



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(9):80-93
(<http://derpharmachemica.com/archive.html>)

New copolymer based on carbazole and terphenyle (PECz-Ter) for optoelectronic devices. Structure–properties correlation

H. Sadki^a, M. N. Bennani^a and M. Bouachrine^{b*}

^aLaboratory of Chemistry and Biology Applied to the Environment, Faculty of Sciences, My Ismail University, BP – 11201 Zitoune, Meknès, Morocco

^bMEM, High School of Technology (ESTM), University Moulay Ismail, Meknes, Morocco

ABSTRACT

Geometrical parameters, electronic structures, optoelectronic and photovoltaic properties of new copolymers poly(Ethylcarbazole-Terphenyl) (PECz-Ter) containing Ethylcarbazole as a donor group and Terphenyl rings as electron acceptors, have been investigated through Density Functional Theory, has been theoretically studied using the density functional theory (DFT) with the hybrid B3LYP exchange correlation function and the split valence 6-31G (d,p) basis set. The theoretical results including the geometries optimization of (PECz-Ter)_n was carried out, showing a reduction in the band gap when going from n=1 to the n=5 monomer. Structural parameters, optoelectronic and photovoltaic properties have been analyzed and discussed in terms of conjugative pathway between the electron-donating and electron-accepting moieties. Optical properties of the studied oligomers of PECz-Ter (n=1-5) characterized by the bathochromic effect and the decreases value of the wavelength λ_{abs} with increasing the chain length from n=1 to n=5 monomer. From these results, the correlation structure-properties are better understood. Furthermore, the copolymers PECz-Ter, which is blended with fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and derivatives, seems to be a good active layer in bulk heterojunction solar cells in the case of the studied oligomers of (PECz-Ter) blended with C₆₀ or C₇₀. The subject of this work is to design novel materials for organic solar cells, and help to understand the structure–properties relationship of these new systems.

Keywords: DFT, Ethylcarbazole, Terphenyl, B3LYP, ZINDO/s, PCBM, structure–properties.

INTRODUCTION

Considerable research efforts have been devoted to the study the conjugated organic polymers from chemistry and physics science. With a booming in research effort to develop cost-effective renewable energy devices, dye sensitized solar cells (DSSC), also known as Grätzel cells [1] have been the topic of more than a thousand published papers just in 2010 [2], such as organic light emitting diodes (OLEDs) [3,4], field-effect transistors [5-7] (OTFTs), photovoltaic cells [8-10], portable electronic [11], lasers [12,13bouras]. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are desired in optoelectronic applications such as LEDs or solar cells [14].

Two waves of interest in carbazole containing polymers can be distinguished. The beginning of the first wave dates back to the sixth decade of the last century. A lot of interest in these polymers was caused by the discovery of photoconductivity in poly(N-vinylcarbazole) (PVK) by H. Hoegl [15,16]. In 1957, he has established that PVK sensitized with suitable electron acceptors showed high enough levels of photoconductivity to be useful in practical applications like electrophotography. As a result of the following activities, IBM introduced its Copier I series in 1970, in which an organic photoconductor, the charge transfer complex of PVK with 2,4,7-trinitrofluorenone (TNF),

was used for the first time [17]. Since then numerous carbazole containing polymers have been described in scientific literature and especially as patents.

The peak current interest in polymers containing carbazole or derivatives namely Ethylcarbazole (ECz) are mainly related to the discovery of organic light emitting diodes (OLEDs) [18], and organic photorefractive materials [19]. In recent surveys of organic electroluminescent (EL) devices and photorefractive materials an important role belongs to polymers containing carbazole. Outside electrophotographic photoreceptors [20], light emitting diodes, and photorefractive materials carbazole containing polymers are considered as components of photovoltaic devices [21]. In all of these fields of application of the photoconductive properties of carbazole containing polymers or their capacity to transport positive charges (holes) are exploited.

For these reasons the basic principles of photoconductivity are briefly discussed at the beginning of this article. Ethylcarbazole-based polymers are attractive as photoconductors or charge-transporting materials from the following reasons:

- † Ethylcarbazole groups easily forms relatively stable radical cations (holes);
- † Some Ethylcarbazole containing compounds exhibit relatively high charge carrier mobilities;
- † Different substituents can be easily introduced into the carbazole ring;
- † Ethylcarbazole containing compounds exhibit high thermal and photochemical stability;
- † Ethylcarbazole is a cheap raw material readily available from coal–tar distillation.

This materials become the most promising materials for the optoelectronic device applications [22]. Since then, there have been increasing interests and research activities in synthesis and design of new polymeric materials for organic electronic devices. However, their properties and related devices are still poorly understood.

On the other hand since the new experimental results on these new materials [23], these materials offer advantages over polymeric systems in terms of easy synthesis and purification, and generally exhibit high charge carrier mobility. In parallel with recent experimental work on these new materials, theoretical efforts have indeed begun to constitute an important source of valuable information which supplements the experimental studies, thereby contributing to the understanding of the molecular electronic structure as well as the nature of absorption and photoluminescence [24]. Therefore, theoretical investigation should be helpful to understanding of the structural information of this Ethylcarbazole-based copolymerization. In this study, the torsional energy curves for the poly(Ethylcarbazole-Terphenyl) (PECz-Ter) (Figure 1) were investigated using various theoretical approaches and basis sets. The theoretical knowledge of the electronic structures has given great contributions to the rationalization of the properties of known materials and to the properties prediction those of yet unknown ones. In this context, quantum-chemical methods have been increasingly applied to predict the band gap and other electronic properties of conjugated systems [25].

As a result, one of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are desired in optoelectronic applications such as LEDs or solar cells [26]. Significant efforts have been devoted to develop methods for controlling the band gaps of conjugated materials with the goal of producing technologically useful low band gap polymers. A powerful approach towards designing low band gap polymers is to synthesize alternating electron-rich (donor) and electron-deficient units (acceptor) to form internal Donor–Acceptor (D–A) structures along the polymer backbone [27-30]. Plastic solar cells have been synthesized through a low band gap alternating copolymer of fluorene and a donor-acceptor-donor moiety [31]. A common strategy to enhance the power conversion efficiency of the photovoltaic device is the development of low band gap conjugated polymers as an alternating (D-A) structure in the main polymer backbone, because this improves the exciton charge transfer and transport [32]. Ethylcarbazole-based alternating D–A copolymers have been of particular recent interest producing low band gap useful in technological field novel materials, by adjusting the HOMO and LUMO levels [33-35]. The HOMO and LUMO energy levels of these systems are very important factors to determine whether the effective charge transfer in the luminescent devices [36-38]. In this work, we use the density functional theory (DFT) (B3LYP/6-31G (d,p) and ZINDO/s to study the ground state and related electronic structures and various opto-electronic properties of these co-polymers, such as HOMOs, LUMOs, E_{gap}, the electronic absorption spectrum is calculated and discussed. So, we can save time and money in choosing the adequate organic materials to optimize photovoltaic device properties.

Research into new conjugated systems with high electro-optical properties have led us to synthesize regular copolymers and polymer blends containing aromatic and hetero-aromatic rings [39,40]. Thus, copolymers containing both Ethylcarbazole and p-Terphenyl units have also proved to be of interest in combining the properties associated to the two different conjugated rings [41-43].

This work is focused at completing theoretically the structure, optical and photovoltaic properties of new soluble co-polymers poly(Ethylcarbazole-Terphenyl) (PECz-Ter), in order to investigate its properties for an adequate optoelectronic application.

THEORETICAL METHODOLOGY

All computations of the studied co-polymers in this work were carried out with the Gaussian 09 program package [44] on an Intel Pentium IV 3.3 GHz PC running Linux. For the geometry optimizations at ground, excited, and doped states were performed under no constraints in the framework of the DFT methods. These methods have become very popular in recent years because they can reach similar precision to other methods in less time and less cost from the computational point of view. Using the B3LYP functional [Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP)] exchange correlation functional [45,46]. The 6-31G (d,p) basis set was used for all calculations, and was chosen as a compromise between the quality of the theoretical approach and the high computational cost associated with the high number of dimensions to the problem for all atoms [47,48]. In the conformational part, calculation was done by varying the torsion angle by 20° steps between $\theta = 0^\circ$ and $\theta = 180^\circ$. For each conformer, the dihedral angle was held fixed while the remainder of the molecule was optimized (the rigid-rotor approximation was not applied). The energy differences are always relative to the corresponding absolute minimum conformation and the potential energy surfaces were drawn.

