning in a rigorous sense. For instance, Roald Hoffmann and his

coworker investigated in detail the Kohn-Sham (KS) orbitals and eigenvalues recently and compared them to those of Hartree-Fock (HF) and one-electron extended Hückel (eH) calculations, and with experimental results [75]. They calculated Kohn-Sham orbitals and eigenvalues with gradient-corrected functionals for a set of small molecules, varying basis sets and functionals. They found that shape and symmetry properties of KS orbitals are very similar to those calculated with RHF (Restricted Hartree-Fock) and eH methods (Scheme 12). Although KS orbitals are compressed relative to the HF levels, the energy order of occupied orbitals is in most cases in agreement among the various methods (Scheme 13). Hoffmann et al. concluded that KS orbitals are a good basis for qualitative interpretation of molecular orbitals [75].



Scheme 12: Calculated contour plots (*xy* plane) of the a_1 , b_2 , a_1 , and b_1 orbitals of water with BP86/3-21G, BP86/6-31G*, RHF/3-21G, RHF/6-31G*, and eH methods [75].



Scheme 13: (a) Calculated occupied valence and virtual orbitals for the nitrogen by BP86/6-31g*, RHF/6-31g*, and eH methods, and experimental values. The compression of the KS levels relative to HF levels is highlighted by dashed lines [75].

(b) Calculated occupied and virtual orbitals for CrH_6^{-6} by BP86/LANDZL1, RHF/LANDZL1, and eH methods. The Fermi level is indicated by a dotted line [75].

The meaning of orbital energies is also a matter of controversy. Mathematical proof exists only that the negative energy of the HOMO is the IP, provided that the exact functional is used. Unfortunately, approximate functionals do not produce values anywhere near the IP. For example the HOMO of the hydrogen atom lies at around 0.25 a.u. with GGA and at about 0.36 a.u with hybrid functionals. The exact value is 0.5 a.u. Excitation energies are usually underestimated when DFT orbital energies are used [73].

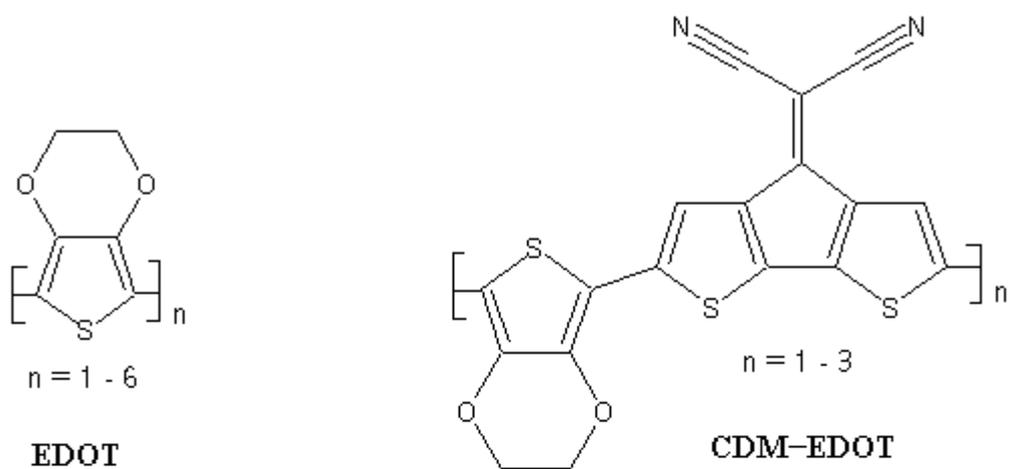
2.1.3.3 Problems of DFT with respect to Band Structure Calculations

Despite problems with orbital energies, DFT methods are widely used in band structure calculations by physicists. In general, band gaps are underestimated by about 50% with LSDA and GGA. Investigation on molecular π -systems have shown that hybrid functionals, which are not available in solid state programs, increase the energy and produce values close to λ_{\max} from absorption spectroscopy [76]. The performance also depends somewhat on the size of the system. A study on oligomers of increasing size [77] showed that the best extrapolated band gap values are obtained with hybrid functionals containing 30% of HF exchange in combination with the P86 correlation functional. The good prediction of the band gaps is due to error cancellation since IP and EA are both too low compared with experiment. The error is about 1 eV. Energy gaps of small oligomers are overestimated and the decrease with increasing chain length is somewhat too large. The method has been tested for numerous π -systems and was shown to reproduce the band gap in every case.

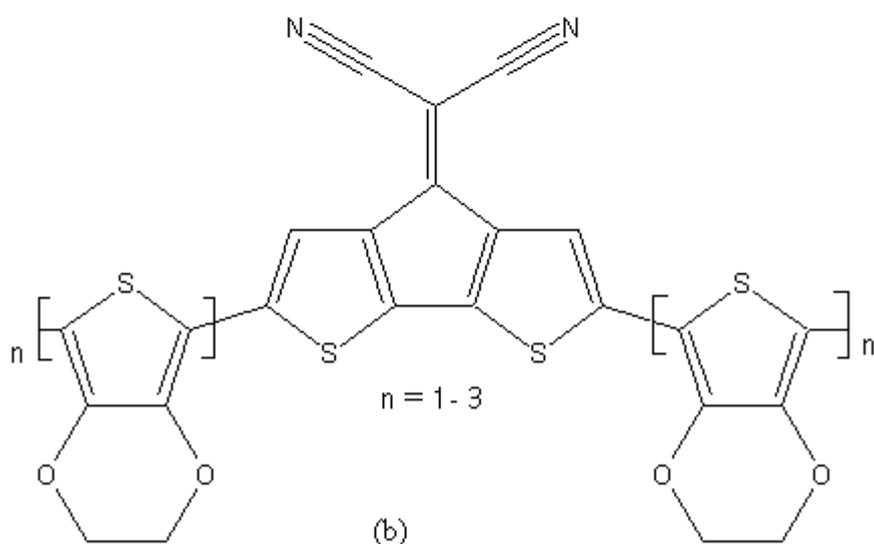
2.2 The Method Used in this Study

In this study we employed G98W [78] to perform DFT calculations. Orbital contours were plotted with the g-openmol program [79]. Origin 5.0 and xmgr programs are used to sketch the graphs. We used the B3P86-functional [80,81] with a weight of 30% of the HF exchange. The basis sets are of split valence quality and pseudo potentials by Stevens-Basch-Krauss are employed for the cores [82,83]. Monomer through hexamer of EDOT and oligomers of (CDM-EDOT) for $n=1$ to 3 (Scheme 14a) were optimized. In order to determine the effect of the EDOT/CDM ratio, we connected EDOT units to the right and to the left of CDM unit, $(\text{EDOT})_n\text{CDM}(\text{EDOT})_n$, and calculated the molecules for $n=1$ to 3 (Scheme 14b).

Except for CDM-EDOT oligomers, the molecules are calculated under C_2 symmetry restriction. Although ethylenedioxy groups are twisted, and C_2 does not require the backbone to be planar, all oligomers were found to be planar. The C-C bond that belongs to ethylenedioxy group makes an angle of 26° with the plane of the thiophene ring [5].



(a)



Scheme 14: (a) Building blocks of polymers, which are calculated with DFT method.
 (b) EDOT units connected CDM unit, which are calculated for $n=1$ up to 3. For $n=1$ (E)₁C(E)₁, for $n=2$ (E)₂C(E)₂, for $n=3$ (E)₃C(E)₃.

3. RESULTS AND DISCUSSION

3.1 Geometries

3.1.1 EDOT

EDOT has a non-planar structure. The sp^3 hybridized carbon atoms connected to the oxygen atoms do not lie on the same plane as the rest of the molecule. There are two possibilities for the space orientation of these carbon atoms. Both carbon atoms can be above or below the molecular plane (kinked), or one of the carbon atoms is above and the other is below of the molecular plane (twisted). The twisted structure has C_2 symmetry, the kinked one has C_s symmetry. The twisted structure is 7.5 kcal/mole more stable than the kinked structure. In the kinked structure, the oxygen atoms are 4.7° above the thiophene backbone. However, in the twisted structure, the oxygen atoms are only 0.8° above and below the backbone, which indicates that the

p-lone pairs of the oxygen atoms make slightly better π -orbital interaction with the conjugated system. The HOMO-LUMO energy difference for the kinked structure is 6.50 eV, 0.07 eV larger than that for the twisted form. The LUMO energies of both structures are very close in energy (kinked : -0.59 eV, twisted : -0.58 eV). However, the HOMO energy of the twisted conformation is 0.07 eV higher than that of the kinked one. To sum up, the twisted conformation is energetically favored and has a slightly lower HOMO-LUMO difference than the kinked conformation.

For the dimer only the twisted structure turned out to be stable. The kinked form converted to the twisted one during the geometry optimization. For larger oligomers only the twisted form of EDOT was considered. For the even-numbered oligomers of EDOT there are two possible conformations, which give rise to two different symmetries. For example, for the dimer of EDOT one can propose two conformations, one with C_2 symmetry and one with C_i (i) symmetry. Our calculations showed that the dimer of EDOT, which has C_i symmetry, is a little more stable (0.10 kcal/mole) than the other conformation, which has C_2 symmetry. For the tetramer of EDOT, the situation is very similar, the conformation, which has C_i conformation, is 0.26 kcal/mole more stable than the C_2 form. The molecular orbital energies are very close in both forms. For instance, the HOMO energy of dimer of EDOT is differing by only 0.0008 eV for the two conformations.

Figure 1 shows bond lengths in the monomer of EDOT and in the inner rings of the hexamer. As the size of oligomer increases, carbon single and double bonds are shortening and lengthening, respectively, as a result of conjugation in the thiophene backbone. The change in the bond lengths decreases rapidly with

increasing chain length. For example, when we go from the monomer of EDOT to the dimer, C=C bond is lengthening by 0.0111 Å. When going from pentamer to the hexamer of EDOT the C=C bond length changes very little. The small changes in the bond lengths between the larger oligomers show that the geometries of the inner rings of the pentamers have converged to the polymer values.

