

DFT/TDDFT approach: an incredible success story in prediction of organic materials properties for photovoltaic application

D. Khlaifia^{(a,b)*}, M. Chemek^(b), K. Alimi^(b)

^(a)Physics department, Faculty of Arts and Sciences, Jouf University, Qurayyat 77451, KSA.

^(b)Laboratoire de Recherche 18ES19 "Synthèse Asymétrique et Ingénierie Moléculaire des Matériaux Organiques pour l'Electronique Organique" (SI2MEO), Faculté des Sciences, Université de Monastir, 1002 Monastir, Tunisia.

* Corresponding author:

dalilakhlaifia@yahoo.fr

Received 20 Nov 2019,

Revised 23 Jun 2020

Accepted 26 Jun 2020

Abstract

In the quest to improve the performance of organic solar cells (OSCs), the distinction of the critical factors limiting their power conversion efficiency (PCE) with a view to rationalizing the relationship between the structures of the active layers, their morphology, and the electronic processes taking place at their interface is required. In this review, we give an overview of the role of computational approaches based on density functional theory (DFT) in describing and predicting the structure of OSC active materials at molecular level and characterizing their various properties. We first discuss the key success of DFT calculations in establishing and understanding the relationship between the structure and the optoelectronics properties of some organic compounds. A second section deals with the power of DFT calculations in the molecular design of potential donor materials for photovoltaic applications which is beneficial for chemists to have an estimate of the photophysical properties of the target before carrying out a multistep synthesis.

Keywords: Photovoltaic application; Conjugated organic materials; DFT calculations; Structure-property relationship; Design

1.Introduction

The need to produce more cost efficient electronic devices with simple processing techniques has fostered the development of new materials to become an attractive and useful alternative to inorganic semiconductors. Recently, organic materials, including conjugated polymers, organic small molecules (SMs) and self-assembling organic semiconductors, have intrigued an increasing attention because of their potential to enable the fabrication of flexible, light weight, semi transparency and large-area devices [1-3]. These advantages prove attractive for organic and printable electronics industries which have been on an exponential growth curve for many years and variety of applications has expanded such as organic photovoltaic cells (OPVs), organic light-emitting diodes (OLEDs), flexible displays, integrated Smart systems and various sensors [4-6]. Particularly, OPVs composed of organic materials have recently brought considerable attention to their potential to become an economically viable source of affordable, clean, and renewable energy [7-9]. Generally, in a functioning bulk-heterojunction solar cells (BHJSCs) consisting of donor and acceptor materials, the conversion process involves four fundamental steps [10,11]; (1) creation of the excitons upon absorption of photon from sunlight, (2) dissociation of the exciton at the D/A materials interface into free charges forming charge transfer (CT) states, (3) transport of the charges under an electric field, and (4) collection of charges by electrodes. The availability of precisely defined structure of organic materials will be useful to give a comprehensive understanding of these processes and then to rationalize and optimize the PCE of BHJSCs. Quantum chemical modelling by DFT and time-dependant DFT (TDDFT) has become a powerful tool to allow qualitative and quantitative studies of materials at the molecular level. Herein, we will try presenting an overview of the successes and opportunities in using DFT and TDDFT in the OSC research [12-14]. Firstly, DFT has been employed successfully to explain and predict detailed morphological information for known conjugated organic molecules, such as molecular geometries, electronic structure, frontier molecular orbital (FMO) energy levels, absorption spectra, and intramolecular charge transfer (ICT). These properties strongly affect the open-circuit voltage (V_{OC}), the short circuit current (J_{SC}), the charge separation at the donor/acceptor interface, and the absorption of the solar photons [15,16]. This was previously confirmed by our research group for several conjugated monomeric and oligomeric model structures such as poly(3-hexylthiophene) (P3HT) oligomers [17], Oligofuran (OFu)-bridged oligomers [18], a donor-acceptor (D-A) copolymer denoted carbazole-benzothiadiazole (Cz-5Bzt)₂ [19], a D-A small band-gap copolymer denoted (fluorine-2-1-3-benzothiadiazole) (PFBT) [20], some [2,1,3]-benzothiadiazole based alternating copolymers [21], and a series of 4-(methoxyphenyl) acetonitrile]_n (n-MPA) oligomers [22]. The examination of geometric structures, electronic, optical and vibrational properties of these compounds are carried out by DFT and TDDFT calculations promoting a reasonable interpretation of the experimental results and subsequently better understanding of the relationship between the structure and resulting properties. The ground states structure of each compound was optimized and the geometric parameters (dihedral angles), HOMO and LUMO energy levels, energy gaps, ionization potentials (IPs), electron affinities (EAs) and vibrational spectra have been investigated on the base of the optimized molecular structures. Moreover, the absorption spectra, lowest excitation energy gaps and oscillator strength have been studied on the excited states via TDDFT method. On the other hand, the exploration of novel donor materials is identified as one of the powerful strategies to enhance the PCEs of OPVs devices. In this context, molecular modelling techniques, especially DFT, form a valuable support in materials design by providing experimentally inaccessible data, which can help experimentalists to develop novel-high performance materials by relying on easily reachable high-end simulations and reduce the development cost of new materials and limit the material production cycle. Several molecules have been designed and modelled with a target of improved photoconversion by using an interpenetrating network [23-25]. These molecules have been exploited as donor materials for a heterojunction with

[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), a fullerene derivative, as the electron acceptor. The purpose was double: to increase the spectral range of absorption and to optimize the energy levels with those of PCBM [26,27]. Generally, the design of high-efficiency donor materials with excellent electronic and optical properties using computational methods consists of many steps. The first step is to evaluate the geometric structure, electronic properties, and other factors related to OPVs such as absorption spectra and intramolecular transferred charges of the designed materials. Next, an in-depth theoretical investigation of the dynamics of charge transfer and charge recombination occurring at the D/A interface can be carried out in order to select more efficient donor materials versus specific acceptors. Finally, based on various empirical approaches, the performance of the OPV device based on the designed donor material and potential acceptor can be predicated.

2. Theoretical Methods

Throughout this review, DFT will be the modelling method of choice to investigate the electronic structure and photovoltaic properties of many-body system such as organic molecules, conjugated polymers and D/A complexes. The excited state of these systems such excitation energies, oscillator strengths and the absorption characteristics has been predicted using the TDDFT methods. The application of this method as a powerful tool to calculate the excitation energies started after the groundbreaking work of Casida [28] and Petersilka et al. [29]. All the DFT and TDDFT calculations presented here were carried out using Gaussian program package [30]. Solvation effects were implicitly taken into consideration using the polarizable continuum model (PCM) [31,32]. It is well known that, in DFT, the total energy of a many-body system is the sum of the classical energy of the charge distribution (ion-electron potential energy, ion-ion potential energy, electron-electron energy and kinetic energy) and the exchange-correlation energies. Consequently, a good choice of the exchange-correlation functional is essential for correct description of the structural and electronic properties of a many-body system. In this context, various methods have, for some time, been the standard choice for the study of the electronic structure and optical properties of isolated molecules and D/A complexes such as presented here. In general, the so-called hybrid exchange-correlation functionals, which include a mixture of Hartree-Fock exchange with DFT exchange-correlation (e.g. B3LYP [33], B3PW91 [34], PBE0 [35]), have been shown to give qualitative accuracy in modelling the electronic structure. However, these functionals still not suitable for modelling the system's physical properties since they do not include any corrected long-range effects, which play a critical role in investigating the charge transfer excited states [36,37]. This emphasizes the importance of long range corrected functionals to describe correctly the excited states such as CAM-B3LYP [38]. The description of the charge transfer excited state can be described using functionals including empirical dispersion forces such as WB97X(D) [39]. With these functionals, several polarized basis sets such as 3-21G(d), 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p), etc. have been developed. Amongst these basis set, the 6-31G(d) basis set has been proved to be useful in the study of the ground and excited states of organic semiconductors.