The 3D structures of the molecules were generated using the Gauss View software program (version 5.0.8) and the graphical molecular orbital. The HOMO, LUMO and gap's energies were also deduced from the stable structure of the neutral form, where the energy E_{gap} is evaluated as the difference between LUMO and HOMO energies. In this paper, the transition energies were calculated at the ground-state geometries using ZINDO/s method calculations on the fully optimized geometries. The results obtained gave us the absorption, their corresponding transition energies, and the factor oscillation.

Finally, the nature and the energy of vertical electron transitions (the main singlet–singlet electron transitions with highest oscillator strengths) of molecular orbital wave functions were presented. Then, the theoretical simulated absorption spectrum was calculated using the SWizard program [49] into simulated spectra as described in the literature [50]. The electronic absorption in vacuum was carried out using ZINDO/s method on the basis of the optimized ground structures.

RESULTS AND DISCUSSION

3.1. Conformational study

The torsional angle (θ) is defined as the angle between the planes formed by the two heterocyclic Ethylcarbazole-phenyl and biphenyl. In order to present models structures of the co-polymer studied, and identify thus different properties which result, we found it useful to start with the most stable conformation via determination of the potential energy surface (PES).

First, it has been clear that Theory of the density functional (DFT) was used to determine the torsion angle which corresponds to the minimum relative energy which the conformer is more stable, using the B3LYP density function and 6-31G (d,p) basis set. This method tend to predict geometries closer to planarity than the conventional ab initio correlation methods [51, 52] and it been also performed on the phenyl-dimer (Ph)₂ and Ethylcarbazole-phenyl (ECz-Ph) compounds. Torsional energy curves, relative energies and torsional angles for (Ph)₂ and (ECz-Ph) molecules are shown in Figure 2A. Structures at various torsional angles (from $\theta = 0^\circ$ to 180° in steps of 20°) were partially optimized. $\theta = 0^\circ$ corresponds to the syn or cis structure. All stationary points located on the torsional energy were characterized as minima by harmonic frequency calculations (for minimum energy structures all frequencies are real).

In the case of terphenyl copolymerized with Ethylcarbazole, the twisted conformers were found with two torsion angles θ_1 and θ_2 to about 40° and 140° respectively, in which two compounds are more stable. The corresponding stable conformations are shown in Figure 2B. These results indicate that (Ph)₂ and Ecbz-Ph are non-planar in its ground states. The stable molecular geometries, corresponding to the energy minima on potential energy surface (PES), were obtained separately by releasing the constraints of the torsional angles θ .

3.2. Geometry parameters

The (PECz-Ter) copolymer prepared in this research is sufficiently long to consider the translation as a symmetry operation. In order to be coherent with experimental results, and in the geometric structure of this copolymer, we

have chosen an oligomer model with five successive monomers units. The optimized ground state geometry structure of this model with respect to the torsion angles of both ECbz-Ph and Ph-Ph compounds.

In order to determine the geometrical parameters (inter-ring bond lengths (d_i) and dihedral angles (θ_i)), the most stable conformations were fully optimized in their ground using DFT/B3LYP/6-31G (d,p) method. The twisting of the chain backbone was investigated by the dihedral angle's variety indicated in the Table 1. The optimized geometrical structure of (ECz-Ter)₅ model and their geometric parameters, with all labeled atoms are displayed in Figure 3. Based on these optimized structures, the access to the characteristic parameters of the copolymer becomes simple by considering the corresponding representation, or the dihedral angle (θ) is the deviation from coplanarity between the donor and acceptor units and inter- ring bond lengths (d_i) is the bond length between the donor and acceptor.

Considering the most stable conformation, we can deduce that the optimized structure of the PECbz-Ter appears under a twisted configuration with a large torsional angle (θ). This suggests that a strong steric hindrance effect exists between the donor and acceptor moieties.

The results of the optimized structures for the studied molecules show that all molecules possess planar structures. The inter-ring bond lengths and bond angles do not suffer appreciable variation with the oligomer size and it suggests that we can describe the basic structures of the polymers as their oligomers. As shown in Table 1, the inter-ring bond lengths (d_i) are in the average of 1.483 Å and the dihedral angles (θ_i , $i = 1 - 9$). The inter-ring torsions in the case of the longest oligomer (ECbz-Ter) 5 were evaluated to be about (θ_i , $i = 1 - 9$) = 143.28°. It is obvious that the torsional angles and barriers to internal rotation depend on the balance of two interactions, as a consequent of the p-electrons conjugation between two adjacent monomers, the molecules tend to remain planar, whereas the steric repulsion between hydrogens causes the molecules to twist or non planar [53].

3.3. Optoelectronic properties

The opto-electronic properties depend essentially on the appropriate HOMO and LUMO energy levels and the electron and hole mobilities. It is known that (E_{gap}) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is an important parameter which determines the molecular admittance because it is a measure of the electron density hardness. Generally, in theory the band gap is estimated as the difference between the HOMO and the LUMO level energies ($E_g = \Delta E_{\text{HOMO-LUMO}}$) when the repeated unit number is infinite [54]. The oligomer geometries and their corresponding band gap calculations were performed using DFT/B3LYP method with 6-31G/ (d,p) basis sets. In our case, the band gap of (PECz-Ter)_n ($n = 1-5$) oligomers is listed in Table 2. By using the linear extrapolation technique [55], it can be seen from Figure 4A, that this value decreases with increasing the chain length from $n=1$ to $n=5$ monomer. The experiment showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry [56-57]. But in the theory, the HOMO and LUMO energies can be calculated by DFT calculation. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers [58].

For a better understanding of the electronic properties of the studied oligomers, we present in Table 2, the calculated HOMO and LUMO energy levels, and the energies E_{gap} . In Figure 4, we have plotted HOMO, LUMO energetic levels and their corresponding optical energy differences ($\Delta H-L$) against the inverse of the number n of the monomer units. A good linear relationship was obtained. The extrapolated HOMO and LUMO energy levels and associated optical gaps (E_g) were determined (Table 2 and Figure 4). They lie at -4.979 eV, -1.219 eV and 3.76 eV, respectively. Consequently, the LUMO level energy significantly decreases and is responsible for the optical gap reduction. As a result, the energy gap decreases suggesting the maximum absorption peak in UV-vis spectra will red shift. The low HOMO energy level of the PECz-Ter copolymer suggests that the compound has high stability and potential application for hole injection and transport material in optoelectronic.

Electronic structures of PECz-Ter copolymer ($n = 1-5$) were displayed in Figure 5. The evolution of the calculated HOMO and LUMO energies as a function of reciprocal chain length for the copolymers of (ECz-Ter) n . It is known that in the case of the π -conjugated systems, the HOMO energies destabilized with the increasing of the conjugation length, whereas the LUMO energies decreased [59]. There is systematical decrease of the electronic calculated E_{gap} of (ECz-Ter)_n oligomers as the number of chain length increased (Figure 4B). These results indicate that the chain length of polymers have more effect on the electronic transition. Finally, it is relevant to note that the energy difference between consecutive π (π^* levels) levels becomes smaller and smaller as the chain gets longer. At the limit of an infinite chain, the change between levels is infinitely small. This results in continuous energy zones for

the π and π^* levels leading to energy bands, as often the case of conjugated polymer and inorganic semiconductors [60].

It will be useful to examine the highest occupied and the lowest unoccupied molecular orbitals of these oligomers, because the relative ordering of the occupied and unoccupied molecular orbital provides a reasonable quantitative indication of the excitation properties and the ability of electron or hole transport [61], and because the first dipole-allowed electron transitions, the strongest electron transitions with largest oscillator strength, correspond almost exclusively to the promotion of an electron from HOMO to LUMO. Electron density isocontour plots of the HOMO and LUMO of these oligomers are depicted in Figure 6. In the HOMO orbital representation, the C=C segments are π -bonding and have anti-bonding phase with respect to their neighboring C=C units. Whereas, in the case of the LUMO orbital, the C=C units are antibonding and bonding in the bridge single bonds. We also deduce that the frontier orbitals of all compounds are spread over the whole π -conjugated backbone. In general, excitation of π -electron from HOMO to LUMO leads to increase localization of electron density on the acceptor part of the molecule. Here, the promotion of one electron from HOMO to LUMO is explained by the frontier molecular orbital. For each structure, the LUMO favors the inter-ring mobility of electrons, while the HOMO only promotes the intra-ring mobility of electrons [62].