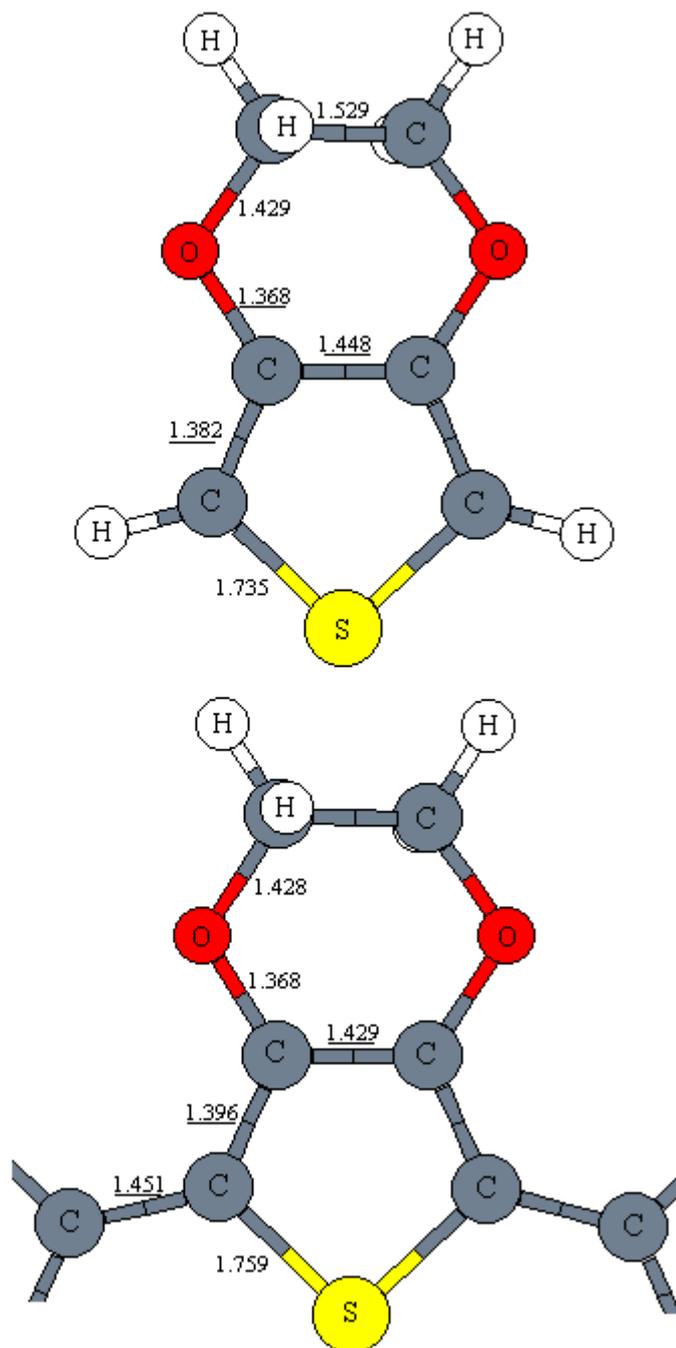


Figure 1: Bond lengths in monomer of EDOT and in the inner ring of hexamer of EDOT.

For comparing the bond lengths of different polymers, we used the bonds in the inner rings of the oligomers, which have converged to polymer values. At the terminal rings, monomeric geometrical features are found. For instance, C=C bond length is 1.396 Å in the inner part of the hexamer of EDOT, and 1.381 Å at the end of the oligomer close to the C=C bond (1.382 Å) length estimated in the monomer of EDOT.

The long bonds connecting the rings and short bonds in the thiophene ring show that the structures are aromatic. C=C and C-C bonds in monomer are 1.382 Å and 1.448 Å, where the corresponding bonds are 1.396 Å and 1.429 Å long in hexamer which shows effective conjugation in thiophene backbone. As we discussed in the introduction part (section 1.3), bond length alternation is an important factor that affects the value of band gap. So, in low band gap conjugated polymers, the value of maximum bond lengths alternation is desired to be small. The maximum bond lengths alternation between the C=C and C-C bonds (which connects the monomers) for hexamer of EDOT is predicted to be 0.055 Å.

The C-O bonds which are bound to sp^2 hybridized C atoms (1.368 Å) are much shorter than the C-O bonds whose carbons are sp^3 hybridized (1.429 Å). The dihedral angle between the oxygen atoms and the carbon backbone is 179.2°, which means oxygen atoms lie on the same plane as carbon backbone. This indicates that the lone pairs of the oxygen atoms have the same orientation as the p-orbitals of the carbon atoms in the π -system. Therefore, the oxygen p-orbitals are part of the conjugated system.

The sp^2 hybridized carbon atoms have bond angles around $120\pm 8^\circ$. The C-S-C angle is approximately 93° for all of the EDOT oligomers. The C-O-C angle is close to the bond angles of sp^3 hybridized carbon atoms, which have bond angles of around 111° . Bond angles in the thiophene ring are changing a few degrees upon polymerization, because bond lengths are changing within the ring. The other bond angles are mostly remaining constant. In order to minimize the effect of E^θ (section 1.3), the carbon backbone should be planar. It is important to emphasize that although planarity is not imposed on the backbones of the EDOT oligomers, all of the oligomers are calculated to be planar with dihedral angles of $180\pm 1^\circ$.

3.1.2 CDM-EDOT

Previous theoretical studies showed that CDM has a planar structure [7]. Since all the carbon atoms are either sp^2 or sp hybridized, the structure becomes completely planar with dihedral angles close to 180° . For the co-oligomers of CDM and EDOT the situation is similar. The angle between the planes of the EDOT and CDM units in monomeric CDM-EDOT is 179.2° . This angle is a little larger in the dimer (177.4°) and in the trimer (178.2°) of CDM-EDOT. Thus, co-oligomers of EDOT and CDM are almost planar.

Figure 2 compares the bond length changes in monomer and trimer of CDM-EDOT. The carbon-carbon single and double bond lengths are changing less compared to the corresponding bond length changes, which we observed in EDOT oligomers. This happens because the monomer of CDM-EDOT has more single and double bonds in its conjugated backbone, that is, it is already conjugated to some

extent within the structure itself. The maximum increase in double bond lengths is 0.002 Å, the maximum decrease in single bond lengths is 0.006 Å. Other bonds, which do not participate in the alternating single-double bond chain, are changing even less. The C=C bond which connects the dicyanomethylene group to the bithiophene ring is 1.382 Å long, and is only 0.001 Å shorter in the trimer of CDM-EDOT. The carbon-nitrogen triple bond length is short (1.174 Å) and remains essentially constant. The N-C-C angle is 179.2°, which is due to the sp hybridized carbon atom connected to the nitrogen. The sp² hybridized carbon atoms have bond angles of around 120±8°, the C-S-C angle is around 92±1°.

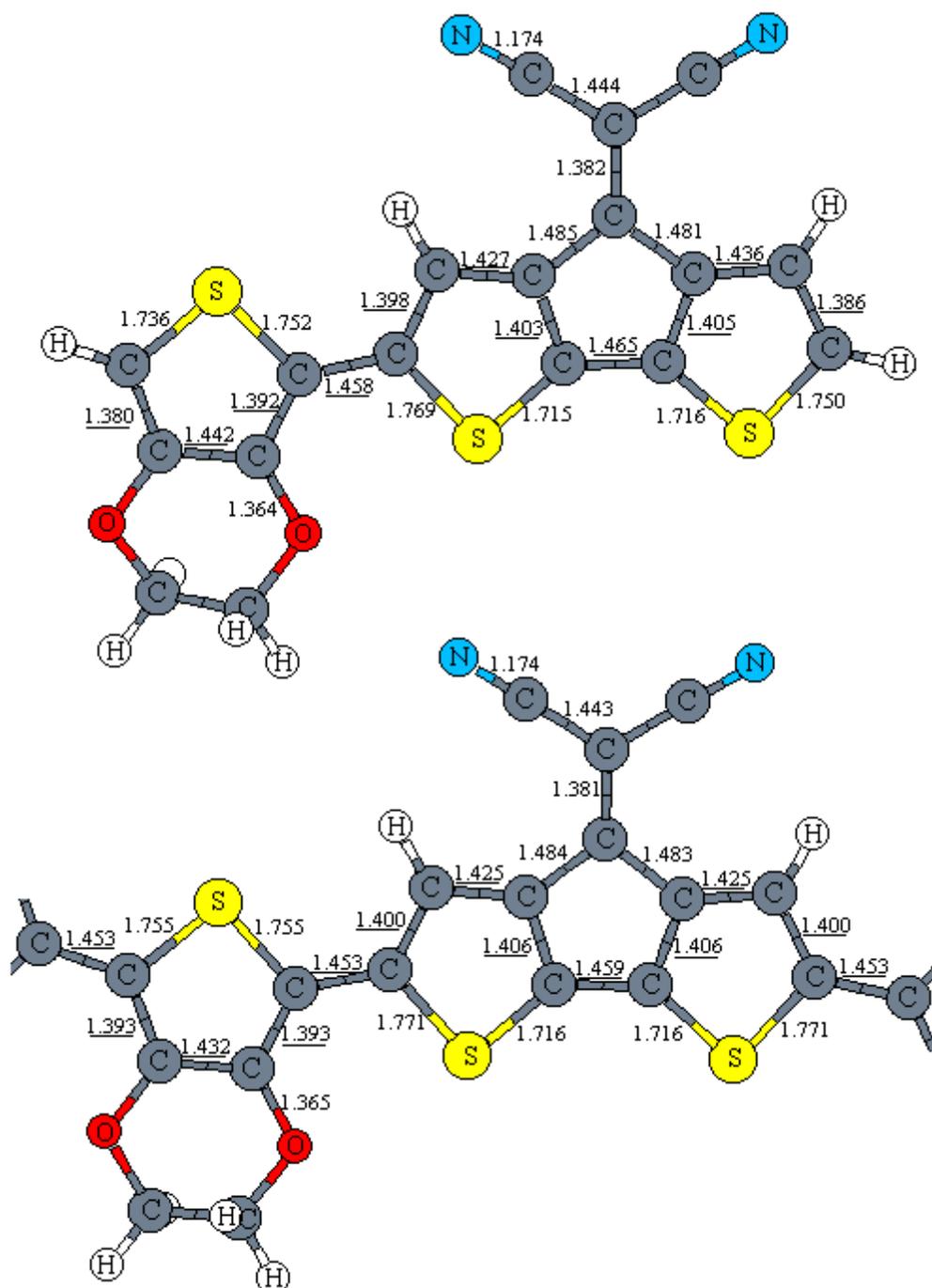


Figure 2: Bond lengths in the monomer and the trimer of CDM-EDOT oligomers.