3. DFT for a reliable structure-property relationship of organic materials

3.1. Conformational analysis

Conformational analysis is extremely important for experimentalists and theoreticians to develop a clear picture of how molecules behave in different phases of matter. Recently, we have carried out a conformational analysis in gas phase by varying the dihedral angle in steps of 10° from $\theta=0^\circ$ to $\theta=180^\circ$ to determine the ground-state geometry of a series of P3HT oligomers [17]. A preliminary benchmark step has been performed to verify the reliability of the DFT computational methods in anticipating ground state geometries (torsional potential energy). Figure 1 (a) shows the torsional potential energy curves of P3HT oligomers containing 2, 6 and 10 monomer units as a function of θ , using

three different functionals: B3LYP (black symbols), CAM-B3LYP (blue symbols), and WB97X(D) (red symbols) with 6-31G(d) as a basis set. Generally, the B3LYP has been the choice for the examination of the ground and excited states of P3HT oligomers model structures [40,41]. Here, the same calculation was done with two other functionals, which overcome some of the limitations of B3LYP, notably through incorporating of long-range corrections (CAM-B3LYP) and empirical dispersion forces (WB97X(D)). It can be seen in figure 1(a) that calculations with the different functionals identify approximately the same torsional angle for the ground state structure at $\sim 40^\circ$, which indicates that the most stable structure of each P3HT oligomer corresponds to a twisted conformation with $\theta=40^\circ$. This result was found to be in good agreement with the observations by Cui and Kertesz [42]. Another important result is that long-range corrections and dispersion effects are minor. As observed in Figure 1 (b), despite its low gap energy compared to other configurations, the alkyl chains in the molecule $(3HT)_8$ at $\theta = 180^\circ$ are on the same side which is not beneficial to the formation of well ordered chains in thin film, as observed experimentally when $\theta = 0^\circ$.

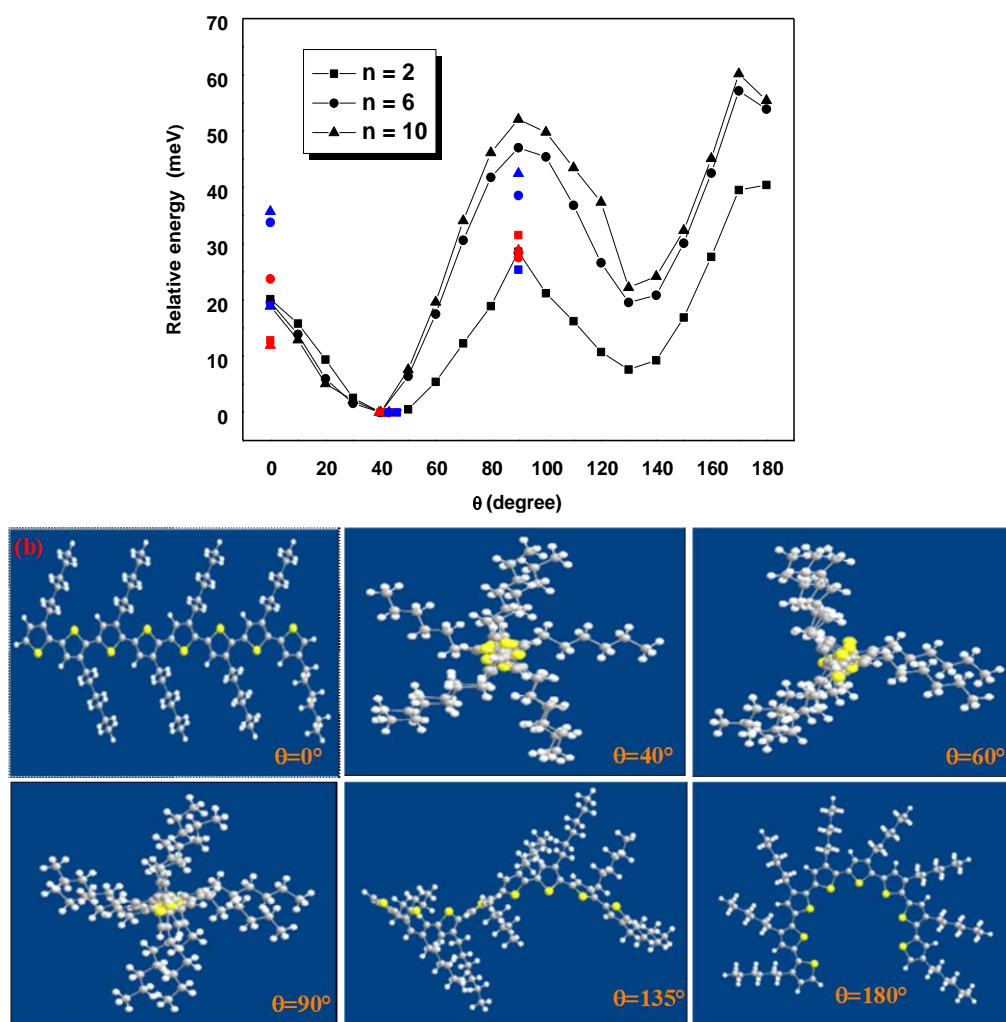


Figure 1: (a) Torsional potential energy curves of P3HT oligomers containing 2, 6 and 10 monomer units as a function of θ , using three different functionals: B3LYP (black symbols), CAM-B3LYP (blue symbols), and WB97X(D) (red symbols) (Figure taken from reference [17]). (b) Optimized structures of a P3HT oligomer ($n=8$) at different conformations ($\theta=0^\circ$, 40° , 60° , 90° , 135° and 180°).

Using a similar approach, a conformational analysis was carried out by Taouali et al. [22] at DFT/B3LYP/6-311G(d,p) level of theory on a dimer 2-MPA to see the favorite linkage between C_1-C_1 and C_1-C_2 during the

chemical synthesis. The results of the dihedral angle show that both configurations scans have a minimum energy at θ in the range of 60-70°. However, the configuration C₁-C₂ is more stable than C₁-C₁ with an energy difference of about 1.49 kcal mol⁻¹, which is in good agreement with the experimental results showing the predomination of the configuration C₁-C₂ during the synthesis process of oligophenylene [43].

3.2. HOMO and LUMO levels and energy gaps

In the discussion that follows, we define the electronic gap given by E_g = HOMO-LUMO, the energy difference between the HOMO (Highest occupied molecular orbital) and LUMO (Lowest occupied molecular orbital), as the minimum energy required for the electronic excitation process, which is a key factor to reflect the electrical characteristics of conjugated polymers [44,45]. The HOMO-LUMO energy gaps of P3HT oligomers at different conformations (θ = 0°, 40°, 60°, 90°, 135° and 180°) (figure 1(b)) were calculated at the B3LYP/6-31G(d) level of theory in the gas phase [17]. Additionally, the E_g energy gaps of the infinite P3HT chains were extrapolated using a Kuhn fit [46-48] and compared to that of regioregular P3HT (RR-P3HT) in thin film measured experimentally at about 2.1 eV [49]. The E_g for the cis-planar P3HT infinite chain (θ =0°) calculated at about 2.02 eV is in excellent agreement with the experimental value, however a large discrepancy was observed in the case of the fully relaxed ($\theta \approx 37$ -42°) infinite chain ($E_g \approx 3$ eV). Interestingly, this result indicates that the P3HT backbone aligns towards 0° when it is coated in thin film, which is in a good agreement with most experimental studies showing that the P3HT chain is planar [50-52].

Additionally, Mabrouk et al. [20] have calculated the HOMO, LUMO and E_g energy gaps of PFBT oligomers. The authors have predicted the band gaps of PFBT infinite chain using the linear extrapolation tool. They found that the energy gaps calculated with 3-21G(d) and 6-31G(d) are in good agreement with the experiment measured values. On the other hand, whatever the used basis set, PFBT show a reduction in band gap compared to that of polyfluorene (PF). This has been addressed to the donor-acceptor alternating structure which allows efficient electron delocalization along the molecular structure.