3.3. Photovoltaic properties

Photovoltaic devices or solar cells convert the solar energy into electric energy. The process of conversion is based on photovoltaic effect, by which electrons and holes are produced as the result of photoexcited electron transfer between donor and acceptor, followed by the transport of created charges to the electrodes. Several types of 'plastic' solar cells have been developed [63]. Here, we studied the photovoltaic properties of the studied oligomers (PECz-Ter)_n (n=1-5) as donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), which are the most broadly used as an acceptor in solar cell devices. The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. As shown in Table 3, the change of the electron-donor shows a great effect on the HOMO and LUMO levels. Figure 7 shows detailed data of absolute energy of the frontier orbitals for the studied compounds and PCBM derivatives. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/LUMO energies in agreement with their electron character.

Figure 7 lists the calculated frontier orbital energies and energy E_{gap} between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the E_{gap} energy of the studied molecules, also the open circuit voltage V_{oc} (eV) and The difference between both the energy levels LUMO of the donor and acceptor.

Table 3: Energy values of E_{LUMO} (eV), E_{HOMO} (eV), E_{gap} (eV), α and the open circuit voltage V_{oc} (eV) of the studied molecules obtained by B3LYP/6-31G (d, p) level.

On the other hand and from the above analysis, we know that the LUMO energy levels of the studied compounds are much higher than that of the ITO conduction band edge (-4.7 eV). Thus, the studied oligomers of (PECz-Ter) have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [64]; this latter reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the HOMO level of several acceptor PCBM. (C_{60} , C_{70} , C_{76} , C_{78-C2V} , C_{78-D3} , C_{84-D3} , C_{84-D2} , C_{84-D2d}) (Figure 8).

It is known that the architecture of photoactive layer is one of the principle factors of efficiencies of solar cells. The most efficient technique to generate free charge carriers is bulk heterojunction where the π -conjugated compounds donors are blended with fullerene derivatives us acceptor [65]. In our study, PCBM and derivatives (C_{60} , C_{70} , C_{76} , C_{78-C2V} , C_{78-D3} , C_{84-D3} , C_{84-D2} , C_{84-D2d}) were included for comparison purposes.

As shown in Table 3, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. It should be noted that the LUMO levels of all studied compounds are higher than that of PCBM derivatives which varies in literature from -4.0 to -3.47 eV (C_{60} (-3.47 eV); C_{70} (-3.54 eV); C_{76} (-3.79 eV); C_{78-C2V} (-3.94 eV); C_{78-D3} (-4.0 eV); C_{84-D2} (-3.98 eV) and C_{84-D2d} (-3.95 eV) [66].

The most efficient cell design, leading to the highest power conversion efficiencies, is the bulk-heterojunction (BHJ) solar cell [67]. The active layer of BHJ solar cells consists of an interpenetrating network of two types of organic materials, an electron donor and an electron acceptor, and is formed through the control of the phase separation between the donor and acceptor parts in the bulk. Accordingly, the large donor acceptor area can favour charge separation and, hence, increases the conversion efficiency of the cell [68].

On the other hand and knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor [69]. The power conversion efficiency (PCE) was calculated according to the following equation (1):

$$PCE = \frac{1}{P_{in} (FF \cdot V_{oc} \cdot J_{sc})} \quad (1)$$

Where P_{in} is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, and FF denotes the fill factor.

To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of the proposed acceptors, the HOMO and LUMO levels are compared. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor. The maximum open circuit voltage (V_{oc}) of the Bulk Hetero Junction solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor (PECz-Ter) $_n$ and the LUMO of the electron acceptor (PCBM derivatives), taking into account the energy lost during the photo-charge generation [70]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression (2):

$$V_{oc} = |E_{HOMO} (Donor)| - |E_{LUMO} (Acceptor)| - 0.3 \quad (2)$$

The theoretical values of the open circuit voltage V_{oc} of the studied compounds calculated according to the equation (2) range from (1.022 eV to 1.174 eV) for PCBM C₆₀(A); (1.252 eV to 1.404 eV) for PCBM C₆₀; (1.182 eV to 1.334 eV) for PCBM C₇₀; (0.932 eV to 1.084 eV) for PCBM C₇₆; (0.782 eV to 0.934 eV) for PCBM C_{78-C2V}; (0.722 eV to 0.874 eV) for PCBM C_{78-D3}; (0.742 eV to 0.894 eV) for PCBM C_{84-D2}; (0.772 eV to 0.924 eV) for PCBM C_{84-D2d} (Table 3).

These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as organic solar cell sensitizers because the electron injection process from the excited molecule to the conduction band of the acceptor (PCBM derivatives) and the subsequent regeneration is possible. We noted that the best values of V_{oc} are indicated for the studied oligomers of (PECz-Ter) blended with C60 or C70 (1.404 eV) and (1.334 eV) respectively.

3.4. Absorption properties

The absorption properties of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. The ZINDO/s method has been used on the basis of the optimized geometry to obtain the energy of the singlet-singlet electronic transitions and absorption properties (λ_{max}) of PECz-Ter. The corresponding simulated UV-Vis absorption spectra of the studied oligomers of PECz-Ter (n=1-5), presented as oscillator strength against wavelength are shown in Figure 9. As illustrated in Table 4, we can find the values of calculated absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of all studied oligomers.

The calculated wavelength λ_{abs} of the studied oligomers decreases in the following order ECz-Ter5 > ECz-Ter4 > ECz-Ter3 > ECz-Ter2 > ECz-Ter1, this value decreases with increasing the chain length from n=1 to n=5 monomer. This bathochromic effect from ECz-Ter1 ($\lambda_{max} = 321.95$ nm) to ECz-Ter5 ($\lambda_{max} = 343.03$ nm) is obviously due to a higher mean conjugation length, and to inter-chain electronic coupling [71]. Those interesting points are seen both in the studying the electronic and absorption properties.

In addition, we note that the broader absorption peak means that there is a distribution of energy level corresponding to the π - π^* transition. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the S1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. As in the case of the oscillator strength, the absorption wavelengths arising from S0→S1 electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in S0→S1 electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

Table 1 Geometric parameters (bond length (in Å) and inter-ring twisting angles (°)) for all studies co-oligomers (n = 1–5)

| Unit number | d1 θ1 | d2 θ2 | d3 θ3 | d4 θ4 | d5 θ5 | d6 θ6 | d7 θ7 | d8 θ8 | d9 θ9 |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| ECz-Ter1 | 1.483 142.6 | | | | | | | | |
| ECz-Ter2 | 1.483 143.02 | 1.484 143.03 | 1.483 143.04 | | | | | | |
| ECz-Ter3 | 1.483 143.33 | 1.483 143.52 | 1.483 143.15 | 1.483 143.04 | 1.483 143.31 | | | | |
| ECz-Ter4 | 1.483 143.19 | 1.483 143.14 | 1.484 142.72 | 1.484 142.72 | 1.483 142.97 | 1.483 143.30 | 1.484 143.22 | | |
| ECz-Ter5 | 1.483 143.62 | 1.483 143.49 | 1.483 143.28 | 1.483 143.36 | 1.483 143.28 | 1.483 143.60 | 1.483 143.57 | 1.483 143.25 | 1.483 143.27 |

Table 2 Optoelectronic parameters the HOMO, LUMO and {En (HOMO) - En(LUMO)} gaps energies (eV) of (ECbz-Ter)n obtained at B3LYP/6-31G(d,p)

| Unit number | -ε _{HOMO} | -ε _{LUMO} | E _g (eV) |
|-------------|--------------------|--------------------|---------------------|
| ECz-Ter1 | 5.174 | 1.069 | 4.105 |
| ECz-Ter2 | 5.070 | 1.140 | 3.930 |
| ECz-Ter3 | 5.039 | 1.174 | 3.865 |
| ECz-Ter4 | 5.029 | 1.182 | 3.847 |
| ECz-Ter5 | 5.022 | 1.186 | 3.836 |
| ∞ | 4.979 | 1.219 | 3.760 |