The thiophene rings are aromatic in the co-oligomer structures. The maximum bond lengths alternation for the trimer of CDM-EDOT is predicted to be 0.066 Å, 0.011 Å larger than the maximum bond lengths alternation of EDOT. To estimate the effect of this bond length alternation on the band gap, we compare it to that in

polyacetylene where the band gap is due to bond length alternation alone. Thus, a bond length alternation of 0.6 Å gives rise to a band gap of 1.4 eV. For poly-EDOT the band gap due to $E^{\delta r}$ is therefore slightly smaller than 1.4 eV, for the copolymer it is slightly larger.

Not only single and double bonds give valuable information about the band structure of the system, but also C-O (which connects the ethylenedioxy group to the thiophene ring) bond length. This C-O bond is 1.368 Å long, 0.061 Å shorter than the C-O bond with the ethylene bridge. This confirms that the ethylenedioxy group significantly interacts with the conjugated backbone. The lone pairs on the oxygen atoms contribute to the π -system by increasing both HOMO and LUMO levels. The coefficients on the oxygen atoms in molecular orbital pictures of EDOT (Figures 8 and 9 in 3.4 Band Widths section) show this effect clearly.

3.2 Ionization Potentials (IPs) and Electron Affinities (EAs)

IPs and EAs are summarized and extrapolated to polymer values in Table 1. The data for thiophene and CDM are taken from a previous study, carried out at the same level of theory [35]. IPs and EAs of all oligomers are plotted against to $1/n$ (number of oligomers), and polymeric IPs and EAs are obtained by extrapolation. All points on the curves are fitted according to second order polynomial fitting, because correlation is improved with polynomial fitting compared to linear fitting, and correlation coefficients of these curves are found to be 0.999 or better.

The comparison of HOMO and LUMO levels of thiophene and EDOT oligomers reveals that EDOT and its oligomers have higher HOMO energies (lower IPs) and higher LUMO energies (lower EAs) than thiophene oligomers. The HOMO of EDOT lies 0.47 eV above that of thiophene, the extrapolated HOMO of poly-EDOT is 1.08 eV above that of polythiophene, showing a stronger decrease of the IP upon polymerization. The LUMO level of EDOT is -0.58 eV, 0.17 eV higher in energy than the LUMO level of thiophene. However, LUMO of poly-EDOT lies 0.90 eV higher than that of polythiophene, showing a smaller increase of the EA upon polymerization compared to thiophene.

In order to compare the changes in the IP and EA values of thiophene and EDOT with those of CDM upon polymerization, we should take bithiophene and bi-EDOT as repeating units, since CDM includes two thiophene rings in its monomer. The HOMO of CDM lies 1.21 eV or 0.22 eV lower than the HOMO levels of bi-EDOT and bithiophene respectively. The IP of poly-CDM is 1.9 eV and

Table 1: Energy levels for oligomers of thiophene, EDOT, CDM, CDM-EDOT.

# of repeat units	lower valence band edge	HOMO	LUMO	upper conduction band edge	E _g
Thiophene					
1	-7.48			-0.75	6.73
2	-8.65	-6.59	-1.78	-0.10	4.81
3	-9.14	-6.22	-2.22	0.18	4.00
4	-9.39	-6.04	-2.46	0.33	3.58
5	-9.55	-5.93	-2.61	0.42	3.32
6	-9.66	-5.86	-2.71	0.49	3.15
∞	-10.23	-5.45	-3.25	0.83	2.20
Band Width : 2.32 eV (evaluated poly-bithiophene)		Band Width : 1.96 eV (evaluated poly-bithiophene)			
EDOT					
1	-7.01			-0.58	6.43
2	-7.99	-6.00	-1.32	0.38	4.68
3	-8.30	-5.53	-1.63	0.77	3.90
4	-8.43	-5.26	-1.80	0.98	3.46
5	-8.49	-5.10	-1.91	1.10	3.19
6	-8.52	-4.98	-1.97	1.19	3.01
∞	-8.76	-4.37	-2.35	1.64	2.02
Band Width : 2.35 eV (evaluated for poly-bi-EDOT)		Band Width : 2.19 eV (evaluated for poly-bi-EDOT)			
CDM					
1	-7.21			-3.98	3.23
2	-7.89	-6.72	-4.19	-4.15	2.53
3	-8.17	-6.55	-4.34	-4.19	2.21
4	-8.32	-6.48	-4.40	-4.22	2.08
5	-8.41	-6.45	-4.44	-4.23	2.01
∞	-8.80	-6.27	-4.66	-4.28	1.61
Band Width : 2.53 eV		Band Width : 0.38 eV			
CDM-EDOT					
1	-6.41			-3.82	2.59
2	-6.73	-5.99	-3.88	-3.80	2.11
3	-6.86	-5.85	-3.90	-3.79	1.95
∞	-7.15	-5.57	-3.94	-3.77	1.63
Band Width : 1.58 eV		Band Width : 0.17 eV			

0.82 eV lower in energy than the HOMO levels of poly-EDOT and polythiophene, respectively. The LUMO value of CDM is -3.98 eV, the LUMO level of bi-EDOT is -1.32 eV, and that of bithiophene is -1.78 eV. The LUMO of poly-CDM (-4.66 eV) is also differing very much from the LUMO levels of poly-EDOT (-2.35 eV) and of polythiophene (-3.25 eV).

To sum up, poly-EDOT has both high-lying HOMO and LUMO in comparison with polythiophene and poly-CDM. The HOMO of poly-EDOT is 1.08 eV and 1.90 eV above those of polythiophene and poly-CDM, respectively. Similarly, LUMO of poly-EDOT is 0.90 eV and 2.31 eV above those of polythiophene and poly-CDM, respectively. Experimental results support our calculations. Because of its low ionization potential, poly-EDOT is air stable in the p-doped form. Poly-CDM has the highest IP and EA values compared to polythiophene and poly-EDOT.

IP and EA of the copolymer lie between the IPs and EAs of their constituent homopolymers (Table 1). Poly-CDM-EDOT has a HOMO level of -5.57 eV, which is in between the HOMO levels of poly-EDOT (-4.37 eV) and of poly-CDM (-6.27 eV). The LUMO level of poly-CDM-EDOT is -3.94 eV, which is also in between the LUMO levels of poly-EDOT (-2.35 eV) and of poly-CDM (-4.66 eV).

Huang and Pickup reported [24] that the onset of n-doping is relatively insensitive to composition while the onset of p-doping shifts to lower potentials as the content of EDOT is increased [24]. Table 2 summarizes the IPs and EAs of $(E)_n C(E)_n$ co-oligomers with increasing number of EDOT rings connected to the ends of CDM

monomer. In fact, it is difficult to compare IPs and EAs of $(E)_nC(E)_n$ co-oligomers with the oligomers of CDM-EDOT, because both CDM-EDOT and $(E)_nC(E)_n$ co-oligomers have different number of thiophene rings in their repeat units, which make the situation difficult to compare directly. However, the extrapolated HOMO energy of poly-CDM-EDOT, -5.57 eV, is lower than the HOMO of $(E)_3C(E)_3$ co-oligomer (-5.28 eV). This indicates that the ionization potential of $(E)_3C(E)_3$ co-oligomer is already less than the IP of poly-CDM-EDOT. This is consistent with the experimental finding that the onset of p-doping shifts to lower potentials as the content of EDOT is increased in the composition of copolymer.

Table 2: *IPs, EAs, and E_g values for $(E)_nC(E)_n$ co-oligomers*

n	HOMO	LUMO	E_g
1	-6.03	-3.71	2.32
2	-5.54	-3.60	1.94
3	-5.28	-3.54	1.74

The donor/acceptor concept predicts the IP of the copolymer to be close to the IP of the donor, and the EA of the copolymer to be close to that of the acceptor. Our calculations showed that the frontier orbital energy levels of CDM-EDOT and $(E)_nC(E)_n$ oligomers have values lying between those of similar sized homooligomers. In order to understand the nature of averaged values, we estimated HOMO and LUMO levels of co-oligomers by simply taking into account the number of thiophene rings in EDOT and CDM. CDM includes two thiophene rings in its monomer, and EDOT has one. Averaging HOMO and LUMO levels of the hexamer of EDOT and the trimer of CDM by 1 to 2 gives estimated average levels for repeat unit 2 of CDM-EDOT and the $(E)_2C(E)_2$ co-oligomer. The results are shown in Table 3. Averaged HOMO levels of co-oligomers are very close to our theoretically calculated HOMO

levels. However, averaged LUMO levels of co-oligomers differ from the calculated ones. The calculated LUMO levels are closest to the LUMO level of trimer of CDM.

Table 3: Comparison of HOMO and LUMO levels of co-oligomers with estimated average values.