3.3. UV-Visible absorption and lowest excited energy

Optical properties such as absorption spectra and optical band gap can provide an additional means of structure validation. The best example is the study of the relationship between the chain conformation and the optical properties of 3-hexylthiophene (3HT) oligomers and the corresponding polymer P3HT [17]. In this study, the optical absorption spectra at TDDFT/B3LYP/6-31G(d) of the longest oligomer (n=10) for θ = 0°, 10°, 20°, and 40° in chloroform have been simulated and compared with the experimental spectra of P3HT in the solution and in thin film. The calculated absorption maximum at 442 nm for n=10 oligomer at θ = 40° is very close to the experimental value of P3HT in chloroform (λ_{max} = 451 nm). Furthermore, the E_g^{opt} for an infinite twisted (θ = 40°) P3HT chain is estimated using a Kuhn fit to be 2.67 eV, which is in a good agreement with 2.74 eV measured for P3HT in solution (CHCl₃) [53, 54]. This indicates that the twisted conformation is the main configuration of P3HT in solution. Similarly, TDDFT calculations on a quatramer (n=4) of PFBT have shown that the B3LYP/3-21G(d) method gives a maximum absorption wavelength of 472 nm, in good accordance with the experimental value at 450 nm [20]. The shape of absorption spectrum of PFBT oligomer (n=4) appears to be similar to the traditional model for other D-A molecules exhibiting two absorption bands, which is different from the single broad absorption peak observed in traditional π -conjugated polymers. The lowest-energy band in the absorption spectrum is probably assigned to an intramolecular charge transfer (ICT) between the donor and acceptor moieties. This behavior agrees with the model suggested for

other D-A molecules, where it has been proved that the ICT is a dominant character resulting from a push of electrons from donor core to the electron-rich unit.

4.DFT calculations: A powerful tool for materials design

4.1. Some preliminary notes

It is well known that PCE ($PCE = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}}$) of an OSC is fundamentally governed by three important factors [55-57]: the open circuit voltage V_{OC} , the short circuit current density J_{SC} and the fill factor FF. To optimize the PCE, it is important to find an efficient combination of donor/acceptor (D/A) materials in terms of electronic, optical and morphological properties, which can be realized via rational design of new materials. From this regard, the following points required to be carefully addressed.

- First, to maximize the number of generated excitons and then to increase the J_{SC} , the D/A heterojunction should possess a large and strong absorption in the region from 380 (3.26 eV) to 900 nm (1.38 eV) of solar spectrum. Since acceptor material has a deficient absorption in this region, an ideal donor material has to act as the main light absorber with a relatively low optical band gap.
- Second, as proposed by Scharber and co-workers [58], the V_{OC} of an OSC device is directly proportional to the difference of energy levels between the HOMO of the donor and LUMO of the acceptor and it could be expressed by the following empirical equation:

$$V_{OC} = \frac{1}{e} (|E_{HOMO}(D)| - |E_{LUMO}(A)|) - 0.3V \quad (1)$$

where e is the elementary charge, $E_{HOMO}(D)$ is the HOMO energy level of the donor, $E_{LUMO}(A)$ is the LUMO energy level of the acceptor, and the value of 0.3 V is an empirical factor, corresponding to the exciton binding energy (bound electron-hole pair) following the charge transfer [58]. In a typical BHJSC, the donor material should possess a low lying HOMO energy level, while the acceptor should possess high LUMO to offer high V_{OC} . Moreover, the LUMO offset between the donor and the acceptor materials should be controlled. Indeed, Scharber and co-workers [58] and Marks and co-workers [59] have considered that a driving force $\Delta E_{L-L} = 0.3 - 0.5$ eV is sufficient for efficient charge separation.

- Third, an ideal D/A pair should possess high charge carrier mobilities in order to avoid as much as possible charge recombination, which causes a decrease in the FF and then in the efficiency of the BHJ device.
- Fourth, the donor and acceptor materials should have good long-term stability for longevity of service of BHJ device.

4.2. A brief history of the development of donor and acceptor materials for polymer solar cells

Great progress has been reached in both donor and acceptor materials development, witnessed by the significant increase in devices power conversion efficiency (PCE) from less than 2% before 2008 to over than 10% in recent years [60-64]. However, the number of high performance acceptor materials is limited compared to donor materials. Fullerene and their derivatives have been extensively used as acceptor materials within BHJ devices because of their important electronic properties such as small reorganization energy, high electron mobility and affinity [65-67]. In addition, PDI molecules have been shown to possess many desirable design features for OPV electron acceptors such as strong red absorption, well matched LUMO energy level with those of many conjugated donors and high electron mobilities similar to that of fullerene derivatives [68,69]. Thus, material design work is concentrated on the design of

novel donor materials versus the reported acceptor materials. These materials can be classified according to their molecular weight into two main categories, polymers and SMs. There are three key factors for designing ideal donor material: (i) a low-lying highest occupied molecular orbital (HOMO) energy level to get a high V_{OC} ; (ii) a suitable band gap for a large and strong absorption spectrum in the visible and near-infrared region; (iii) a coplanar structure and a good crystalline properties to improve the charge transport efficiency and consequently to increase the fill factor (FF) of the OPVs [70]. In this context, the use of alternating structure of donors and acceptors units in the main chain has been proved to be an effective way to address these needs. In such D-A molecule, the donor moiety shows a destabilized HOMO energy level and consequently a small ionization potential, while the high electron affinity of the acceptor (A) moiety results in a stabilized lowest-unoccupied molecular orbital (LUMO) energy level [71-74]. The resultant D-A coupling could then potentially lead to a lower HOMO-LUMO gap and a smaller optical gap compared to either unit individually.

4.3. Databases for design of high-throughput donor materials

In this section, we will focus our attention on the role of DFT and TDDFT calculations to provide rapid and reliable answers for a range of questions related to photovoltaic donor materials design. To elaborate this point, we mainly focus on the donor materials with an alternation of donor and acceptor units (D-A) and those with more complicated sequences than D-A such as (A-D-A) and (D₁-A-D₂-A-D₁).

4.3.1. Required structural features of donor and acceptor units toward ideal donor materials

Recently, there has been an intense effort to enable computationally-guided design of potential donor materials in BHJSCS by generating a huge number of hypothetical donor and acceptor units. However, in a conjugated polymer/SM with an alternating donor and acceptor building blocks, the HOMO and LUMO energy levels are generally determined by the electron donating and the electron accepting moieties, respectively. Thus, it deserves to predicate the behaviour HOMO and LUMO energy levels of the donor and acceptor fragments to make a rational design of donor materials for efficient photovoltaic applications. Such DFT precalculations are thus very useful to produce a data basis for the quest of a large space of possible molecular configurations and select suitable combinations donor-acceptor pairs. The best example comes in 2011 by Brédas and co-workers [75] who designed a series of 144 D-A copolymers using DFT calculations and examined their photophysical behaviours as a function of donor and acceptor units. As seen in figure 2, twelve commonly used acceptors were chosen and coupled with the donor core (CPDT or CPDP) either directly or via bis-thiophene linkages (denoted Y and T-Y-T). The calculated results show that the DFT/B3LYP/6-31G(d) optimized ground-state geometries of the D-A oligomers are very much affected by the choice of the donor and acceptor units. Indeed, X/CPDT-Y oligomers exhibit a more linear structure compared to X/CPDP-Y oligomers. Furthermore, it was found that the introduction of thiophene rings as spacer between the donor and acceptor units along the oligomeric chain leads to an increase in coplanarity. Thus, the HOMO/LUMO overlap, the decrease of optical band gaps and the increase of the oscillator strengths of X/CPDP-T-Y-T and X/CPDT-T-Y-T oligomers can be understood geometrically, since they are the most planar, i.e. the most conjugated. Finally, the authors have examined the relationship between the LUMO energies of the designed D-A tetramers and that of PC₆₁BM. It was found that D-A tetramers based on B2T and PX as acceptor units possess energetically stabilized LUMOs compared to that of PC₆₁BM, which denotes that BHJ based on these molecules will have the poor capacity of electron transfer from donor material to acceptor material (PC₆₁BM).