Table 3 Energy values of E_{LUMO} (eV), E_{HOMO} (eV), E_{gap} (eV), α and the open circuit voltage Voc (eV) of the studied molecules obtained by B3LYP/6-31G (d, p) level

| Molecules | E _{HOMO} (eV) | E _{LUMO} (eV) | E _{gap} (eV) | PCBM C ₆₀ (A) | | PCBM C ₆₀ | | PCBM C ₇₀ | | PCBM C ₇₆ | |
|--------------------------|------------------------|------------------------|-----------------------|--------------------------|--------|----------------------|--------|----------------------|--------|----------------------|--------|
| | | | | Voc (eV) | α (eV) | Voc (eV) | α (eV) | Voc (eV) | α (eV) | Voc (eV) | α (eV) |
| ECz-Ter1 | -5.174 | -1.069 | 4.105 | 1,174 | 2,631 | 1,404 | 2,401 | 1,334 | 2,471 | 1,084 | 2,721 |
| ECz-Ter2 | -5.07 | -1.14 | 3.93 | 1,070 | 2,560 | 1,300 | 2,330 | 1,230 | 2,400 | 0,980 | 2,650 |
| ECz-Ter3 | -5.039 | -1.174 | 3.865 | 1,039 | 2,526 | 1,269 | 2,296 | 1,199 | 2,366 | 0,949 | 2,616 |
| ECz-Ter4 | -5.029 | -1.182 | 3.847 | 1,029 | 2,518 | 1,259 | 2,288 | 1,189 | 2,358 | 0,939 | 2,608 |
| ECz-Ter5 | -5.022 | -1.186 | 3.836 | 1,022 | 2,514 | 1,252 | 2,284 | 1,182 | 2,354 | 0,932 | 2,604 |
| PCBM C ₆₀ (A) | -6.1 | -3.700 | | | | | | | | | |
| PCBM C ₆₀ | - | -3.470 | | | | | | | | | |
| PCBM C ₇₀ | - | -3.540 | | | | | | | | | |
| PCBM C ₇₆ | - | -3.790 | | | | | | | | | |

| Molecules | E _{HOMO} (eV) | E _{LUMO} (eV) | E _{gap} (eV) | PCBM C _{78-C2V} | | PCBM C _{78-D3} | | PCBM C _{84-D2} | | PCBM C _{84-D2d} | |
|--------------------------|------------------------|------------------------|-----------------------|--------------------------|--------|-------------------------|--------|-------------------------|--------|--------------------------|--------|
| | | | | Voc (eV) | α (eV) | Voc (eV) | α (eV) | Voc (eV) | α (eV) | Voc (eV) | α (eV) |
| ECz-Ter1 | -5.174 | -1.069 | 4.105 | 0,934 | 2,871 | 0,874 | 2,931 | 0,894 | 2,911 | 0,924 | 2,881 |
| ECz-Ter2 | -5.07 | -1.14 | 3.93 | 0,830 | 2,800 | 0,770 | 2,860 | 0,790 | 2,840 | 0,820 | 2,810 |
| ECz-Ter3 | -5.039 | -1.174 | 3.865 | 0,799 | 2,766 | 0,739 | 2,826 | 0,759 | 2,806 | 0,789 | 2,776 |
| ECz-Ter4 | -5.029 | -1.182 | 3.847 | 0,789 | 2,758 | 0,729 | 2,818 | 0,749 | 2,798 | 0,779 | 2,768 |
| ECz-Ter5 | -5.022 | -1.186 | 3.836 | 0,782 | 2,754 | 0,722 | 2,814 | 0,742 | 2,794 | 0,772 | 2,764 |
| PCBM C _{78-C2V} | - | -3.94 | | | | | | | | | |
| PCBM C _{78-D3} | - | -4.00 | | | | | | | | | |
| PCBM C _{84-D2} | - | -3.98 | | | | | | | | | |
| PCBM C _{84-D2d} | - | -3.95 | | | | | | | | | |

Table 4 Main transition states, their assignments, the corresponding wavelength and oscillator strength for the title oligomers by ZINDO/s method

| Monomers | Transition | Wavelength (λ, nm) | E _a (eV) | O.S | MO/character |
|----------|--------------------------------|--------------------|---------------------|--------|-----------------|
| ECz-Ter1 | S ₀ →S ₁ | 321.95 | 3.8510 | 1.5725 | HOMO→LUMO (65%) |
| ECz-Ter2 | S ₀ →S ₁ | 335.73 | 3.6929 | 1.2913 | HOMO→LUMO (27%) |
| ECz-Ter3 | S ₀ →S ₁ | 340.41 | 3.6422 | 3.5276 | HOMO→LUMO (32%) |
| ECz-Ter4 | S ₀ →S ₁ | 342.01 | 3.6251 | 4.8203 | HOMO→LUMO (24%) |
| ECz-Ter5 | S ₀ →S ₁ | 343.03 | 3.6144 | 6.0906 | HOMO→LUMO (19%) |

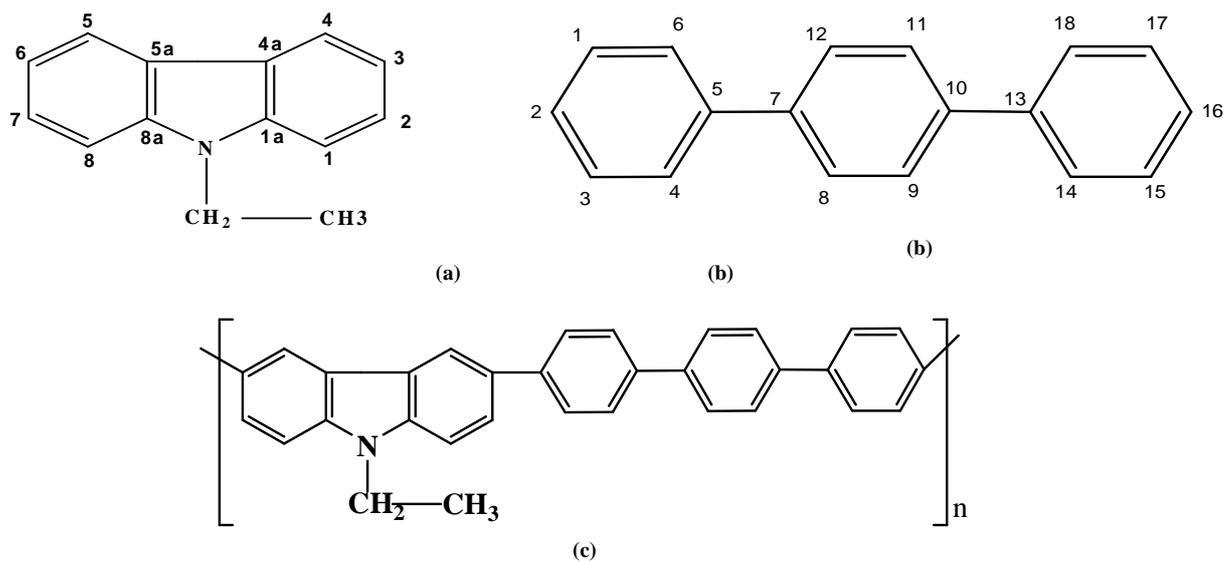


Fig. 1. Chemical structure of: (a) PECz, (b) p-Terphenyl (Ter), and (c) PECz-Ter

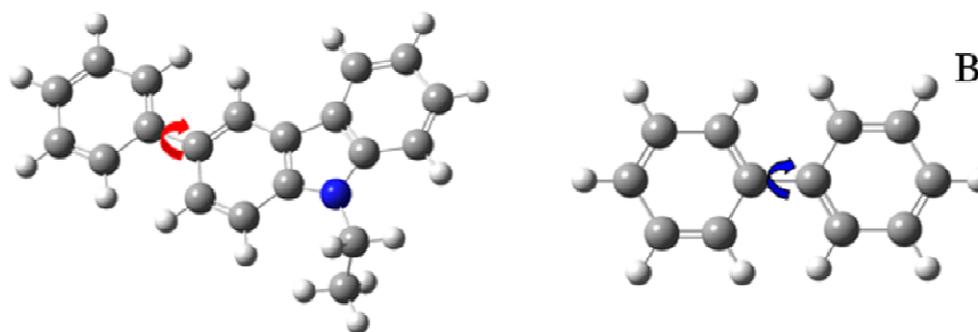
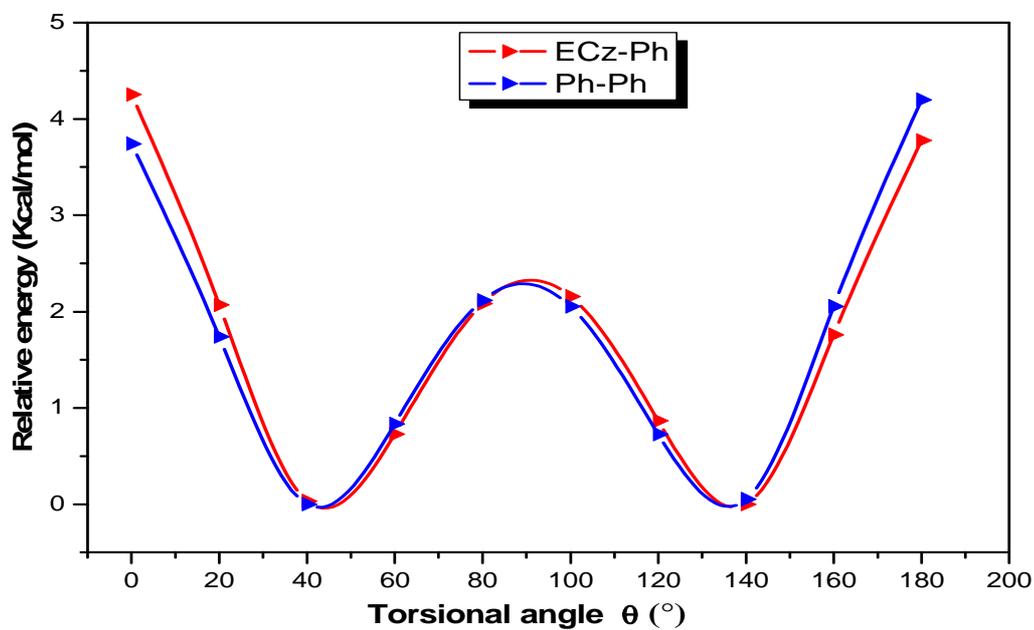