	CDM-EDOT [dimer]	(E) ₂ C(E) ₂
Theoretically calculated HOMO	-5.99	-5.54
Estimated average value of HOMO	-6.02	-5.50
Theoretically calculated LUMO	-3.88	-3.60
Estimated average value of LUMO	-3.55	-2.76

The donor/acceptor concept requires copolymerization of a donor with low IP and an acceptor with high EA. EDOT qualifies as donor since IP and EA are low. CDM is a good acceptor, since its EA is unusually large. However, there is only a 0.2 eV difference between the IP of EDOT and that of CDM. That the IP are so close is due to several effects. EDOT has an electron-donating group connected to a thiophene ring, which increases HOMO level. CDM has two thiophene rings in its monomer, which increases its HOMO level as a result of its larger size compared to EDOT, while the dicyanomethylene group decreases the HOMO. Since the IPs of EDOT and CDM are about the same, a donor-acceptor type interaction can not be expected for valence band. However, the EAs of EDOT and CDM differ by of 3.4 eV. Hence, we can expect a donor-acceptor type interaction for the conduction band of the copolymer.

To compare and to see the changes in HOMO and LUMO levels of homo-oligomers and co-oligomers, we sketched Figure 3 for the oligomers, which have 12-double bonds in their conjugated backbone. When we go from hexamer of thiophene

to hexamer of EDOT, we observe an increase in the highest occupied and lowest unoccupied levels. The trimer of CDM has lower HOMO and LUMO levels than the hexamer of EDOT. When we combine EDOT and CDM in one to one ratio and in different ratios, the levels are found to be between the HOMO and LUMO levels of hexamer of EDOT and trimer of CDM as explained above.

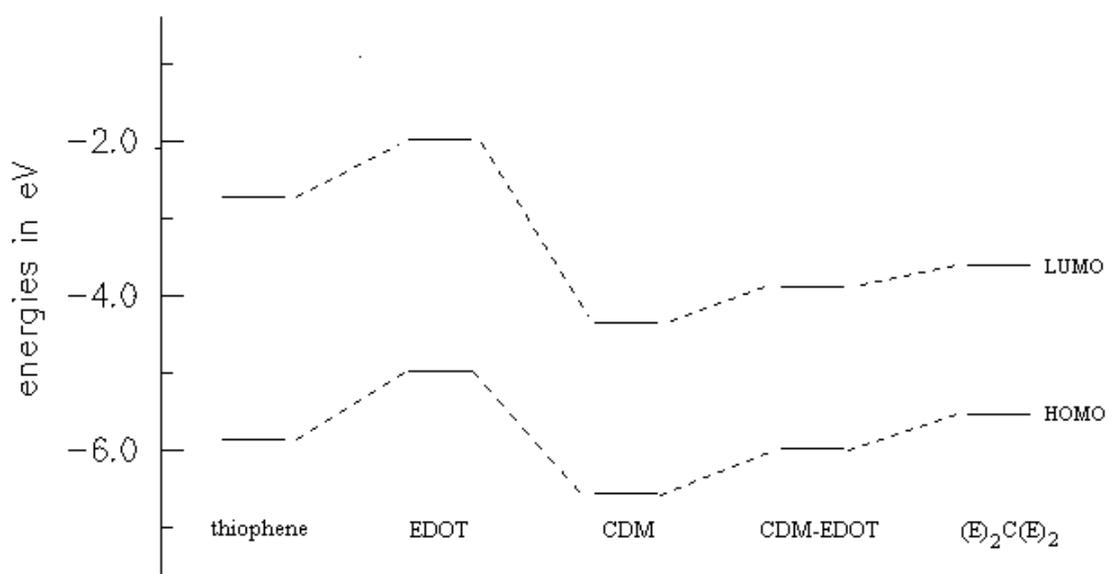


Figure 3: Changes in the HOMO and LUMO levels of thiophene (hexamer), of EDOT (hexamer), of CDM (trimer), of CDM-EDOT (dimer), and of (E)₂C(E)₂ respectively. (They all have the same number of double bonds (12) in their conjugated backbone.)

3.3 Band Gaps

Energy levels and development of bands for oligomers of thiophene, EDOT, and CDM-EDOT are sketched in Figures 4, 5, and 6, respectively. In order to figure out these bands, we sketched all of the molecular orbitals of each oligomer and used only the π -orbitals and their energy levels. Since EDOT has only C_2 symmetry, a strict separation between π and σ orbitals is not possible. Inspection of orbital plots showed that the frontier orbitals are nonetheless almost pure π -orbitals. Therefore, EDOT has more π -orbitals than thiophene since one of the oxygen lone pairs is an almost pure π -orbital and conjugates with the backbone (Figure 5). However, we could not identify all of the low and high lying π -orbitals, since ' σ - π '-mixing is significant for low and high lying orbitals. After careful search for the correct orbitals, we selected only the π -orbital energy levels, which will form energy bands at infinite chain length. As the size of oligomers increases, the number of energy levels corresponding to that oligomer are also increasing. For thiophene and EDOT, we calculated the oligomers starting from the monomer to the hexamer (Figure 4 and 5). For CDM-EDOT, we were able to calculate the oligomers up to trimer (Figure 6). This is because as the size of the system increases, computational cost of calculation time increases rapidly [72]. By using these energy levels, we obtained band widths and band gap values for the polymers and the copolymer by extrapolation (Table 1).

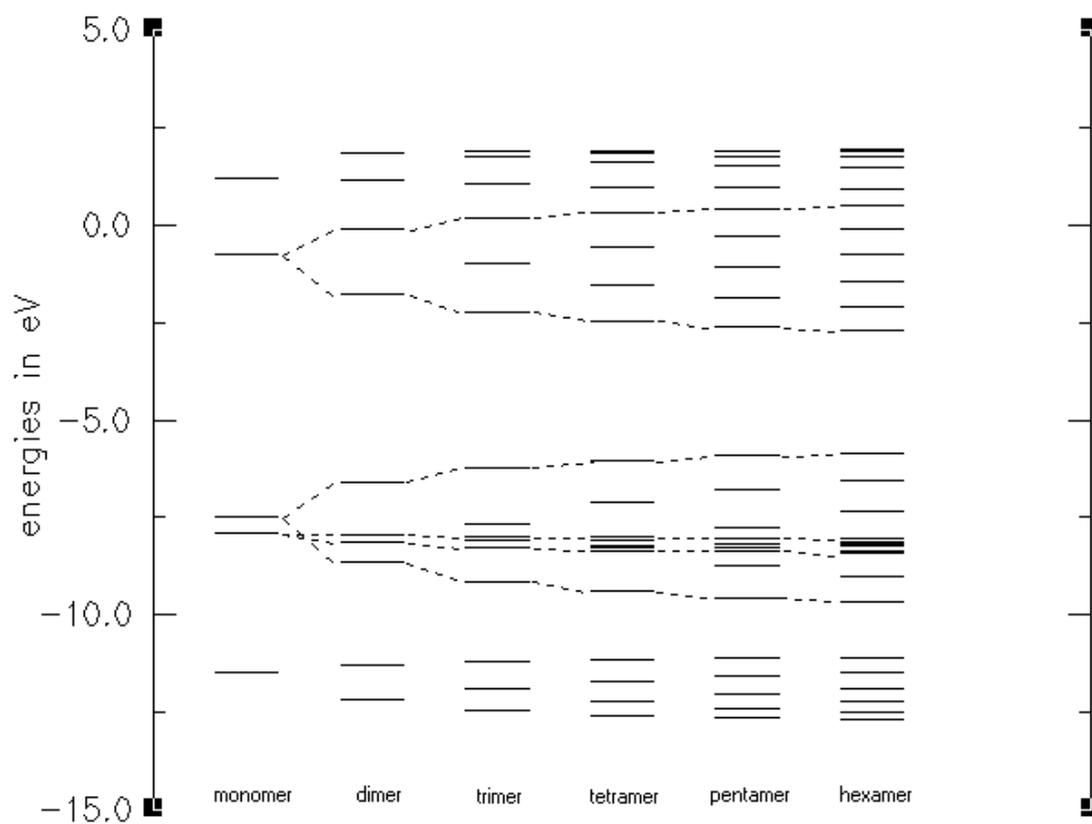


Figure 4: Energy levels and development of bands for oligomers of thiophene.

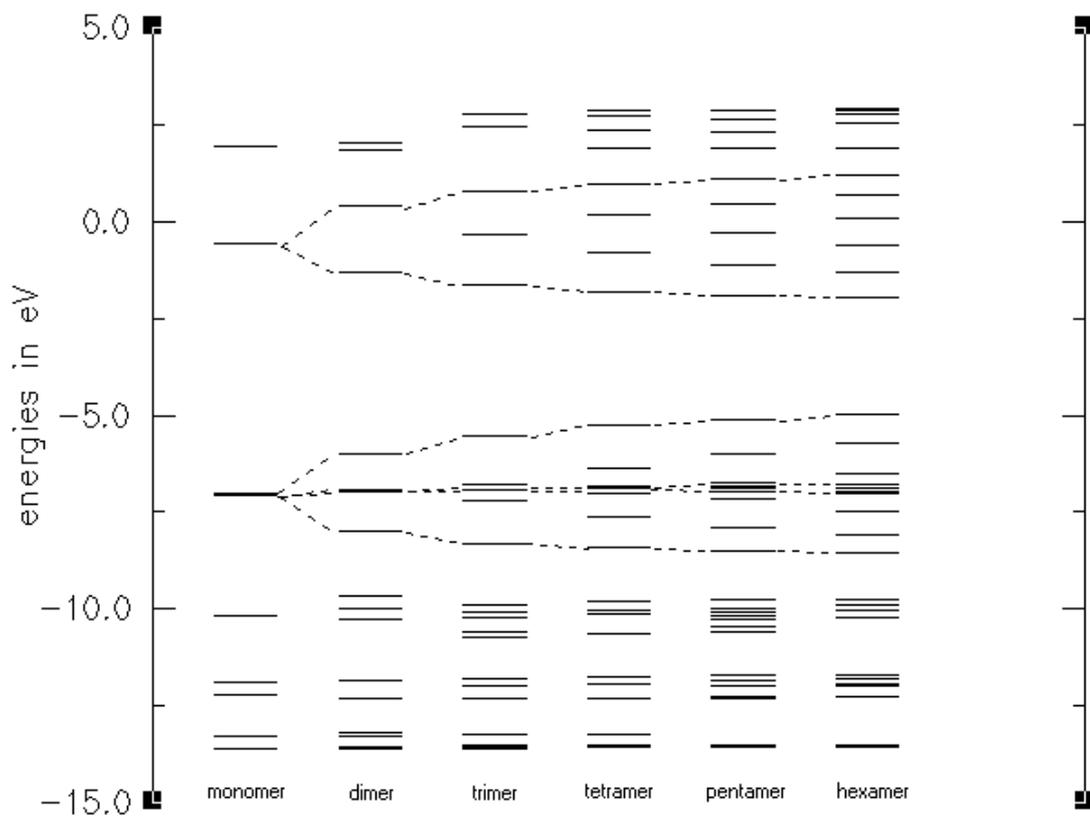


Figure 5: Energy levels and development of bands for oligomers of EDOT.