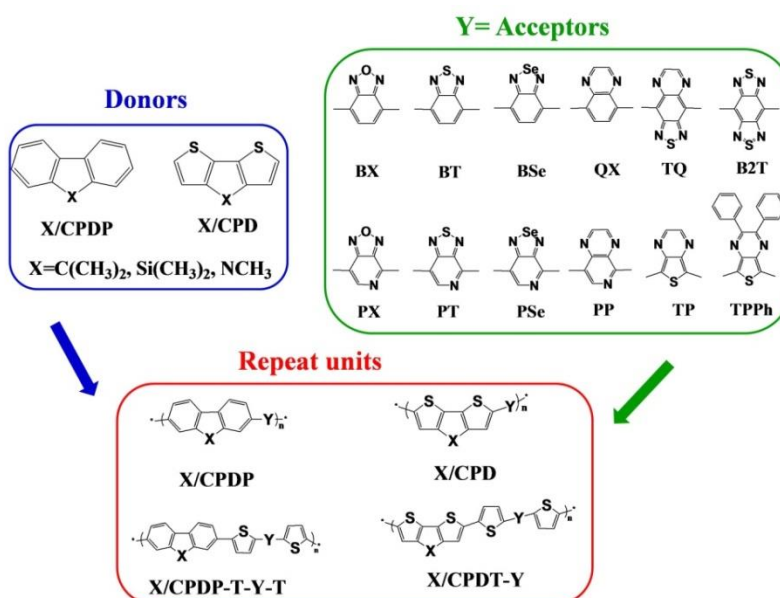


Figure 2. Chemical structures of the donors (X/CPDP, X/CPDT) and acceptors (isolated (Y) and bis-thiophene substituent (T-Y-T)) and copolymer repeat units [75].

4.3.2. Prediction of electronic, optical and photovoltaic properties of donor materials

DFT calculations are the basis upon several predictive models are developed and help to predict the electronic, optical and photovoltaic behaviours of candidate materials. The first and foremost task to gain insight the parameters related to the solar cells performance such as, V_{oc} of device, the charge separation ability in donor/acceptor interface and the energetic driving force (ΔE_{L-L}) is to investigate the FMO energy levels of the donor and acceptor materials. The absorption properties of the donor material should be investigated to better understand the physical processes contributed in the photocurrent generation. Recently, important attempts to design potential donor conjugated polymers/SMs for BHJ devices and predict their photophysical properties using DFT calculations have been undertaken. A good example is the study by Ghomrasni et al. [76] of new class of conjugated systems (P_1 , P_2 , and P_3) with acceptor-donor-acceptor (A-D-A) structure for use as potential donor materials for OPVs devices. DFT calculations based on B3LYP/6-31G(d) level of theory were performed to investigate the optoelectronic behaviours of these systems. In addition, Su et al. [77] have designed and investigated a series of bithiopheneimide (BTI)-based D-A copolymers (denoted 2-5) based on the experimental system (PDTSBTI (1)) at the PBE0/6-31G(d) and the TD-PBE0/6-31G(d) levels. The choice of the functional PBE0 has been explained by its validity for conjugated thiophene derivatives as demonstrated in previous studies [78,79]. Their initial DFT and TDDFT calculations show good accordance with experimental data, which encourages them to use the dimer model to simulate the electronic and optical properties of the new designed copolymers. Electronically, the designed molecules are calculated to have deeper FMO energy levels compared to those of $PC_{71}BM$ which can positively impact the electron transfer between donor and acceptor materials and charge separation in the D/A interface. Amongst the designed copolymers, the authors selected the most promising molecule (4) containing cyanomethylene-CPDT as donor unit with BTI as acceptor unit, showing a higher V_{oc} , extended absorption in the UV-Visible region and smaller reorganization energy compared to the experimental system (1). One of the major challenges in designing OPVs devices is achieving maximum charge transfer at the D/A interface, consequently increasing exciton dissociation (inter-CT) and decreasing non radiative recombination (inter-CR) [80,81]. Therefore, a detailed description of the dynamics of charge transfer will be very useful for rational design of new materials and devices with good performance. In that context, semi-

classical Marcus theory, explained in great details elsewhere and largely applied in several works intended for the organic solar cells, can correctly evaluate the charge transfer rates in the D/A interface. According to this formalism, the charge carrier mobility can be related with the rate of electron transfer $k_{inter-CT}$ and $k_{inter-CR}$ between two adjacent molecules, which can be expressed by the following equation [82]:

$$k = |V_{DA}|^2 \frac{1}{h} \sqrt{\frac{4\pi^3}{\lambda k_B T}} \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right) \quad (2)$$

where V_{DA} , is the electronic coupling (charge transfer integral) between D and A molecules, λ , is the reorganization energy, ΔG is the free energy change during electron transfer reaction, h is the Planck's constant, k_B , is the Boltzmann constant and T is the temperature. It should be mentioned that k is governed by two important parameters: V_{DA} , which needs to be maximized, and λ , which needs to be minimized for an optimal charge transfer rate. Numerous methods have been developed to compute the electronic coupling, amongst them the generalized Mulliken-Hush (GMH) formalism is the most commonly used in the past few years [83,84]. The reorganization energy λ includes the internal reorganization energy (λ_{int}) and external reorganization energy (λ_{ext}) [85,86]. The λ_{int} arises from the change in the molecular geometry of donor (D) and acceptor (A) due to the gain or loss of electronic charge throughout electron transfer process. The λ_{int} can be estimated with [87]:

$$\lambda_{int} = [E(A^-) - E(A)] + [E(D) - E(D^+)] \quad (3)$$

where $E(A^-)$ and $E(A)$ are the energies of the neutral acceptor at the anionic geometry and optimal ground state geometry, respectively. $E(D)$ and $E(D^+)$ are the energies of the cationic electron donor at the neutral geometry and optimal cation geometry, respectively. The λ_{ext} designates the variation in the surrounding medium due to the electronic and nuclear polarizations effects [87-89]. However, it is confirmed that it is not easy to estimate quantitatively the λ_{ext} in solid state. For the heterojunction P3HT/PC₆₁BM, the reorganization energy λ_{ext} is 0.11 eV [90].

During charge transfer and charge recombination process, the free energy change $\Delta G = \Delta G_{CT}$ and ΔG_{CR} , respectively. The ΔG_{CR} can be evaluated by [91]:

$$\Delta G_{CR} = E_{IP}(D) - E_{EA}(A) \quad (4)$$

here, the $E_{IP}(D)$ is the ionization potential of the donor and $E_{EA}(A)$ is the electron affinity of the acceptor. The ΔG_{CT} can be evaluated by the Rehm-Weller equation [92]:

$$\Delta G_{CT} = -\Delta_{GR} - \Delta E_{H-L} \quad (5)$$

where, ΔE_{H-L} is the electronic band-gap of the donor material.

In an attempt to explain the low performance measured experimentally for the devices using PDI derivatives as acceptor, Yi et al. [93] have employed Marcus-Levich-Jortner rate equation to evaluate the charge transfer and recombination rates in oligothiophene/fullerene and oligothiophene/PDI complexes. Their DFT/B3LYP/6-31G(d,p) and TDDFT/B3LYP/6-31G(d,p) calculated results showed that the inter-CR rate is faster in the complex oligothiophene/PDI compared to that in the fullerene based complex which may explain the low performance of the PDI-based devices. Furthermore, in 2011, theoretical calculations have been conducted to evaluate the rates of charge transfer and charge recombination in P3HT/PCBM-based OSCs devices by Troisi and co-workers [90] using Marcus theory. Many functionals such as B3LYP, and PBE0 have been demonstrated to be a reliable method for the calculation of the Marcus parameters. For example, Li et al. [87] have employed B3LYP to calculate the inter-CT and

inter-CR rates of a new designed complex BDDTT/PC₆₀BM. Using the Marcus's theory, the authors predicted that the designed D/A complex possess fast inter-CT rate ($5.77 \times 10^{11} \text{ s}^{-1}$) and slow inter-CR rate ($3.76 \times 10^5 \text{ s}^{-1}$). Recently, DFT calculations at PBE0/6-31G(d) level of theory were performed by Li et al. [94] to calculate the inter-CT and inter-CR hopping rates of four heterojunctions based on four new engineered molecules as donor materials with the PCBM as an acceptor material.