Fig. 2. (A): Torsional energy curves of ECz-Ter based molecules as obtained by B3LYP calculations using 6-31G (d,p) as basis set and (B): The most stable conformations of (Ph)₂ and ECz-Ph

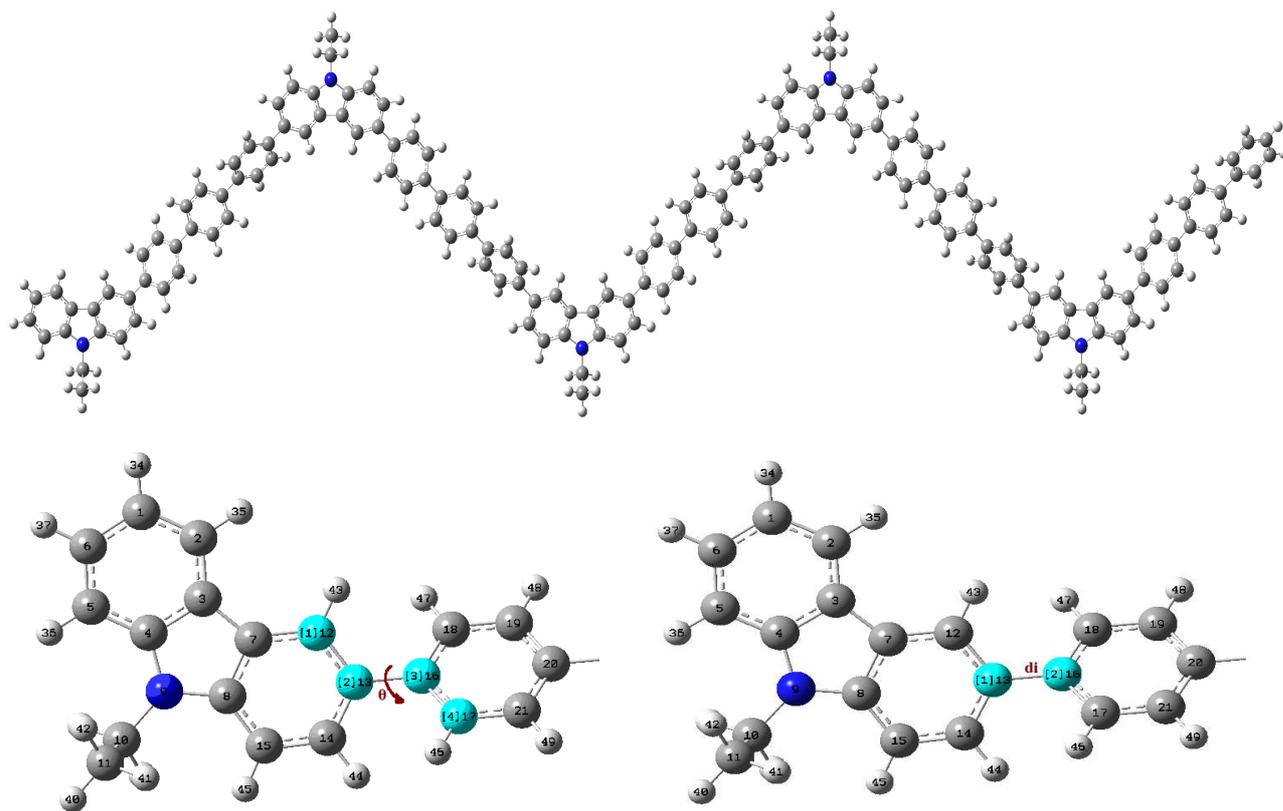


Fig. 3. Optimized structure obtained by DFT/B3LYP/6-31G (d,p) method and schematic representation of characteristic parameters of $(\text{PECz-Ter})_5$ copolymer

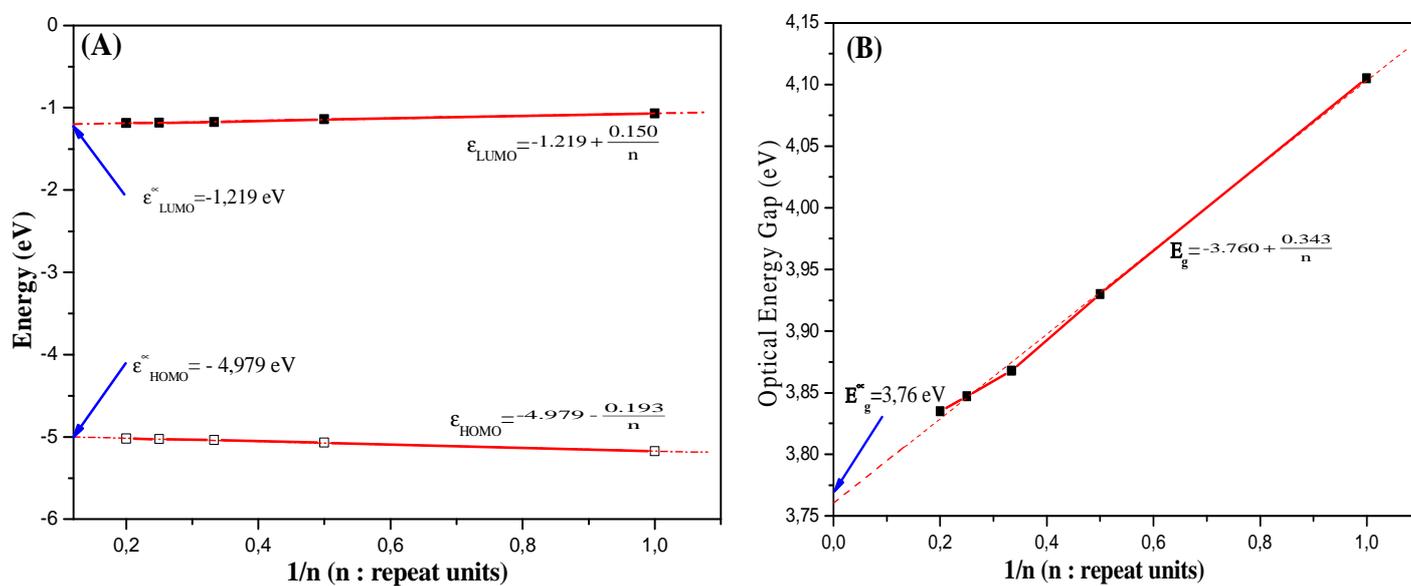


Fig. 4. Plot of HOMO, LUMO energetic levels (A) and their associated gap (E_g) (B) against the inverse number of repeat units. Linear fits and extrapolated parameters for infinite chain of PECz-Ter copolymer are also given