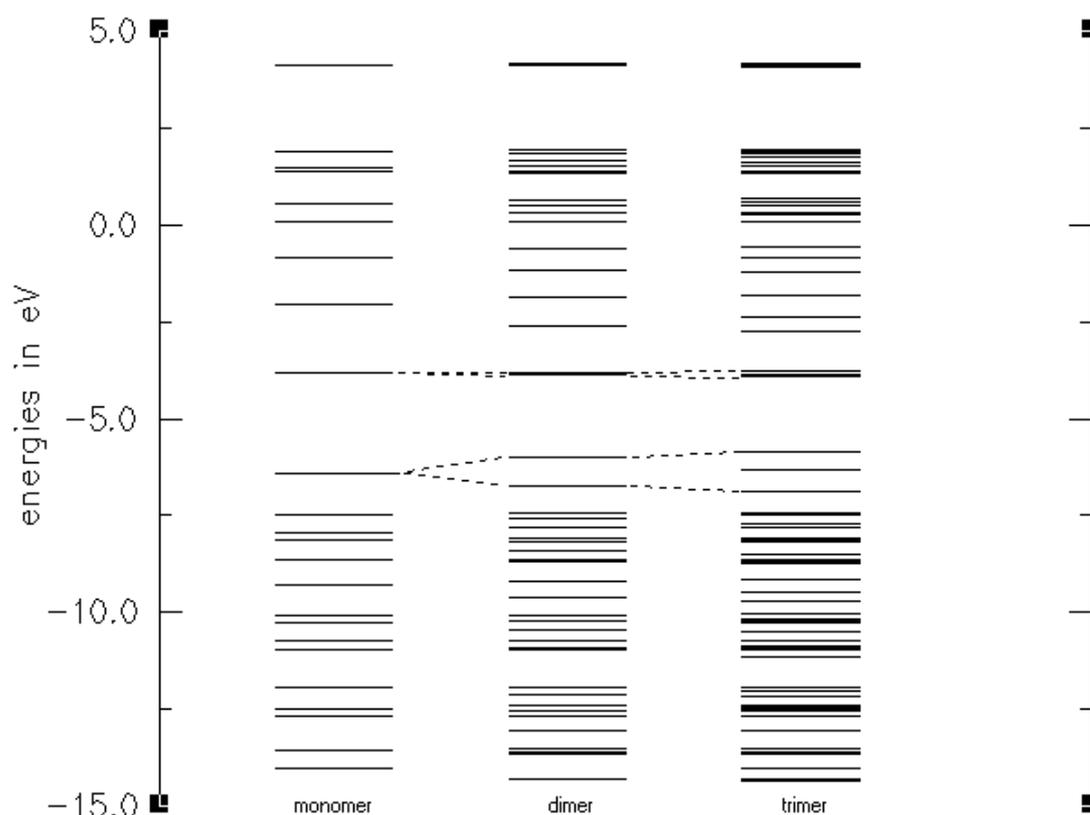


Figure 6: Energy levels and development of bands for oligomers of CDM-EDOT.

The copolymer of EDOT and CDM has about the same energy gap as poly-CDM. Plotting the HOMO-LUMO energy differences against $1/n$ and extrapolating to infinite chain length by using second-order polynomial fitting (Figure 7) predicts the band gaps of polythiophene, poly-EDOT, poly-CDM, and poly-CDM-EDOT to be 2.20 eV, 2.02 eV, 1.61 eV, and 1.63 eV, respectively. Absorption maxima (λ_{\max}) for polythiophene and poly-EDOT are 2.30 eV [84] and between 2.00 eV and 2.43 eV (Table 4) respectively. The electrochemical band gap of poly-CDM is 0.8 eV [25], and that of poly-CDM-EDOT is 0.19 eV [24].

Table 4: Absorption maxima and highest conductivity values for *p*-doped poly-EDOT reported in the literature.

Reference Number	Absorption Maximum	Highest Conductivity
48	2 eV	200 S/cm
51	2.03 eV	600 S/cm
61	2.13 eV	-
44	-	20 S/cm
62	2.43 eV	8.3 S/cm
56	-	13.0 S/cm
58	-	230 S/cm
59	2.1 eV	-

Experimental optical band gap values are taken as the onset of absorption where theoretical estimates for band gap calculations correspond to λ_{\max} . According to the Franck-Condon principle, the highest intensity (λ_{\max}) in absorption spectra corresponds to a vertical excitation since the electronic excitation is fast with respect to nuclear relaxation. For polyenes and aromatic heterocycles, the lowest allowed excitations are singlet $\pi \rightarrow \pi^*$ transitions. Thus, the HOMO-LUMO gaps for our oligomers estimate λ_{\max} [77]. The difference between the onset of absorption and λ_{\max} is usually about 0.5 eV. For example, in case of poly-EDOT, absorption begins at around 1.5 eV, reaching maximum at around 2 eV-2.13 eV, with exception of the larger number of reference 62. Different research groups also reported varying values for the onset of absorption of poly-EDOT, which are lying between 1.5 to 1.7 eV [48,54,61,62].

We searched the crystal lattice structure of poly-EDOT from the literature. Poly-EDOT has flat main chains, which stack on top of each other, and the distance between two chains is 3.4 Å which gives rise to an important conductivity along the axis perpendicular to the chain axis due to orbital overlap [47]. Hence, this orbital overlap might change the band gap of poly-EDOT (This maybe the reason why

different research groups measured different band gap values for poly-EDOT). Experimental conditions, crystal structures, extend of conjugation might significantly alter the value of λ_{\max} and the onset of absorption.

The varying conductivity values and the absorption maxima for poly-EDOT are summarized in Table 4. Electrochemical band gap of poly-EDOT is 1.2 eV [24] making a difference of 0.3-0.5 eV between optical and electrochemical band gap. Thus, there is a difference of 0.8-1.0 eV between the electrochemical band gap and absorption maximum.

While comparing our theoretical band gap estimates with the experimental ones, we take absorption maxima as a reference of comparison. Ultrathin polythiophene films showed a λ_{\max} value of 2.30 eV [84]. So, the theoretical estimate for polythiophene is only 0.10 eV larger than the experimental value, where for the poly-EDOT case, our prediction is within the range of the experimental values. Unfortunately, we do not have λ_{\max} values for poly-CDM and poly-CDM-EDOT. So, we have to compare our theoretical band gap estimates with the electrochemical band gaps. As we stated in the previous paragraph, there is approximately 0.8-1.0 eV difference between absorption maximum and electrochemical band gap. Thus, our electrochemical band gap estimates for poly-CDM and poly-CDM-EDOT are between 0.6 and 0.8 eV. Electrochemical band gap of poly-CDM is 0.8 eV, which agrees well with our theoretical calculation. However, for poly-CDM-EDOT, our estimate is 0.4-0.6 eV larger than the experimental value. This casts reasonable doubt on the low electrochemical band gap value reported for poly-CDM-EDOT [24].

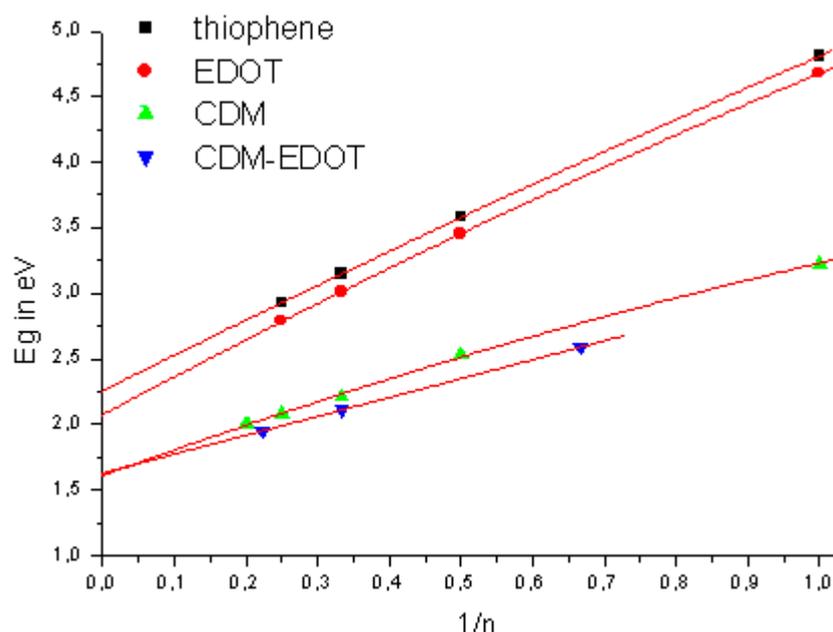


Figure 7: Energy gaps vs $1/\text{number of repeat units}$ of thiophene, of EDOT, of CDM, and of CDM-EDOT.