4.3.3. OPVs performance prediction: empirical approaches

In the effort to direct scientists to design new materials and device configurations, several empirical and theoretical models that estimate the maximum practically achievable efficiency in OPV devices have been developed. Particular attention was paid to the absorption spectrum, the FMOs energy levels of donor and acceptor materials to estimate the open-circuit voltage V_{oc} , and the driving force (ΔE_{L-L}) for charge transfer. Scharber and coworkers were first to propose a design rules to estimate the PCE of BHJSCs based on PCBM as common acceptor [58]. Scharber model, which assumes a charge carrier mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an FF of 0.65, evaluates the PCE of the PCBM-based BHJSC from the optical band gap and the LUMO energy level of the donor polymer. Figure 3 shows that efficiency of over 10% can be reached for an ideal donor material with $E_{LUMO} < -3.9 \text{ eV}$ and $1.65 < E_g < 1.35 \text{ eV}$.

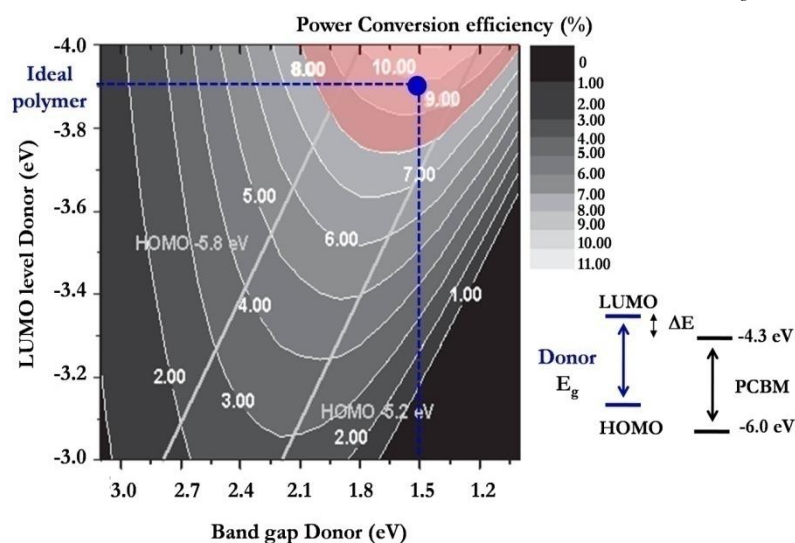


Figure 3. Scharber diagram showing the calculated energy-conversion efficiency of an ideal donor material. A schematic energy diagram of a donor PCBM system with bandgap energy (E_g) and the energy difference (ΔE_{L-L}) is also shown [58].

Liu et al. [95] have performed computational work using DFT methods on the design of two types of new (D-A) copolymers (Pb1-Pb3 and Pc1-Pc3) starting from three reported systems (Pa1-Pa3) based on C-, Si-, N-bridged bithiophene as donor core and thienopyrroledione (TPD) as acceptor core (figure 4). The calculated results show that the new designed copolymers show better performance with higher hole mobility compared to the reported systems Pa1-Pa3. Indeed, according to the Scharber diagram, the PCEs of the BHJ devices based on the newly designed copolymers (Pb1, Pb2, Pb3, Pc1, Pc2, and Pc3) and PCBM are predicted to be $\sim 8.8\%$, $\sim 10.0\%$, $\sim 8.4\%$, $\sim 8.5\%$, $\sim 9.9\%$ and $\sim 7.9\%$, respectively.

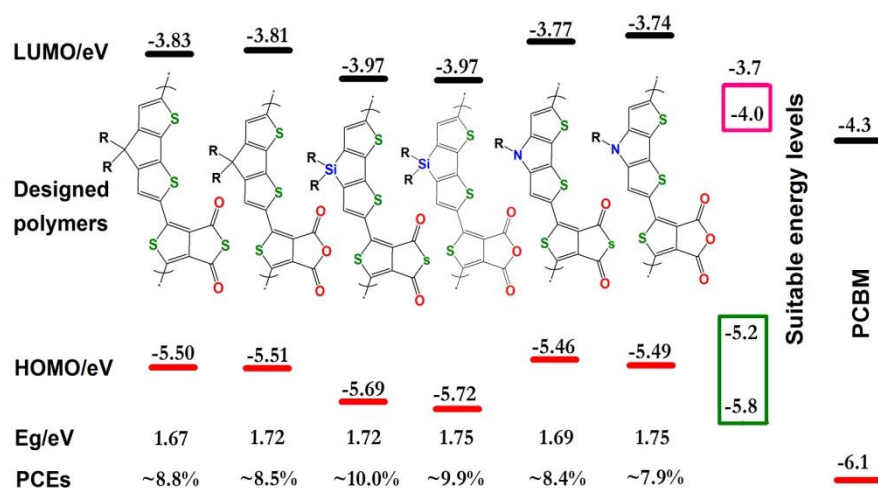


Figure 4. FMOs energy levels (HOMO and LUMO) and band gap (E_g) of Pb1-Pc3 evaluated at DFT/PBE0/6-31G(d) with those of PCBM measured experimentally. The performances of Pb1-Pc3 predicted according to Scharber diagrams are presented [95].

The main drawback in Scharber model is that it limited the acceptor materials to the fullerene derivatives. However, as above mentioned, there is an increasing interest in developing new non-fullerene acceptors to be employed with large number of polymeric and SMs donor materials in photovoltaic applications [68]. Some of these candidates have been shown to outperform fullerene derivatives in similar devices. Therefore, a reliable theoretical model for the PCE prediction of these devices is required. Recently, in 2009, Marks et al. [59] advanced a practical efficiency limit of OPVs (figure 5), where the J-V curve is assumed to be described by the classical diode model including series and parallel resistances. In their work, they treat the electrical fill factor (FF) as a function of LUMO offset (ΔE_{L-L}). By applying similar assumptions about the V_{oc} as Scharber et al. [58], a practical efficiency limit of ~ 14% is predicted for systems where the charge generation process occurs efficiently at $\Delta E_{L-L} = 0.3-0.4$ eV [59,96].

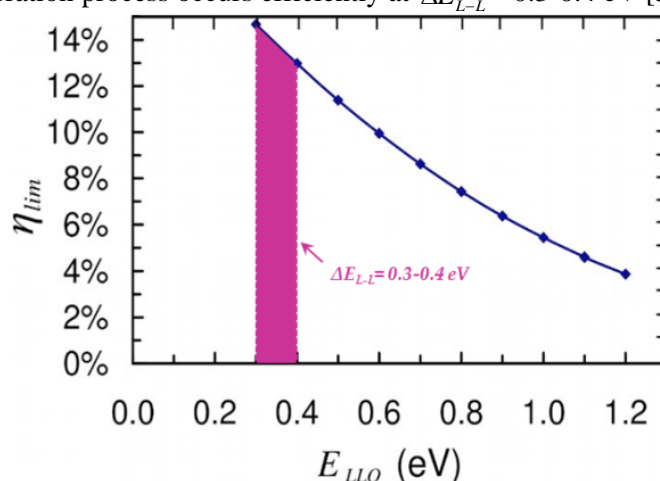


Figure 5. Practical efficiency limit (η_{min}) of bulk-heterojunction photovoltaic devices versus the LUMO offset (ΔE_{L-L}) (solid squares). The line is added as a guide to the eye [59].

5. Conclusions

Computational calculations based on DFT have become a powerful tool to investigate materials for the OSC research. In this review, we have distinguished the role of DFT calculations in the understanding of the structure-properties

relationship of known materials as well as the design of novel organic materials. Furthermore, we have learned that the dramatically power of DFT in understanding and predicting properties of organic materials is not only provoked by the increased availability of computational power, but also by emergence of robust and versatile computational methods. In the first part of the review, we have detailed a number of combined theoretical and experimental studies where DFT calculations have guided experimental results. Detailed investigations of the structural, energetic and spectroscopic characteristics of some organic systems were determined based on the preferentially adopted conformations in the ground states. For the fully studied models, there is a good agreement between experimental and theoretical results, which leads to a clear identification of the structure-property relationship. However, DFT calculations have not only used for studying some selected materials with a given composition, but they are very useful to generate a data basis for looking for a wide space of possible structural configurations. In most cases, the structure of a newly designed donor material is determined experimentally through trial and error. However, there is a need for methodologies of true computational prediction to guide the synthesis of novel donor materials. The different studies detailed in the second part of this review highlight the key success and contribution of DFT in the molecular design of potential photovoltaic donor materials for OSCs. They have demonstrated that DFT calculations are able to provide a detailed understanding of the geometric structure, electronic properties and other factors related to OPVs such as, V_{OC} , absorption spectra, driving forces ΔE_{L-L} , PCEs as well as the dynamics of charge transfer and charge recombination in the BHJSCs. Thus, rational design strategies may stimulate experimentalists to synthesize novel materials with forecasted properties.