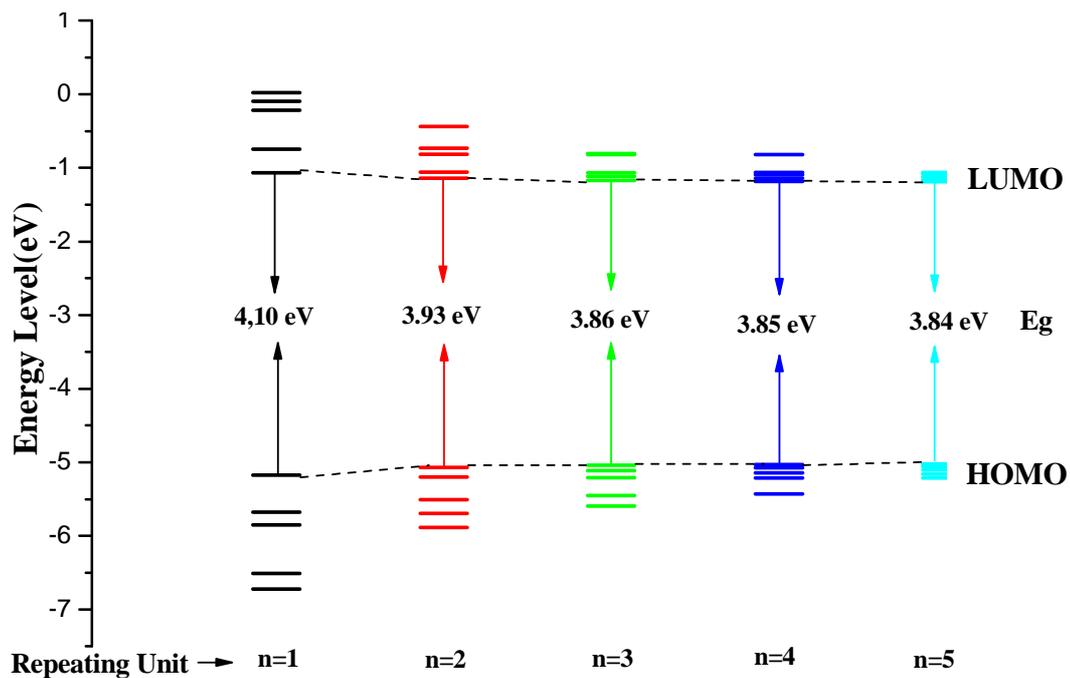


Fig. 5. The DFT//B3LYP/6-31G (d,p) electronic structures of co-oligomers (n = 1–5)

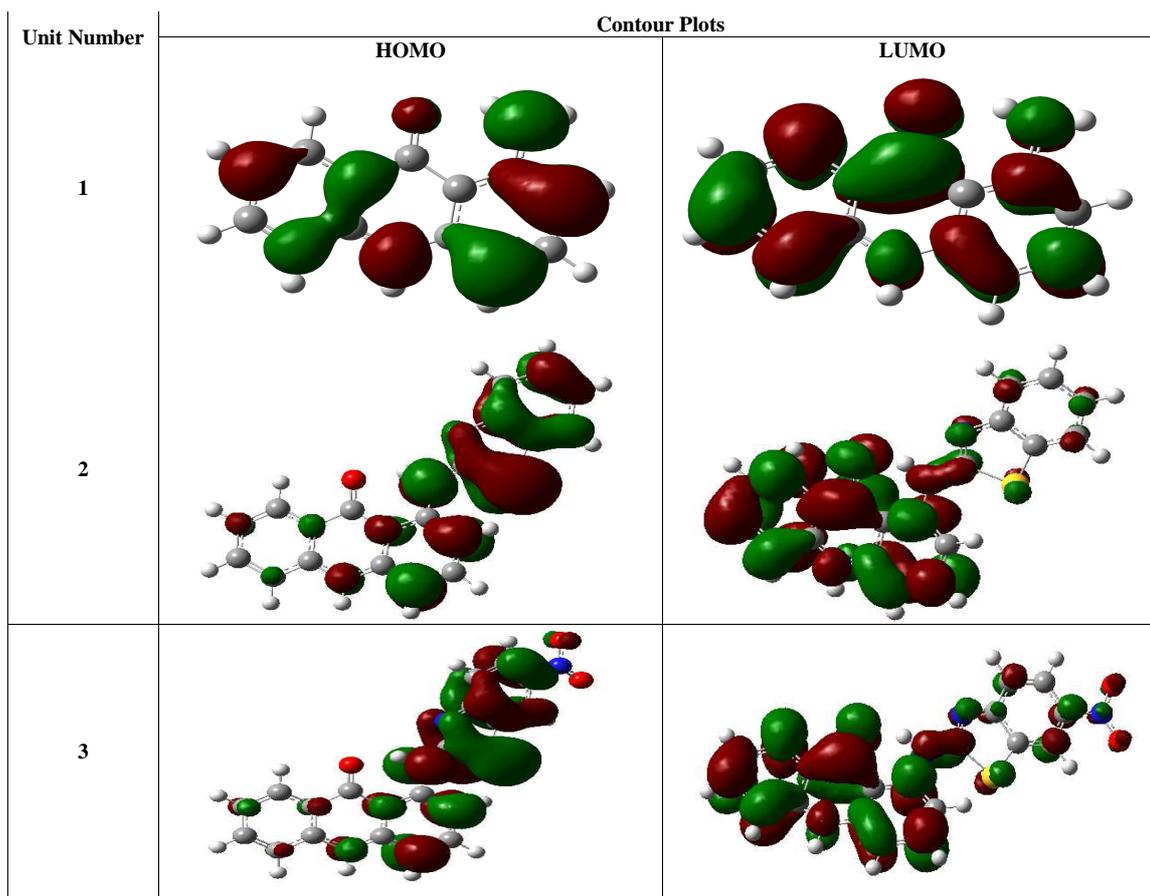


Fig. 6. Frontier molecular orbitals significantly contributing to the electronic transitions of co-oligomers(n=1-3)

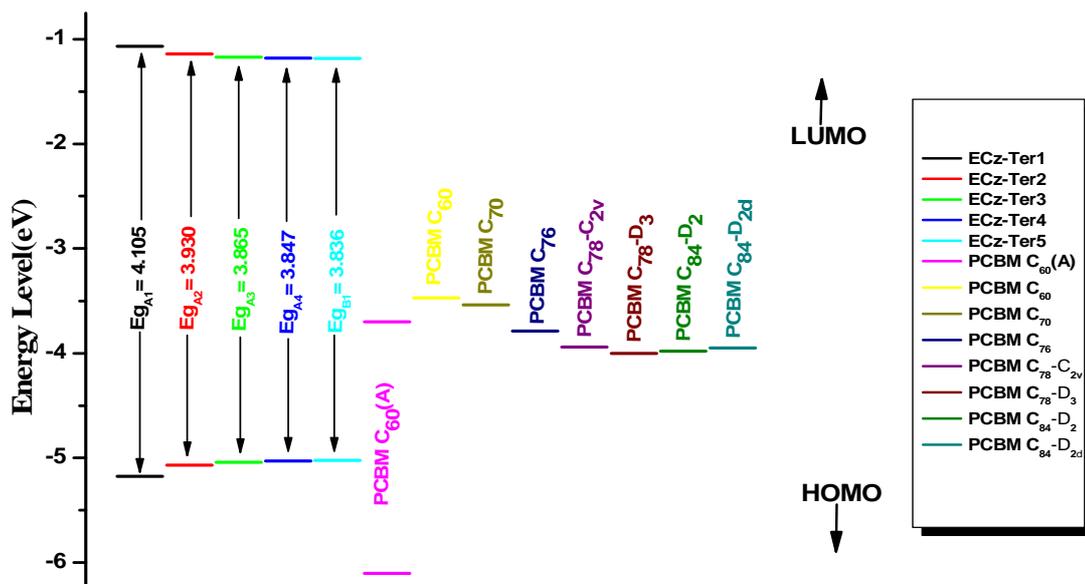


Fig. 7. Sketch of B3LYP/6-31G (d, p) calculated energies of the HOMO, LUMO level of studied molecules