The idea of the donor/acceptor concept is that a regular alternation of conjugated donor- and acceptor- moieties in a conjugated chain will induce a small band gap. So, a copolymer of a donor/acceptor system should show a smaller band gap than the corresponding homopolymers. To interpret our system, firstly, we can compare HOMO-LUMO energy differences of monomers. The monomer of EDOT has a HOMO-LUMO energy difference of 6.43 eV, the monomer of CDM has a difference of 3.23 eV and the monomer of CDM-EDOT has a difference of 2.59 eV. So, the repeat unit for copolymer has a HOMO-LUMO difference 0.64 eV smaller than the CDM monomer. Secondly, we can compare band gap values for larger size oligomers. Figure 3 enables us to compare directly the band gaps of oligomers and of co-oligomers. The differences between HOMO and LUMO levels of hexamers of thiophene and EDOT, the trimer of CDM, repeat unit 2 of CDM-EDOT, and the $(E)_2C(E)_2$ co-oligomer are 3.15 eV, 3.01 eV, 2.21 eV, 2.11 eV, and 1.94 eV, respectively. Repeat unit 2 of CDM-EDOT has a 2.11 eV HOMO-LUMO difference,

only 0.1 eV lower than the trimer of CDM. This is only a slight decrease of the HOMO-LUMO energy difference for the co-oligomer. Thirdly, we can compare the polymeric band gap values. Poly-EDOT, poly-CDM and poly-CDM-EDOT have band gaps of 2.02 eV, 1.61 eV and 1.63 eV, respectively. The band gap of the copolymer is almost the same that of poly-CDM. From all these results we can say that the shift of the LUMO levels of the copolymer is very small upon polymerization. Because at the beginning, there was a difference of 0.64 eV between the monomeric oligomers, then this value is decreased to 0.1 eV for large oligomers and for the polymeric values the band gap difference vanished. Thus, we can conclude that IP and EA of the donor-acceptor repeat unit change little, and hence band gap upon polymerization, because of the weak interaction between donor and acceptor units which will be explained in the Donor/Acceptor Model section 3.5 in detail. So, dispersions of valence and/or conduction bands are adversely affected in donor-acceptor systems. If only the HOMOs of donor and acceptor units lie at very different energies, the valence band will be narrow. Similarly, if LUMOs lie at very different energies (like with CDM-EDOT), the conduction band will be narrow. If both IPs and EAs have donor/acceptor type interaction, both valence and conduction band will be narrow. In such a situation, very small band gap polymers could be synthesized with dispersionless bands.

Huang and Pickup [24] reported that if the ratio of EDOT to CDM increases in the composition of copolymer, then the band gap further diminishes and maybe approaches to zero. Our calculations showed that the increasing content of EDOT is causing a little reduction (1.94 eV) in the HOMO-LUMO energy difference, and this

can be attributed to increasing level of HOMO compared to the LUMO level because of high ratio of EDOT to CDM.

Theoretical calculations by using density functional theory give good agreement with experiment for polythiophene (exp : 2.30 eV, DFT : 2.20 eV) and for poly-EDOT (exp: 2.0-2.43 eV, DFT: 2.02 eV). Our estimate range for poly-CDM includes the experimental band gap value 0.8 eV. However, for the band gap of the copolymer, we obtained a larger E_g than the experimental value. In fact, we have doubts for the electrochemical band gap value reported in Huang's paper [24]. Alternatively, this low electrochemical band gap measured for the copolymer might be due to the fact that the experimentally synthesized CDM-EDOT copolymers are random copolymers rather than periodic copolymers. Only the ratio between these two monomer units could be controlled by changing the synthesis potential [24]. Bakhshi et al. stated that saturation in the electronic properties of random copolymers is reached much faster than the periodic copolymers and also random copolymers have lower band gap values than periodic ones [13]. Thus, it is reasonable to calculate larger E_g value for poly-CDM-EDOT theoretically.

3.4 Band Widths

As we stated in the methods section, molecular orbital pictures for Kohn-Sham orbitals are similar to those of RHF methods. However, they are differing from the pictures of eH orbitals, especially near the nuclei; this was expected, since the eH orbitals do not contain the core 1s levels [75]. So, we can say that these MO pictures which are obtained from DFT are very similar to those obtained from other theoretical methods.

In the following pictures, dark-grey areas indicate the parts where the wave-function is positive, and light-grey areas indicate the negative region of the wave-function. The square of the wave-function is proportional to the electron density. If the wave-function has large coefficients everywhere, the electron density is delocalized.

It is essential to examine the molecular orbital pictures of HOMO and LUMO levels of the polymers for a rough understanding of the molecular segments, which contribute to the valence and the conduction bands. Band width values of the valence and the conduction bands for the polymers are estimated and shown in Table 1. Because CDM has two thiophene rings, it has to be compared to bithiophene and bi-EDOT. By this way band widths of the valence and the conduction bands are directly comparable.

Figure 8 shows the orbital plots of the HOMO level and the levels below. There are coefficients concentrated on the double bonds, which indicates that the

HOMO level of hexamer of EDOT favours aromatic structure. Conversely, its LUMO (Figure 9) favours quinoid structure, since the wave-function has the same sign across single bonds along the conjugated backbone. Both valence and conduction bands of poly-EDOT are extensively delocalized and have band widths of 2.35 eV and of 2.19 eV (Table 1), respectively. Valence band width values for poly-EDOT (2.35 eV) and polythiophene (2.32 eV) are very close to each other. The conduction band width of polythiophene is slightly larger (0.13 eV) than that of poly-EDOT.

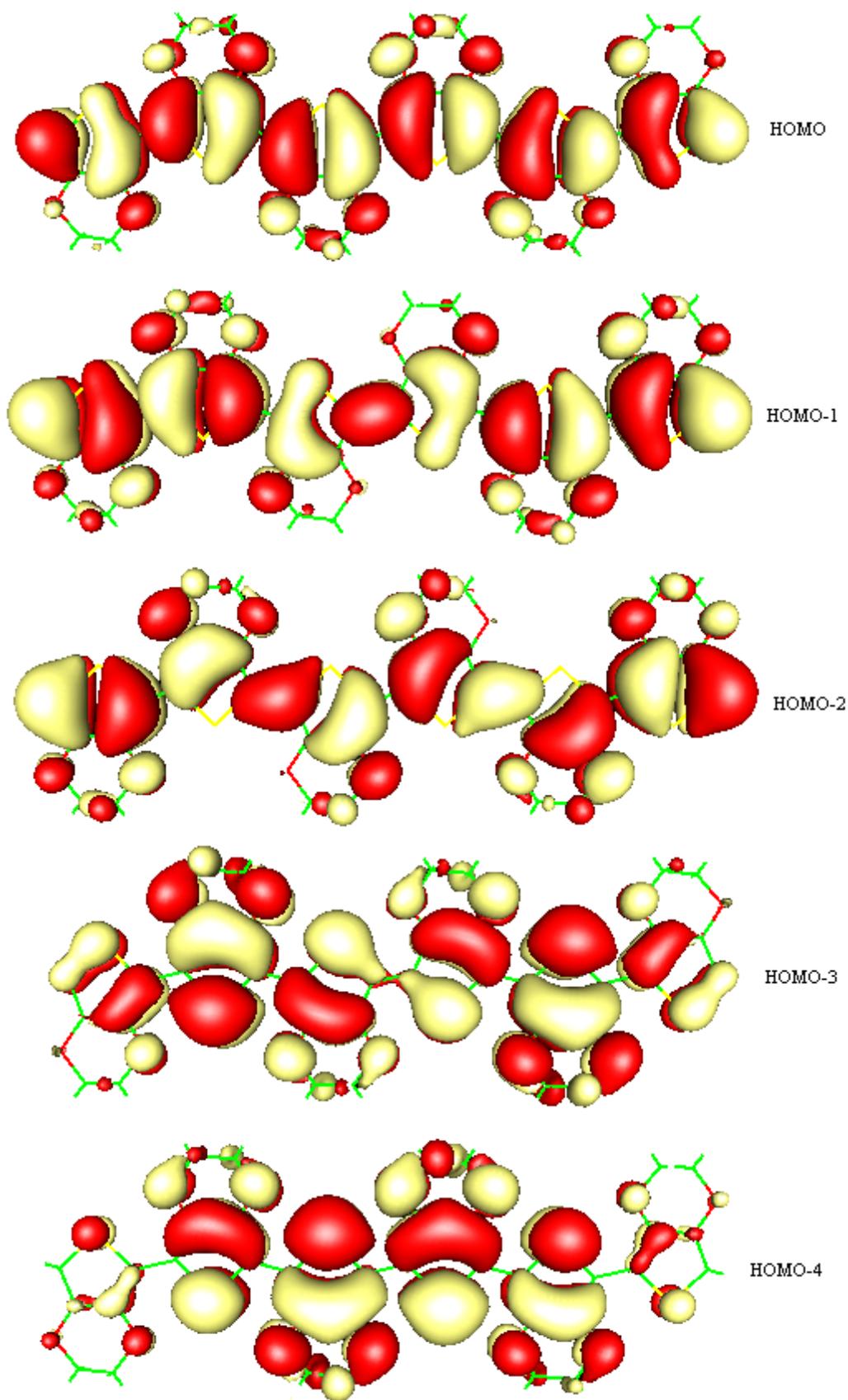


Figure 8: Highest lying occupied π -orbitals of EDOT (hexamer).