References

- [1] R. Kumar, S. Singh, BC. Yadav, Conducting Polymers: Synthesis, Properties and Applications, *International Advanced Research Journal in Science, Eng. Technol.* **2** (2015) 110–124.
- [2] M. S. Vezie, S. Few, I. Meager, G. Pieridou, B. Dörling, R. S. Ashraf, A. R. Goñi, H. Bronstein, I. McCulloch, S. C. Hayes, M. Campoy-Quiles, J. Nelson, Exploring the origin of high optical absorption in conjugated polymers, *Nat. Mater.* **15** (2016) 746–753.
- [3] J. Yan, B. R. Saunders, Third-generation solar cells: a review and comparison of polymer:fullerene, hybrid polymer and perovskite solar cells, *RSC Advances* **4** (2014) 43286–43314.
- [4] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, Materials and Applications for Large Area Electronics: Solution-Based Approaches, *Chem. Rev.* **110** (2010) 3–24.
- [5] P. Meredith, C. J. Bettinger, M. Irimia-Vladu, A. B. Mostert, P. E. Schwenn, Electronic and optoelectronic materials and devices inspired by nature. *Rep. Prog. Phys.* **76** (2013) 34501.
- [6] M. Pagaliaro, G. Palmisano, R. Ciriminna, Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies, In: Brabec CJ, Dyakonov, Vladimir, Scherf, Ullrich, editors. Weinheim: Wiley-VCH; 2008.
- [7] L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao, L. Yu, Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.* **115** (2015) 12666–12731.
- [8] O. A. Abdulrazzaq, V. Saini, S. Bourdo, E. Dervishi, A. S. Biris, Organic Solar Cells: A Review of Materials, Limitations and Possibilities for Improvement, *Particul. Sci. Technol.* **31** (2013) 427–442.
- [9] Q. An, F. Zhang, J. Zhang, W. Tang, Z. Deng, B. Hu, Versatile ternary organic solar cells: a critical review. *Energy Environ. Sci.* **9** (2016) 281–322.
- [10] M. Rita Narayan, J. Singh, Study of the mechanism and rate of exciton dissociation at the donor-acceptor interface in bulk-heterojunction organic solar cells, *J. Appl. Phys.* **114** (2013) 073510.

- [11] L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, Low-Bandgap Near-IR Conjugated Polymers/Molecules for Organic Electronics, *Chem. Rev.* **115** (2015) 12633–12665.
- [12] V. Turkowski, C. A. Ullrich, Time-dependent density-functional theory for electronic excitations in materials: basics and perspectives, *Phys. Astro. publ (MU)*. (2008).
- [13] A. Guillén-López, M. Robles, J. Muñiz, Electronic structure and non-linear optical properties of organic photovoltaic systems with potential applications on solar cell devices: A DFT approach, arXiv. 1701 (2017) 03250.
- [14] A. Rajendran, T. Tsuchiya, S. Hirata, T. D. Iordanov, Predicting Properties of Organic Optoelectronic Materials: Asymptotically Corrected Density Functional Study, *J. Phys. Chem. A*. **116** (2012) 12153–12162.
- [15] D. Khlaifia D, F. Massuyeau, C. P. Ewels, J-L. Duvail, E. Faulques, K. Alimi, DFT Modeling of Novel Donor-Acceptor (D-A) Molecules Incorporating 3-hexylthiophene (3HT) for Bulk Heterojunction Solar Cells, *ChemistrySelect* **2** (2017) 10082-10090.
- [16] D. Baran, T. Kirchartz, S. Wheeler, S. Dimitrov, M. Abdelsamie, J. Gorman, R. S. Ashraf, S. Holliday, A. Wadsworth, N. Gasparini, P. Kaienburg, H. Yan, A. Amassian, C. J. Brabec, J. R. Durrant, I. McCulloch, Reduced voltage loss yield 10% efficient fullerene free organic solar cells with 41 V open circuit voltages, *Energy Environ. Sci.* **9** (2016) 3783–3793.
- [17] D. Khlaifia, C. P. Ewels, F. Massuyeau, M. Chemek, E. Faulques, J-L. Duvail, K. Alimi, Unraveling the real structures of solution-based and surface-bound poly(3-hexylthiophene) (P3HT) oligomers: a combined theoretical and experimental study. *RSC Advances*. **6** (2016) 56174–56182.
- [18] T. Tibaoui, S. Ayachi, M. Chemek, K. Alimi, New bridged oligofuran for optoelectronic applications. *Spectro. Acta A* **142** (2015) 25–33.
- [19] N. Bouzayen, B. Zaidi, A. Mabrouk, M. Chemek, K. Alimi, Density functional theory studies of new bipolar carbazole-benzothiazole: Electronic and vibrational properties, *Comput. Theor. Chem.* **984** (2012) 1–8.
- [20] A. Mabrouk, A. Azazi, K. Alimi, Molecular Structure-Property Engineering of Low-Band-Gap Copolymers, Based on Fluorene, for Efficient Bulk Heterojunction Solar Cells: A Density Functional Theory Study, *Polym. Eng. Sci.* **53** (2013) 1040–1052.
- [21] A. Azazi, A. Mabrouk, K. Alimi, Theoretical investigation on the photophysical properties of low-band-gap copolymers for photovoltaic devices, *Comput. Theor. Chem.* **978** (2011) 7–15.
- [22] W. Taouali, M. E. Casida, M. Chemek, A. Haj Said, K. Alimi, Theoretical investigation of oligomer structure and optoelectronic properties for [4-methoxyphenyl]acetonitrile]_n (n=1-5). *J. Mol. Model.* **23** (2017) 41.
- [23] A. Hoffman, Computational Chemistry in Rational Material design for Organic Photovoltaics, Western Libraries Undergraduate Research Award, *Paper* **5** (2015).
- [24] X. Yong, J. P. Zhang, Theoretical investigations for organic solar cells. *Mat. Techno.* **28** (2013) 40–64.
- [25] S. Tortorella, M. M. Talamo, A. Cardone, M. Pastore, F. De Angelis, Benchmarking DFT and semi-empirical methods for a reliable and cost-efficient computational screening of benzofulvene derivatives as donor materials for small-molecule organic solar cells. *J. Phys. Cond. Matter.* **28** (2016) 74005.
- [26] Y. Yi, V. Coropceanu, J-L. Brédas, Exciton-Dissociation and Charge-Recombination Processes in Pentacene/C₆₀ Solar Cells: Theoretical Insight into the Impact on Interface Geometry, *J. Am. Chem. Soc.* **131** (2009) 15777–15783.
- [27] M. Mayukh, I. H. Jung, F. He, L. Yu, Incremental Optimization in Donor Polymers for Bulk Heterojunction Organic Solar Cells Exhibiting High Performance. *J. Polym. Sci. Part B: Polym. Phys.* **50** (2012) 1057–1070.
- [28] M. E. Casida, Time-dependent density-functional theory for molecules, *Recent Advances in Comput. Chem.* **1** (1995) 155.

