

Review on the DFT Computation of Bulk Heterojunction and Dye-sensitized

Organic Solar Cells Properties

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Abstract

Context

Organic solar cells (OSCs) represent a promising renewable energy technology due to their flexibility, low production cost, and environmental sustainability. To advance OSC efficiency and stability, Density Functional Theory (DFT) has emerged as a powerful computational tool, enabling the prediction and optimization of critical properties at the molecular and device levels. This review highlights the key properties of bulk heterojunction solar (BHJ) solar cells and dye-sensitized solar cells (DSSCs) that can be accurately computed using DFT, including **electronic structure properties** (HOMO-LUMO energy levels, bandgap energies, and exciton binding energies, which influence charge separation and transport); **optical properties** (absorption spectra and light-harvesting efficiency, essential for maximizing photon capture); **charge transport properties** (reorganization energies, electron, and hole mobilities, and charge transfer rates that govern carrier dynamics within devices); **interfacial properties** (energy alignment at donor-acceptor interfaces, contributing to efficient charge separation and minimizing recombination) and **chemical reactivity descriptors** (ionization potential, electron affinity, chemical hardness, and electrophilicity, which facilitate material screening for OSC applications). We also show how to compute OSCs' power conversion efficiency (PCE) from DFT.

Methods

The review also discusses the importance of selecting appropriate exchange-correlation functionals and basis sets to ensure the accuracy of DFT predictions. By providing reliable computational insights, DFT accelerates the rational design of OSC materials, guides experimental efforts, and reduces resource demands. This work underscores DFT's pivotal role in optimizing OSC performance and fostering the development of next-generation photovoltaic technologies.

Keywords: Organic Solar Cells (OSCs); Bulk heterojunction (BHJ) solar cells and Dye-sensitized solar cells (DSSCs); Density Functional Theory (DFT); Optoelectronic properties; Charge transport dynamics; Exciton Dissociation; Energy level alignment.

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Acknowledgements

I. B. thanks the Brazilian agencies CNPq (Grant numbers 304148/2018-0 and 409447/2018-8) and FAPERJ (Grant number E-26/204.294/2024) for funding this research. Nathália M. P. Rosa thanks FAPERJ (grant number E-26/205.922/2022) for a post-doctoral scholarship. Support for this research also came from the National Institute of Science and Technology on Molecular Sciences (INCT-CiMol) grant CNPq 406804/2022-2, and Nano Network grant FAPERJ E-26/200.008/2020

Introduction

The availability of energy has been a transformative factor in human history. Given the substantial increase in global consumption in recent years, transitioning to a more sustainable energy matrix has become crucial to mitigate climate change and ensure global energy security (**Fig.1**) [1–3]. According to the 2024 "Statistical Review of World Energy," global primary energy consumption reached a new record high for the second consecutive year. Renewable energy generation saw significant growth, with a 13% increase in electricity production from renewable sources such as solar and wind [3–6]. Consequently, much research has focused on developing clean fuel technologies and alternative energy sources [6]. In this context, research on solar energy has become particularly attractive, given the abundant daily influx of sunlight reaching the Earth's surface, which far exceeds the planet's annual energy needs [2, 6].