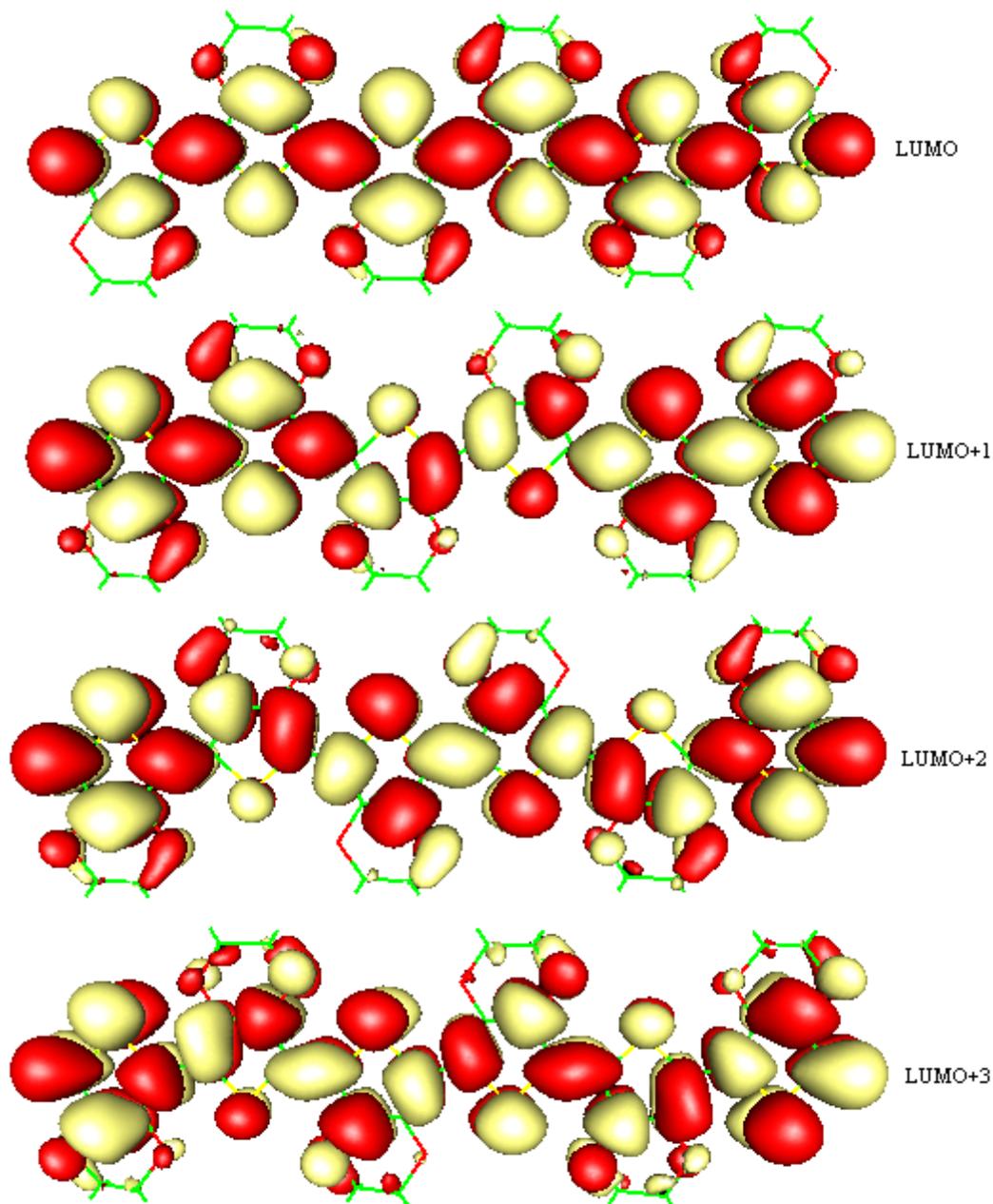


Figure 9: *Lowest lying unoccupied π -orbitals of EDOT (hexamer).*

In a recent study, Salzner studied the electronic structure of thiophene oligomers and plotted their molecular orbital pictures for HOMO and LUMO levels [6]. We compared these pictures with those of EDOT and realized that, if we omit the

effect of ethylenedioxy group on molecular π -orbitals, we are left with the molecular orbital pictures, which are essentially the same as pure molecular π -orbital plots of thiophene. Thiophene and EDOT have very similar electronic structures. Compared to polythiophene, the ethylenedioxy group, which is connected to the thiophene ring, causes upward shifts of the valence and the conduction bands in poly-EDOT.

The valence band width value for poly-CDM is 2.53 eV, approximately 0.2 eV larger than those of poly-bi-EDOT and poly-bithiophene. However, the band width of the conduction band of poly-CDM is only 0.38 eV, approximately 1.8 eV smaller than that of poly-EDOT and 1.6 eV smaller than that of polythiophene. The same behaviour is observed in the copolymer of CDM and EDOT. Although oligomers of poly-CDM-EDOT have three thiophene rings in their repeating units compared to two in bi-EDOT and bithiophene, multiplying the valence and conduction band widths by $3/2$ enables us to make a rough comparison of the band widths of the copolymer and the homopolymers. This crude estimate of the valence band width is 2.37 eV, and for conduction band, it is 0.25 eV. These values are very close to band widths values of poly-CDM. CDM-EDOT has a broad valence band but a very narrow conduction band (Figure 6). Orbital plots show that the valence band is delocalized through conjugated thiophene backbone and there are no coefficients on the dicyanoethylene group (Figure 10). However, the conduction band is mostly determined by the coefficients on the CDM units and there are negligibly small coefficients on the EDOT units (Figure 11).