- [29] M. Petersilka, U. J. Gossmann, E. K. U. Gross, Excitation Energies from Time-dependent Density-Functional Theory, *Phys. Rev. Lett.* 76 (1996) 1212.
- [30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox. Gaussian 09, Revision A.02. Wallingford, CT: *Gaussian, Inc.* (2009).
- [31] V. Barone, M. Cossi, J. Tomasi, A new definition of cavities for the computation of salvation free energies by the polarisable continuum model. *J. Chem. Phys.* 107 (1997) 3210–3221.
- [32] M. Cossi, G. Scalmani, N. Reg, V. Barone, New developments in the polarisable continuum model for quantum mechanical and classical calculations on molecules in solution. *J. Chem. Phys.* 117 (2002) 43–54.
- [33] J. P. Perdew, K. Burke, Y. Wang, Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *J. Am. Phys. Soc.* 54 (1996) 16533- 16539.
- [34] A. D. Becke, Density functional thermochemsitry. III. The role of exact exchange, *J. Chem. Phys.* 98 (1993) 5648–5655.
- [35] C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE₀ model, *J. Chem. Phys.* 110 (1999) 6158–6170.
- [36] S. H. Nabavi, M. H. Khodabandeh, M. Golbabaee, A. Moshaii, M. D. Davari, Excited States Study reveals the Twisted Geometry Induced Large Stokes Shift in DCM Fluorescent Dye, *J. Photochemistry and Photobiology A: Chemistry*. 2017. (In press: <https://doi.org/10.1016/j.jphotochem.2017.05.017>).
- [37] I. Thanopoulos, I. D. Petsalakis, G. Theodorakopoulos, Photoinduced charge transfer in heterofullerene-donor hybrids: A theoretical study, *Chem. Phys. Lett.* 506 (2011) 248–254.
- [38] T. Yanai, D. P. Tew, N. C. Handy, A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chem. Phys. Lett.* 393 (2004) 51–57.
- [39] J.-D. Chai, M. Head-Gordon, Long-range corrected density functional with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* 10 (2008) 6615-6620.
- [40] R. S. Bhatta, M. Tsige, Chain length and torsional dependence of exciton binding energies in P3HT and PTB7 conjugated polymers: A first-principles study, *Polymer* 55 (2014) 2667–2672.
- [41] D. M. Hinkens, Q. Chen, M. K. Siddiki, D. Gosztola, M. A. Tapsak, Q. Qiao, M. Jeffries-EL, S. B. Darling, Model compounds based on poly(p-phenylenevinyleneborane) and terthiophene: Investigating the pen junction in diblock copolymers. *Polymer* 54 (2013) 3510–3520.
- [42] M. Kertesz, C. X. Cui CX, Structural Criteria for Conjugated Polymer Design. In: Kuzmany H, Mehring M, Roth S. Editors Electronic Properties of Polymers, Springer Series in Solid-State Sciences, *Springer, Berlin, Heidelberg*. 107 (1992) 397–400.
- [43] C. Roux, J.-Y. Bergeron, M. Leclerc, Thermochromic properties of polythiophenes: Strutural aspects. *Macromol. Chem. phys.* 194 (1993) 869-877.

- [44] J-L. Brédas, J. P. Calbert, D. A. Silva Filho, J. Cornil, Organic semiconductors: A theoretical characterization of the basic parameters governing charge transport. *Proceedings of the National Academy of Sciences*. 99 (2002) 5804–5809.
- [45] M. Bajpai, R. Srivastava, R. Dhar, R. S. Tiwari, Review on Optical and Electrical Properties of Conducting Polymers. *Ind. J. Mat. Sci.* 201 (2016) 1–8.
- [46] J. Torras, J. Casanovas, C. Alemán, Reviewing Extrapolation Procedures of the Electronic Properties on the π -Conjugated Polymer Limit. *J. Phys. Chem. A*. 116 (2012) 7571–7583.
- [47] S. S. Zade, M. Bendikov, From Oligomer to Polymer: Convergence in the HOMO-LUMO Gaps of Conjugated Oligomers, *Org. Lett.* 8 (2006) 5243–5246.
- [48] J. Gierschner, J. Cornil, H-J. Egelhaaf, Optical Bandgaps of π -Conjugated Organic Materials at the Polymer Limit: Experiment and Theory, *Adv. Mat.* 19 (2007) 173–191.
- [49] S. S. Sharma, G. D. Sharma, J. A. Mikroyannidis, Improved power conversion efficiency of bulk Heterojunction poly(3-hexylthiophene): PCBM photovoltaic devices using small molecule additive, *Sol Energy Mat. Sol. Cell.* 95 (2011) 1219–1223.
- [50] R. Colle, G. Grosso, A. Ronzani, C. M. Zicovich-Wilson, Structure and X-ray spectrum of crystalline poly(3-hexylthiophene) from DFT-van der Waals calculations. *Phys. Status Solidi (b)*. 248 (2011) 1360–1368.
- [51] D. Dudenko, A. Kiersnowski, J. Shu, W. Pisula, D. Sebastiani, H. W. Spiess, M. R. Hansen, A strategy for Revealing the Packing in Semicrystalline π -Conjugated Polymers: Crystal Structure of Bulk Poly-3-hexylthiophene (P3HT). *Angew. Chem.* 124 (2012) 11230–11234.
- [52] R. P. Kurta, L. Grodd, E. Mikayelyan, O. Y. Gorobtsov, I. A. Zaluzhnyy, I. Fratoddi, I. Venditti, M. V. Russo, M. Sprung, I. A. Vartanyants, S. Grigorian, Local structure of semicrystalline P3HT films probed by nanofocused coherent X-rays, *Phys. Chem. Chem. Phys.* 17 (2015) 7404–7410.
- [53] F. P. V. Koch, Synthesis and Physical Chemistry of Poly(3-hexylthiophene) a Monomer-up Approach. *PhD Dissertation No 20912, ETH Zurich*. (2013)
- [54] K. Rahimi, I. Botiz, J. O. Agumba, S. Motamen, N. Stingelin, G. Reiter, Light absorption of poly(3-hexylthiophene) single crystals. *RSC Advances*. 4 (2014) 11121–11123.
- [55] N. K. Elumalai, A. Uddin, Open circuit voltage of organic solar cells, An in-depth review, *Energy Environ. Sci.* 9 (2015) 391–410.
- [56] B. Qiab, J. Wang, Fill factor in organic solar cells, *Phys. Chem. Chem. Phys.* 15 (2013) 8972–8982.
- [57] N. Agrawal, M. Zubair Ansari, A. Majumdar, R. Gahlot, N. Khare, Efficient up-scaling of organic solar cells. *Sol. Energy Mater. Sol. Cell.* 157 (2016) 960–965.
- [58] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, Design Rules for Donors in Bulk-Heterojunction Solar Cells-Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* 18 (2006) 789–794.
- [59] J. D. Servaites, M. A. Ratner, T. J. Marks, Practical efficiency limits in organic photovoltaic cells: Functional dependence of fill factor and external quantum efficiency. *Appl. Phys. Lett.* 95 (2009) 163302.
- [60] Y. Li, Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption, *Acc. Chem. Res.* 45 (2012) 723–733.
- [61] Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, Single-junction polymer solar cells with high efficiency and photovoltage. *Nat. Phot.* 9 (2015) 174–179.
- [62] X. Ouyang, R. Peng, L. Ai, X. Zhang, Z. Ge, Efficient polymer solar cells employing a non-conjugated small-molecule electrolyte. *Nat. Phot.* 9 (2015) 520–524.