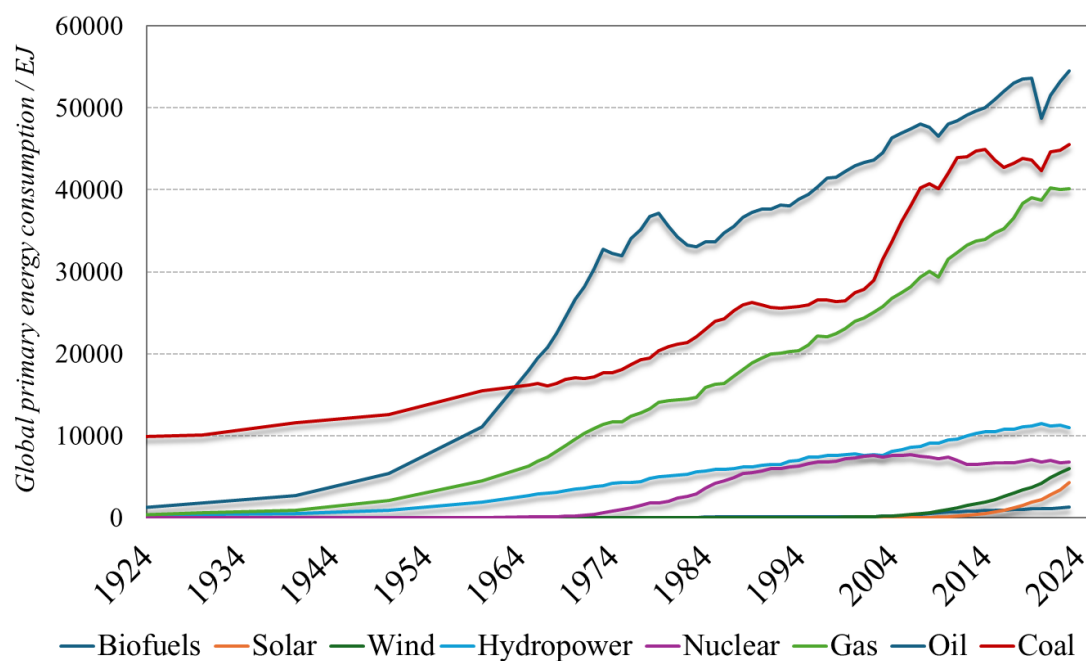


Fig. 1. Global primary energy consumption in the last 100 years by source type [3].

Solar energy is an attractive power source, the most abundant renewable resource available, and can be harnessed directly and indirectly. The solar radiation that reaches the Earth's surface amounts to approximately 3400000 exajoules (EJ) per year, which surpasses all estimated non-renewable energy resources, including fossil fuels and nuclear energy [7]. Considering the vast potential of solar energy, photovoltaic technologies have

evolved significantly over different technological generations, with each advancement aiming for greater efficiency, flexibility, and cost reduction, from conventional silicon cells to modern third-generation organic cells, such as bulk heterojunction (BHJ) and dye-sensitized solar cells (DSSCs).

Photovoltaic devices directly convert solar energy into electricity and encompass many photovoltaic cell technologies [8–10]. Depending on the component materials, these technologies are classified into three generations. First-generation photovoltaic systems utilize crystalline silicon technology, already commercially available. Second-generation systems are based on thin-film photovoltaic technologies, which cells are deposited on flexible substrates, allowing for greater applicability on irregular surfaces. Finally, third-generation photovoltaic systems include organic photovoltaic technologies, still not widely commercialized [8, 9].

Organic optoelectronic materials have been known since the 1910s. Interest in these materials grew significantly during the 1960s and 1970s driven by the discovery of electroluminescence in anthracene crystals, reported by Pope in 1963 [11, 12] and by Helfrich and Schneider in 1965 [13], and with the discovery that π -conjugated polymers, such as hydrocarbon chains with alternating bonds, can achieve high conductivities when doped [14–18]. Currently, these materials are widely studied for applications in electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic solar cells, organic transistors, and sensors [19–25]. Organic photovoltaic materials used in organic solar cells (OSCs) for light absorption and charge transport are based on conjugated organic semiconducting molecules, such as oligomers and polymers [26, 27]. These devices are manufactured more simply and cost-effectively, and although OSC efficiency is still not comparable to traditional photovoltaic technologies, it has improved significantly in recent years [28–34]. OSCs are typically composed of thin films of electron donor (D) and acceptor (A) materials sandwiched between electrodes, one of which must be transparent to allow light to enter [35–37]. Due to the low dielectric constant of organic materials, photoexcitation generates tightly bound excitons (electron-hole pairs), which must be dissociated into free charge carriers, a process that occurs at the D–A interface [26, 38]. The electron and hole carriers are then transported to the

electrodes, generating an electric current. However, charge dissociation and transport are limited by the short diffusion length of excitons in these materials [39].

Although OSC development has made significant advancements, their efficiency is still lower than that of traditional technologies, such as crystalline silicon. Additionally, the degradation of organic materials when exposed to light and oxygen can drastically limit their lifespan, thus requiring improvements in the material's chemistry [40–43]. Devices with efficiencies exceeding 19% have already been reported [34, 44–46]. Recently, OSCs have been reported to achieve a record power conversion efficiency of 20.8%, attributed to an active layer morphology based on an interpenetrating fibril network [47, 48]. The evolution of energy conversion efficiency in solar cells in recent years is summarized in **Fig. 2**, based on data extracted from annual solar cell efficiency tables, listing the highest confirmed efficiencies [49–68]. Scaling up production for large-scale manufacturing also presents a challenge, as while OSCs can be produced more economically through methods like roll-to-roll printing, ensuring uniformity and quality across large surfaces remains a technological barrier [43, 69]. These challenges highlight the need for new approaches, including using theoretical calculations to optimize molecular design and improve the understanding of degradation and charge transport mechanisms.