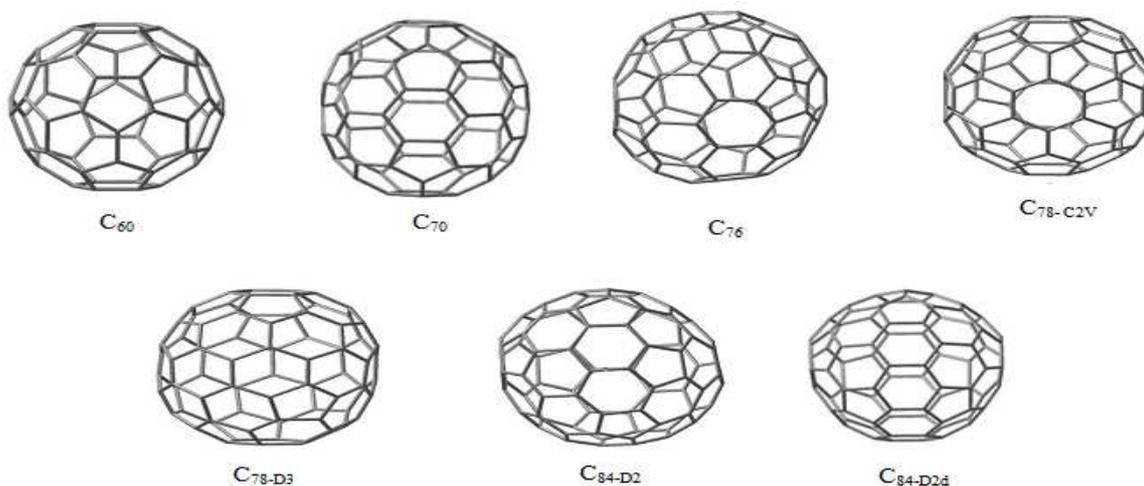


Fig. 8. Structure of the investigated fullerenes

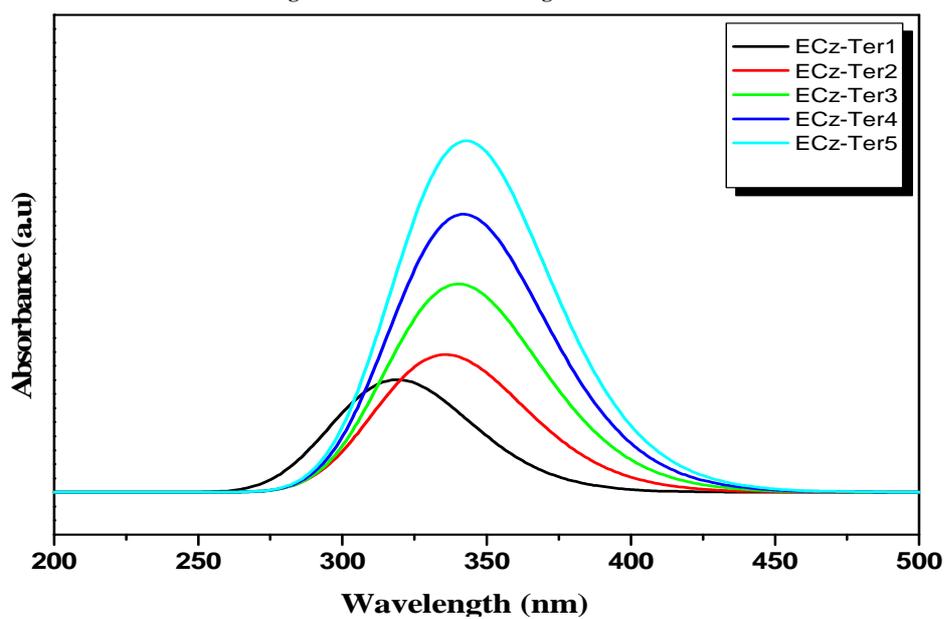


Fig. 9. Optical absorption spectra of (ECz-Ter)*n* (n=1-5) obtained with the ZINDO/s method

CONCLUSION

In this work, we used the Density Functional Theory DFT calculations at B3LYP/6-31G (d,p) level to investigate the geometrical structures, optoelectronic properties, and optical properties of new copolymer based on Ethylcarbazole moieties with attached Terphenyl groups in alternate donor–acceptor structure; The model structure of PECz-Ter copolymer was identified as 5 repeating units (PECz-Ter) n ($n=1-5$). The effect of the number of monomers on chemical structure can significantly improve the electronic and optical properties of perfect copolymers.

It is found that the interactions of the HOMO of the electron-donating moiety (ECz) and the LUMO of the electron-accepting moiety (Ter) cause a systematically change of the HOMO and LUMO energies and the reduction of the band gap as the number of monomer unit increased into the backbone, which enhance the effective charge transfer between donor and acceptor units.

Optical data of this copolymer imply that the calculated values of λ_{abs} shifted in the same direction upon addition of Ethylcarbazole-Terphenyl units and when the conjugation length is increased and thus extending of the conjugation length reduces the optical gap. The absorption maximums of these compounds are in the range 321.95 to 343.03 nm. In fact, the obtained results lead us to suggest that the longest oligomer (PECz-Ter) 5 is a good model to reflect optoelectronic properties for the parent polymer. Moreover, this oligomer were found not only as a conjugated bridge but also by reducing steric interaction between aromatic rings and thus enhancing the effective charge transfer between donor and acceptor units and the low band-gap values 3.61eV is rationalized on the basis of the patterns of their frontier orbitals.

From the calculated values of Voc of the studied oligomers, we can noted that the best values of Voc are indicated for the studied oligomers of (PECz-Ter) blended with C60 or C70 (1.404 eV) and (1.334 eV) respectively. These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of the acceptor and the subsequent regeneration is possible in organic sensitized solar cell.

Finally, we are also convinced that the systematic use of this theoretical approach can be employed to predict the opto-electronic properties on the other oligomers, and further to design novel materials for organic solar cells, and help to understand the structure–properties relationship of these new systems.

Acknowledgements

This work was supported by Volubilis Program (N° MA/11/248), and the convention CNRST/CNRS (Project chimie1009). We are grateful to the “Association Marocaine des Chimistes Théoriciens” (AMCT) for its pertinent help concerning the programs.

REFERENCES

- [1] B. O'Regan, M. Gratzel, *Nature*. 353 (1991) 737–740.
- [2] G.J. Meyer, *J. ACS Nano*. 4 (2010) 4337–4343.
- [3] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Bredas, M. Logdlund, W.R. Salaneck, *J.Nature*. 397 (1999) 121-128.
- [4] R.E.Gill, G.G. Malliaras, J. Wildeman, G. Hadziioannou, *J. Adv. Mater.* 6 (1994) 132.
- [5] C.D. Dimitrakopoulos, P.R.L. Malenfant, *J.Adv. Mater.* 14 (2002) 99-117.
- [6] H.E. Katz, Z. Bao, *J. Phys. Chem. B*.104 (2000) 671-678.
- [7] F. Garnier, G. Horowitz, X. Peng, D. Fichou, *J. Adv. Mater.* 2 (1990) 243.
- [8] J. Hou, C. Yang, J. Qiao, Y. Li, *J. Synth. Met.* 150 (2005) 297–304.
- [9] C. Yang, H. Li, Q. Sun, J. Qiao, Y. Li, Y. Li, D. Zhu, *J. Sol. Energy Mater. Sol. Cells*. 85 (2005) 241–249.
- [10] K. Colladet, M. Nicolas, L. Goris, L. Lutsen, D. Vanderzande, *J.Thin Solid Films*. 451 (2004) 7-11.
- [11] Y.S. Kim, S.C. Ha, Y. Yang, Y.J. Kim, S.M. Cho, H. Yang, Y.T. Kim, *J. Sens. Actuators B*. 108 (2005) 285–291.
- [12] D. Ghosh, G.S. Samal, A.K. Biswas, Y.N. Mohapatra, *J. Thin Solid Films*. 477 (2005) 162-168.
- [13] S. Schrader, A. Penzkofer, W. Holzer, R. Velagapudi, B. Grimm, *J. Lumin.* 110 (2004) 303-308.
- [14] Y. J. Chen, S. H. Yang, C.S .Hsu, Synthesis of conjugated polymers for organic solar cell applications, *J. Chem. Rev.* 109 (2009) 5868-5923 ; G. Wang, S. Qian, J. Xu, W. Wang, X. Liu, X. Lu, F. Li, *J. Physica. Part B*. 279 (2000) 116-119; H. Spanggaard, F.C. Krebs, *J. Sol. Energy Mater. Sol. Cells*. 83 (2004) 125-146.
- [15] H. Hoegl, O. Sus, W. Neugebauer, *J. Ger.Patent*. 1068 (1957) 115.
- [16] H. Hoegl, *J. Phys.Chem.* 69 (1965) 755-766.
- [17] M.D. Schattuck, U. Vahtra, US Patent, 3484327 (1969).