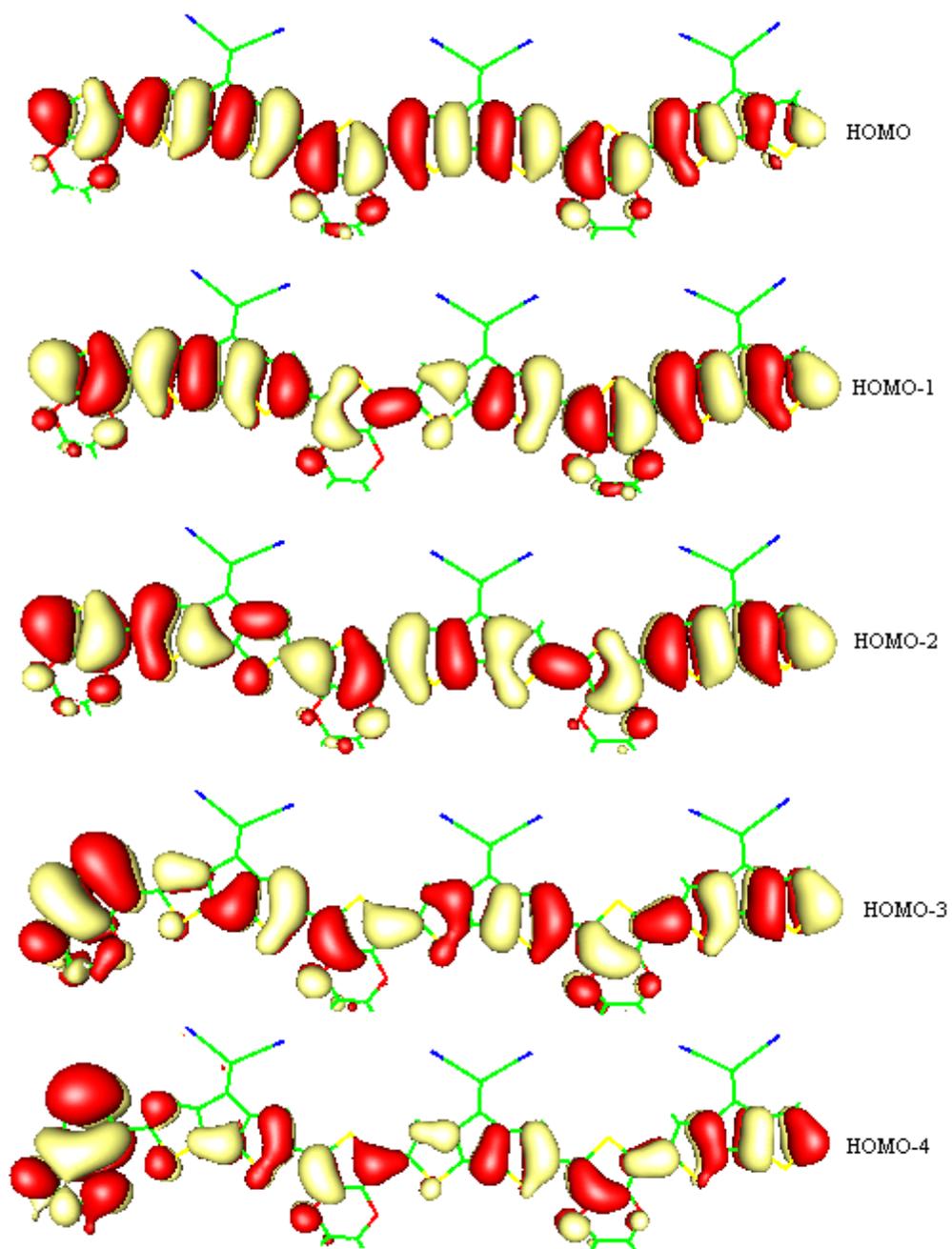


Figure 10: *Highest lying occupied π -orbitals of CDM-EDOT (trimer).*

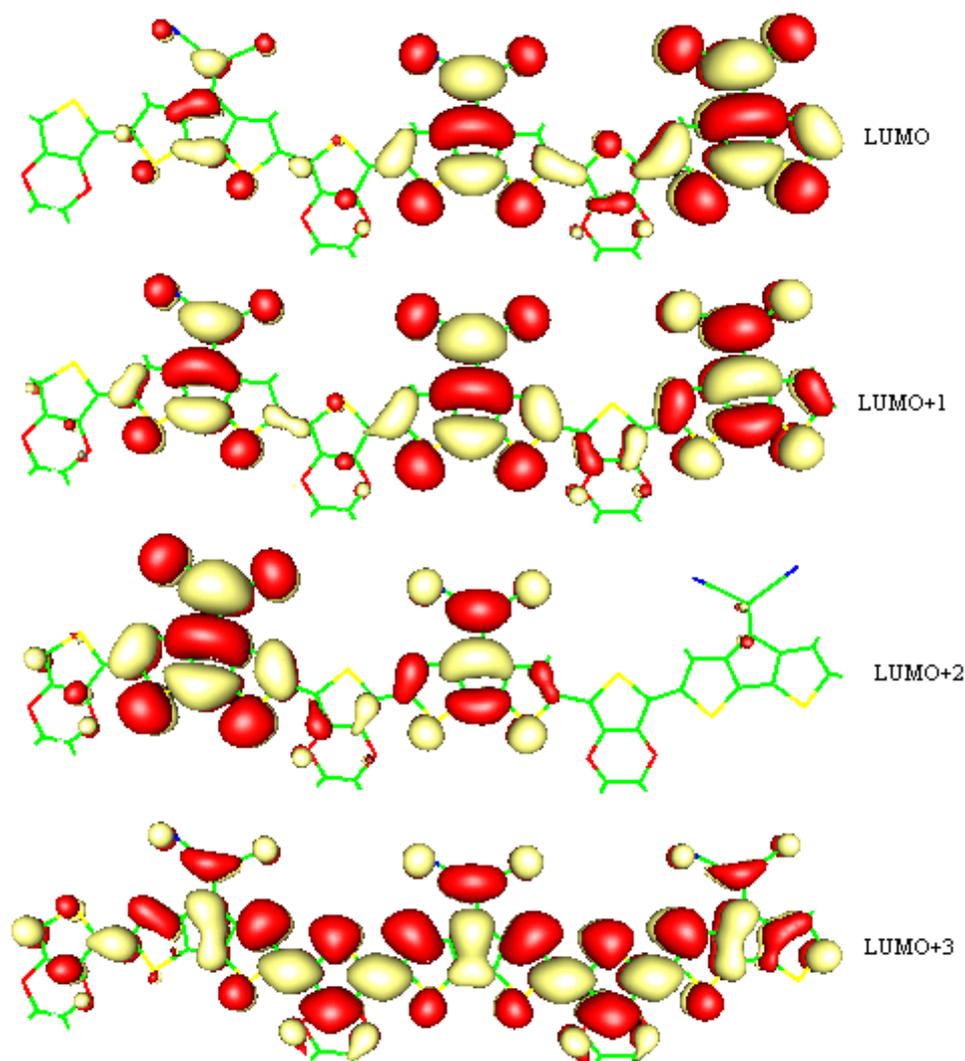


Figure 11: *Lowest lying unoccupied π -orbitals of CDM-EDOT (trimer).*

In the introduction part, we explained how the band width is related to delocalization. To summarize, if the band width of a system is narrow, then this band is constituted from localized states. These localized states prohibit the free movement of the carriers, which play an important role in electrical conduction. Conversely, delocalized states form broad bands. The extent of delocalization determines the mobility of carriers.

Thiophene and EDOT have similar band developments especially for valence and conduction bands and they are giving rise to wide bands. The HOMO-1 levels of thiophene and EDOT are giving rise to a very narrow band inside the band arising from the HOMO. The conduction bands of EDOT and of thiophene are wide. CDM-EDOT has a wide valence band but a flat conduction band.

Huang and Pickup [24] copolymerized EDOT and CDM in order to obtain lower band gaps than the homopolymers. They decreased the band gap of the copolymer to less than 0.16 eV, the intrinsic conductivity of copolymers was 10^{-3} S cm^{-1} . They estimated the ratio of n-type carrier mobility in copolymers to that of p-type as ≈ 0.002 . For poly-CDM, this ratio is measured as 0.025 [25]. The conduction band width of poly-CDM-EDOT is less than that of poly-CDM (0.25 eV vs. 0.38 eV), consistent with a further decrease in from poly-CDM to the copolymer carrier mobility. Thus, the theoretical results rationalize the experimental findings. The low mobility of the n-type carriers and the large mobility of the p-type carriers can be attributed to the narrow conduction band and the wide valence band. It is interesting to note that CDM, which also has a narrow conduction band, showed little conductivity in the n-doped state [25].

3.5 Donor/Acceptor Model

If we apply our explanations to our donor/acceptor (EDOT/CDM) system, we face the following situation (Figure 12). The HOMO of EDOT is -7.01 eV, where HOMO of CDM is -7.21 eV. That is, they are very close in energy and the interaction between these levels will not be donor/acceptor type as we figured out above. So, the resulting molecular orbitals are well separated. However, LUMO of EDOT (-0.58 eV) and LUMO of CDM (-3.98 eV) could have a donor/acceptor type interaction, since their energies are very different from each other. For this reason the LUMO of CDM doesn't interact with LUMO of EDOT.

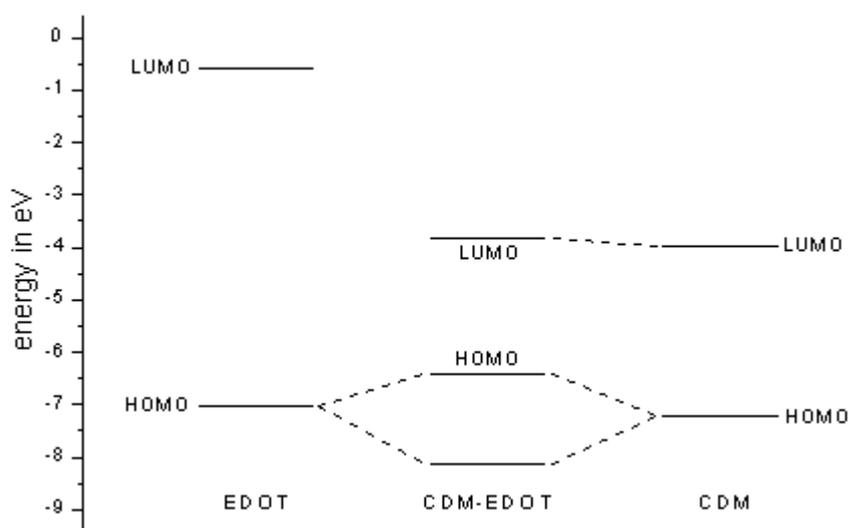


Figure 12: *Interactions between the frontier orbitals of EDOT and of CDM.*

Since the LUMO levels have donor/acceptor type interaction, we should have obtained a broad conduction band for the copolymer as Havinga et al. suggested [23]. In contrast, we calculated a very flat conduction band for the copolymer. The donor/acceptor model fails because of a wrong hypothesis that band broadening

should be observed for the donor/acceptor systems. Instead, we observe localization of states, which lead to narrow bands upon donor/acceptor type interactions.

As a result, the donor/acceptor model applied to one of the bands can be used for synthesizing for n-type or p-type conductors. However, both types of conductivity are not possible for these systems for the same copolymer. Since, for instance, for p-type conducting systems the conduction band will be narrow and hence the mobility of n-type charge carriers will be low. For n-type conducting systems the valence band will be narrow and hence the mobility of p-type charge carriers will be low. If both valence and conduction bands have donor/acceptor type interaction, band gap of the copolymer could be decreased. But then, both, the mobilities of p-type and n-type carriers will be low because of small dispersion of valence and conduction bands. Such a system would be a small band gap insulator.

5. CONCLUSIONS

Our theoretical band gap estimates agree well with the experimental results except for poly-CDM-EDOT, which is overestimated by more than 0.4 eV. Band width values also agree well with the experimental observations. The copolymer has broad valence band and very flat conduction band. This very narrow conduction band is constituted from localized states and prohibits the free movement of n-type carriers.

According to the donor/acceptor concept, combining two systems, one with a high-lying HOMO and one with a low-lying LUMO, in principle, should decrease the band gap. Poly-EDOT has a high-lying HOMO (-4.37 eV; E_g : 2.02 eV) and poly-CDM has a low-lying LUMO (-4.66 eV; E_g : 1.61 eV). Copolymers of CDM and EDOT would be an excellent example of donor/acceptor conjugated systems. However, theoretical investigation of 1:1 copolymer of CDM and EDOT did not show

a decrease in the band gap (1.63 eV) compared to the band gap of one of the homopolymers (poly-CDM).

In our calculations, we found that the HOMO and LUMO levels of co-oligomers are averaged between the HOMO and LUMO of EDOT and CDM oligomers. Nevertheless, LUMOs of co-oligomers are closer in energy to the LUMOs of CDM oligomers, which provide low-lying LUMO levels for co-oligomers.

The donor/acceptor concept can, in principle, be used for decreasing the band gaps of the polymers while sacrificing the dispersion of the bands [11]. These dispersionless bands are constituted from localized states and such localization decreases the mobility of both p-type and n-type carriers so much that then systems become useless for practical applications. For EDOT and CDM containing copolymers, the donor/acceptor approach can not be used to decrease the band gap. Although the HOMO-LUMO energy difference for the monomer of CDM-EDOT is smaller than either that of CDM or EDOT, small dispersion of conduction band in the copolymer causes a band gap for poly-CDM-EDOT that is almost equal to the band gap of poly-CDM. This flat conduction band of poly-CDM-EDOT prevents these kinds of polymers to be n-type conductors. However, p-type conductivity is possible in this copolymer [24].

Low-band gap polymers are of importance for synthesizing intrinsically conducting polymers. However, it is much more important to have mobile charge carriers rather than to have low-band gap systems. By using the donor/acceptor approach, one can synthesize n-type or p-type conductors. Nevertheless, it is not

possible to obtain both n-type and p-type conductivity for the same polymer. Previous studies [68,69] and this study strengthened our claim that the donor/acceptor concept does not work in principle. Different energy levels interact little. This little interaction leads to small decrease in band gap and band width for the donor/acceptor type polymers.

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