- [63] C. Cui, X. Guo, J. Min, B. Guo, X. Cheng, M. Zhang, C. J. Brabec, Y. Li, High-Performance Organic Solar Cells Based on a Small Molecule with Alkylthio-Thienyl-Conjugated Side Chains without Extra Treatments. *Adv. Mater.* 27 (2015) 7469–7475.
- [64] B. Kan, M. Li, Q. Zhang, F. Liu, X. Wan, Y. Wang, W. Ni, G. Long, X. Yang, H. Feng, Y. Zuo, M. Zhang, F. Huang, Y. Cao, T. P. Russell, Y. Chen, A Series of Simple Oligomer-like Small Molecules Based on Oligothiophenes for Solution-Processed Solar Cells with High Efficiency, *J. Am. Chem. Soc.* 137 (2015) 3886–3893.
- [65] Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan, A. J. Heeger, Solution-processed small-molecule solar cells with 6.7% efficiency, *Nat. Mater.* 11 (2011) 44–48.
- [66] Z. Li, X. Zhang, G. Lu, Electron structure and dynamics at poly(3-hexylthiophene)/fullerene photovoltaic heterojunctions, *Appl. Phys. Lett.* 98 (2011) 83303.
- [67] B. Ratier, J-M. Nunzi, M. Aldissi, T. M. Kraft, E. Buncel, Organic solar cell materials and active layer designs-improvements with carbon nanotubes: a review, *Polym. Inter.* 61 (2012) 342–354.
- [68] C. B. Nielsen, S. Holliday, H-Y. Chen, S. J. Cryer, I. McCulloch, Non-fullerene Electron Acceptors for Use in Organic Solar Cells. *Acc. Chem. Res.* 48 (2015) 2803–2812.
- [69] P. Hudhomme, An overview of molecular acceptors for organic solar cells. *EPJ Photov.* 4 (2013) 40401.
- [70] L. Huo, J. Hou, S. Zhang, H-Y. Chen, Y. A. Yang, Polybenzo[1,2-b:4,5-b']dithiophene Derivative with Deep HOMO Level and Its Application in High-Performance Polymer Solar Cells. *Angew. Chem.* 22 (2010) 1542–1545.
- [71] H. Zhou, L. Yang, S. Stoneking, W. You, A Weak Donor-Strong Acceptor Strategy to Design Ideal Polymers for Organic Solar Cells. *ACS Appl. Mater. Interf.* 2 (2010) 1377–1383.
- [72] G. L. Gibson, T. M. McCormick, D. S. Seferos, Atomistic Band Gap Engineering in Donor-Acceptor Polymers. *J. Am. Chem. Soc.* 134 (2012) 539–547.
- [73] K. Müllen, W. Pisula, Donor-Acceptor Polymers, *J. Am. Chem. Soc.* 137 (2015) 9503–9505.
- [74] X. Liu, W. Shen, R. He, Y. Luo, M. Li, A Strategy to Modulate the Electron-Rich Units in Donor-Acceptor Copolymers for Improvements of Organic Photovoltaics, *J. Phys. Chem C.* 118 (2014) 17266–17278.
- [75] L. Pandey, C. Risko, J. E. Norton, J-L. Brédas, Donor-Acceptor Copolymers of Relevance for Organic Photovoltaics: A Theoretical Investigation of the Impact of Chemical Structure Modifications on the Electronic and Optical Properties, *Macromolecules* 45 (2012) 6405–6414.
- [76] S. Ghomrasni, S. Ayachi, K. Alimi, New acceptor-donor (A-D-A) type copolymers for efficient organic photovoltaic devices, *J. Phys. Chem. Solid.* 76 (2015) 105–111.
- [77] S- B. Li, Y-A. Duan, Y. Geng, H-B. Li, J-Z. Zhang, H-L. Xu, M. Zhang, Z-M. Su, A designed bithiopheneimide-based conjugated polymer for organic photovoltaic with ultrafast charge transfer at donor/PC₇₁BM interface: theoretical study and characterization. *Phys. Chem. Chem. Phys.* 16 (2014) 25799–25808.
- [78] Y-A. Duan, Y. Geng, H-B. Li, J-L. Jin, Y. Wu, Z-M. Su, Theoretical Characterization and Design of Small Molecule Donor Material Containing Naphthodithiophene Central Unit for Efficient Organic Solar Cells. *J. Comput. Chem.* 34 (2013) 1611–1619.
- [79] H-B. Li, J. Zhang, Y. Wu, J-L. Jin, Y-A. Duan, Z-M. Su, Y. Geng, Theoretical study and design of triphenylamine-malononitrile-based p-type organic dyes with different p-linkers for dyes-sensitized solar cells. *Dyes and Pigments.* 108 (2014) 106–114.
- [80] S. R. Yost, E. Hontz, D. P. McMahon, T. Van Voorhis, Electronic and Optical Properties at Organic/Organic Interfaces in Organic Solar Cells. *Multiscale Modelling of Organic and Hybrid Photovoltaics.* 352 (2014) 103-150.
- [81] A. Solanki, B. Wu, T. Salim, Y. M. Lam, T. C. Sum, Correlation between blend morphology and recombination dynamics in additives-added P3HT:PCBM solar cells. *Phys. Chem. Chem. Phys.* 17 (2015) 26111–26120.

- [92] R. A. Marcus, Electrontransferreaktionen in der Chemie-Theorie und Experiment (Nobel-Vortrag). *Angew. Chem.* 105 (1993) 1161–1172.
- [83] A. A. Voityuk, Estimation of electronic coupling in π -stacked donor-bridge-acceptor systems: Correction of the two-state model. *J. Chem. Phys.* 124 (2006) 64505.
- [84] C.-P. Hsu, The electronic Coupling in Electron Transfer and Excitation Energy Transfer, *Acc. Chem. Res.* 42 (2009) 509–518.
- [85] P. Song, Y. Li, F. Ma, T. Pullerits, M. Sun, External Electric Field-Dependent Photoinduced Charge Transfer in a Donor-Acceptor System for an Organic Solar Cell, *J. Phys. Chem C.* 117 (2013) 15879–15889.
- [86] V. Lemaire, M. Steel, D. Beljonne, J.-L. Brédas, J. Cornil, Photoinduced Charge Generation and Recombination Dynamics in Model Donor/Acceptor PAIRS FOR Organic Solar Cell Application: A Full Quantum-Chemical Treatment. *J. Am. Chem. Soc.* 127 (2005) 6077–6086.
- [87] Y. Li, T. Pullerits, M. Zhao, M. Sun, Theoretical Characterization of the PC₆₀BM:PDDTT Model for an Organic Solar Cell. *J. Phys. Chem. C.* 115 (2011) 21865–21873.
- [88] S. Tang, J. Zhang, Rational Design of Organic Asymmetric Donors D₁-A-D₂ Possessing Broad Absorption Regions and Suitable Frontier Molecular Orbitals to Match Typical Acceptors toward Solar Cells. *J. Phys. Chem A.* 115 (2011) 5184–5191.
- [89] T. Kawatsu, V. Coropceanu, A. Ye, J.-L. Brédas, Quantum-Chemical Approach to Electronic Coupling: Application to Charge Separation and Charge Recombination Pathways in a Model Molecular Donor-Acceptor System for Organic Solar Cells, *J. Phys. Chem C.* 112 (2008) 3429–3433.
- [90] T. Liu, A. Troisi, Absolute Rate of Charge Separation and Recombination in a Molecular Model of the P3HT/PCBM Interface, *J. Phys. Chem C.* 115 (2011) 2406–2415.
- [91] G. J. Kavarnos, N. J. Turro, Photosensitization by Reversible Electron Transfer: Theories, Experimental Evidence, and Examples, *Chem. Rev.* 86 (1986) 401–449.
- [92] G. D. Scholes, G. Rumbles, Excitons in nanoscale systems, *Nat. Mater.* 5 (2006) 683–696.
- [93] Y. Yi, V. Coropceanu, J.-L. Brédas, A comparative theoretical study of exciton-dissociation and charge-recombination processes in oligothiophene/fullerene and oligothiophene/perylene diimide complexes for organic solar cells. *J. Mater. Chem.* 21 (2011) 1479–1486.
- [94] S.-B. Li, Y.-A. Duan, Y. Geng, H.-Z. Gao, Y.-Q. Qiu, Z.-M. Su, Theoretical Design and Characterization of Pyridalithiadiazole-Based Chromophores with Fast Charge Transfer at Donor/Acceptor Interface toward Small Molecule Organic Photovoltaics. *RSC Advances.* 5 (2015) 29401–29411.
- [95] X. Liu, R. He, W. Shen, M. Li, Molecular design of donor-acceptor conjugated copolymers based on C-, Si- and N-bridged dithiophene and thienopyrroledione derivatives units for organic solar cells. *J. Power Sources.* 245 (2014) 217–223.
- [96] R. A. J. Janssen, J. Nelson, Factors Limiting Device Efficiency in Organic Photovoltaics. *Adv. Mater.* 25 (2013) 1847–1858.