- [18] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *J. Nature*. 347 (1990) 539 – 541.
- [19] K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen and N. Peyghambarian, *J. Nature*. 371 (1994) 497-500.
- [20] Y. Wang, J. Kroschwitz, M. Howe-Grant, editors, 4th ed. Kirk-Othmer Encyclopedia of Chemical Technology, New York: Wiley. 18 (1996) 837.
- [21] G. Wang, S. Qian, J. Xu, W. Wang, X. Liu, X. Lu, F. Li, *Physica B: Condensed Matter*. 279 (2000) 116-119.
- [22] V.C. Nguyen, K. Potje-Kamloth, *J. Thin Solid Films*. 338 (1999) 142; X-G. Li, M-R. Huang, W. Duan, Y-L. Yang, *J. Chem. Rev.* 102 (2002) 2925-3030.
- [23] H. Sadki, M. N. Bennani, K. Alimi, M. Bouachrine, *International Journal of Innovative Research in Science, Engineering and Technology*. 3 (2014) 11600-11611.
- [24] C. Soci, I. Hwang, D. Moses, Z. Zhu, D. Waller, R. Gaudiana, *J. Adv. Funct. Mater.* 17 (2007) 632-636.
- [25] S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, Theoretical investigation of electroluminescent alkoxy substituted 4,4'-bis(2 phenylethenyl)biphenyls as guest in blue OLEDs, *J. Solar Energy Materials & Solar Cells*. 90 (2005) 1393-1402; S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, Density functional theory study of conformational and opto-electronic properties of oligo-para-phenylenes, *J. Molecular Structure: Theochem*. 725 (2005) 39-44; H. Zgou, S.M. Bouzzine, S. Bouzakraoui, M. Hamidi, M. Bouachrine, Etude théorique de propriétés structurales et électroniques d'oligo (thiophène-phénylène) s en comparaison avec oligothiophènes et oligophénylènes, *J. Lettres chinoises chimiques*. 19 (2008) 123-126; S.M. Bouzzine, A. Makayssi, M. Hamidi, M. Bouachrine, *J. Molecular Structure: Theochem*. 851 (2008) 254-262.
- [26] H.J. Snaith, N.C. Greenham, R.H. Friend, *J. Adv. Mater.* 16 (2004) 1640-1645 ; Y. Kim, S. Cook, S.A. Choulis, J. Nelson, J.R. Durrant, D.D.C. Bradley, *J. Chem. Mater.* 16 (2004) 4812- 4818; H. Spanggaard, F.C. Krebs, *J. Sol. Energy Mater. Sol. Cells*. 83 (2004) 125-146.
- [27] X.Y. Pan, S.P. Liu, H.S.O. Chan, S.C. Ng, *J. Macromolecules*. 38 (2005) 7629-7635.
- [28] R. Kroon, M. Lenes, J.C. Hummelen, P.W.M. Blom, B. De Boer, *J. Polym. Rev.* 48 (2008) 531-582.
- [29] C. Kitamura, S. Tanaka, Y. Yamashita, *J. Chem. Lett.* 1 (1996) 63–64.
- [30] K-H. Lee, H-J Lee, K. Morino, A. Sudo, T. Endo, *J. Polym. Sci. Part. A: Polym. Chem.* 49 (2011) 1427-1433.
- [31] B. O'Regan, M. Gratzel, A Low-Cost, *J. Nature*. 353 (1991) 737-740.
- [32] E. Bundgard, F.C. Krebs, *J. Sol. Energy Mater. & Sol. Cells*. 91 (2007) 1019-1025.
- [33] W.L. Yu, H. Meng, J. Pei, W. Huang, *J. Am. Chem. Soc.* 120 (1998) 11808-11809.
- [34] W. Huang, H. Meng, W. Yu, J. Pei, Z. Chen, Y. Lai, *J. Macromolecules*. 32 (1999) 118-126.
- [35] S.C. Ng, M. Ding, H.S.O. Chan, W.L. Yu, *Macromol. J. Chem. Phys.* 202 (2001) 8-13.
- [36] N.J. Watkins, A.J. Mäkinen, Y. Gao, M. Uchida, Z.H. Kafafi, Organic Light- Emitting Materials and Devices VII, in: Zaky H. Kafafi, Paul A. Lane (Eds.), Proceedings of SPIE Bellingham, WA, 5214 (2004).
- [37] L. Yan, Y. Gao, *J. Sol. Films*. 417 (2002) 101-106.
- [38] L-M. Chen, Z. Xu, Z. Hong, Y. Yang, *J. Mater. Chem.* 20 (2010) 2575-2598.
- [39] J.L. Brédas, J. Cornil, A.J. Heeger, *J. Advanced Materials*. 8 (1996) 447-452.
- [40] J. Pei, W.-L. Yu, W. Huang, A.J. Heeger, *J. Macromolecules*. 33 (2000) 2462-2471.
- [41] R.A. Silva, L.A. Cury, A. Marletta, P.S.S. Guimaraes, M. Bouachrine, J.P. Lère- Porte, J.E. Moreau, *F. J. Non-Cryst. Sol.* 352 (2006) 3685-3688.
- [42] J.P. Lère-Porte, J.J.E. Moreau, F. Serein-Spirau, C. Torrelles, A. Righi, J.L. Sauvajol, M. Brunet, *J. Mat. Chem.* 10 (2000) 927-932.
- [43] M. Bouachrine, J. P. Lere-Porte, J. J.E. Moreau, F.S. Spirau, R.A. da Silva, K. Lmimouni, L. Ouchani, C. Dufour, *J. Synthetic Metals*. 126 (2002) 241-244.
- [44] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- [45] A.D. Becke, *Phys. Rev. A*. 38 (1988) 3098-3100.
- [46] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B*. 37 (1988) 785-789.
- [47] M.E. Casida, C. Jamorski, K. C. Casida, D.R. Salahu, *J. Chem. Phys.* 108 (1998) 4439–4449.
- [48] R.E. Stratmann, G.E. Scuseria, M.J. Frisch, *J. Chem. Phys.* 109 (1998) 8218–8224.
- [49] S.I. Gorelsky, SWizard program, <http://www.sg-chem.net/>, University of Ottawa, Ottawa, Canada, 2009.
- [50] S.I. Gorelsky, A.B.P. Lever, *J. Organometallic Chemistry*. 635 (2001) 187-196.
- [51] Z. Gong, J.B. Lagowski, *J. Mol. Struct. Theochem*. 866 (2008) 27-33.
- [52] K. Hasnaoui, H. Zgou, M. Hamidi, M. Bouachrine, *J. Chin. Chem. Lett.* 19 (2008) 488-492.
- [53] E. Faulques, W. Wallnöfer, H. Kuzmany, *J. Chemical Physics*. 90 (1989) 75-85.
- [54] L. Yang, J-K. Feng, A-M. Ren, *polymer*, 46 (2005) 10970-10981.
- [55] H. Cao, J. Ma, G. Zhang, Y. Jiang, *J. Macromolecules*. 38 (2005) 1123-1130.
- [56] J.L. Brédas, R. Silbey, D.S. Boudreaux, R.R. Chance, *J. Am. Chem. SOC.* 105 (1983) 6555-6559.
- [57] F.C. Grozema, L.P. Candeias, M. Swart, P. Van Duijnen, J. Wildemen, G. J. Hadzianon, *J. Chem. Phys.* 117 (2002) 11366-11378.
- [58] J. Huang, Y. Niu, W. Yang, Y. Mo, M. Yang, Y. Cao, *J. Macromolecules*. 35 (2002) 6080-6082.

-
- [59] L. Yang, J. Feng, A. Ren, *J. Polymer*. 46 (2005) 10970-10981
- [60] W.R. Salaneck, R.H. Ami, J.L. Brédas. *J. Phys. Rep.* 319 (1999) 231–251.
- [61] M.A. De Oliveira, H. A. Duarte, J.M.Pernaut, W.B. De Almeida, *J. Phys. Chem. A*. 104 (2000) 8256-8262.
- [62] J. Casanovas, D. Zanuy, C. Alemán, *J. Polymer* 46 (2005) 9452-9460.
- [63] C.J. Brabec, S.N. Saricifitci, *J. Monatshefte Fur Chemie*. 132 (2001) 421-431.
- [64] L. Zhang, Q. Zhang, H. Ren, H. Yan, J. Zhang, H. Zhang, J. Gu, *J. Solar Energy Materials & Solar Cells*. 92 (2007) 581–587.
- [65] H. Derouiche, V. Djara, *J. Solar Energy Materials & Solar Cells*. 91 (2007) 1163–1167.
- [66] P. Morvillo, *J. Solar Energy Materials & Solar Cells*. 93 (2009) 1827–1832.
- [67] G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *J. Science*. 270 (1995) 1789-1791; J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti and A. B. Holmes, *J. Appl. Phys. Lett.* 68 (1996) 3120-3122.
- [68] K. Amro, A.K. Thakur, J.Rault-Berthelot, C. Poriel, L.Hirsch, W.E. Douglas, S.Clément and P. Gerbier, *New J. Chem.* 37 (2012) 464-473.
- [69] Y. He, H.Y Chen, J. Hou, Y. Li, *J. Am. Chem. Soc.* 132 (2010) 1377-1382; F.B. Kooistra, J. Knol, F. Kastenberg, L. M. Popescu, W.J.H. Verhees, J.M. Kroon, J. C. Hummelen, *J. Org. Lett.* 9, (2007) 551-554.
- [70] A. Gadisa, M. Svensson, M. R. Anderson, O. Inganas, *J. Appl. Phys. Lett.* 84 (2004) 1609–1611; M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, *J. Adv. Mater.* 18 (2006) 789-794;
- [71] C. Jia, J. Zhang, J. Bai, L. Zhang, Z. Wan, X. Yao, *J. Dyes and Pigments*. 94 (2012) 403-409.