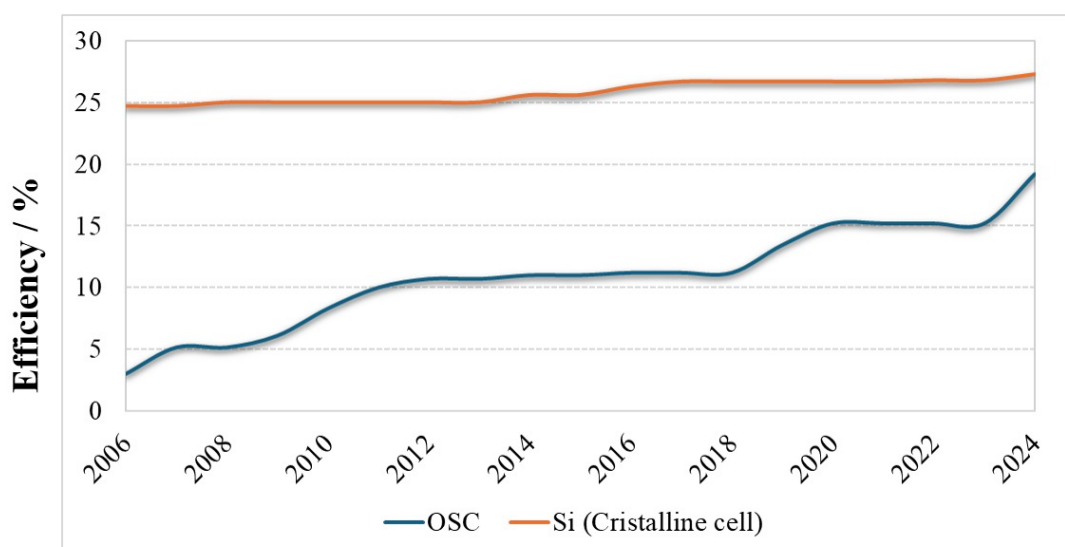


Fig. 2. Reports on energy conversion efficiencies of single-junction organic solar cells and crystalline silicon [49–67].

Density Functional Theory (DFT) calculations play a fundamental role in predicting and evaluating the optoelectronic properties of materials for applications in photovoltaic devices, such as BHJs solar cells and DSSCs [24, 25, 70–75]. DFT provides detailed insights into the electronic structure and optical absorption properties, which are essential for optimizing the performance of these materials in light-harvesting and charge transport processes [76–78]. Compared to experimental methods, DFT offers a more cost-effective and efficient alternative, enabling the rapid screening of potential candidates [78, 79]. Since the synthesis and experimental testing of new materials can be time-consuming and expensive, DFT can be a valuable tool to guide experiments by identifying the most promising candidates in advance, reducing costs and saving time. As a result, DFT can accelerate the development process, optimize resource use, and expand the ability to explore a broader range of materials for photovoltaic applications.

Given the growing interest in organic optoelectronic materials due to their versatility and potential to revolutionize various technologies, from lighting and energy-harvesting devices to sensors and transistors, in this work, we present relevant optoelectronic properties related to efficiency and charge transport in bulk heterojunction and dye-sensitized solar cells and how to compute them using DFT.

Basic working principle of an organic photovoltaic (OPV) device

The fundamental operation principle of an organic photovoltaic device (OPV) is the direct conversion of solar energy into electricity through semiconducting organic materials [80]. These devices consist of an active layer, usually composed of an electron donor and acceptor material, sandwiched between two electrodes, one transparent to allow sunlight to enter [80–82]. When light hits the device, it excites electronically the organic molecules in the active layer, generating tightly bound electron-hole pairs (excitons). These excitons are separated into free charges at the interface between the donor and acceptor materials, allowing electrons to be transported to one electrode and holes to the other, generating an electric current. The efficiency of this process depends

on several factors, including the exciton dissociation capability and the effective transport of charges to the electrodes [81–84].

Organic electronic materials are conjugated polymers in which optical absorption and charge transport are governed by partially delocalized π electrons [83]. This property makes them promising candidates for various photovoltaic applications [24, 70, 71, 85–87]. DSSCs and BHJ-type OSCs are photovoltaic devices that utilize organic materials to absorb sunlight and convert it into electricity, but they differ significantly in their architectures and operational mechanisms. In BHJs, the active layer consists of a blend of donor and acceptor materials, forming an interpenetrating network that facilitates exciton dissociation and charge transport [88]. DSSCs, in contrast, employ a photosensitive dye adsorbed onto the surface of a semiconductor, typically TiO_2 , to capture and transfer electrons [89, 90]. These structural differences influence molecular design strategies and the parameters that determine photovoltaic efficiency, highlighting the need for specific approaches to optimize each type of device. Both technologies offer flexibility, low production costs, and the potential for large-scale manufacturing, positioning them as sustainable and promising alternatives for solar energy generation [89, 91]. Therefore, BHJs and DSSCs can be used on flexible surfaces and portable devices, expanding their potential use in different scenarios.

Bulk heterojunction (BHJ) organic solar cells

The operation of BHJ solar cells relies on the architecture of their active layer. The active layer of a BHJ (**Fig. 3a**) consists of a highly interconnected blend of donor and acceptor materials, forming an interpenetrating amorphous network that maximizes the interface between these components. This architecture enhances exciton dissociation efficiency, generating a more significant electrical current. Despite ongoing challenges related to efficiency and stability, BHJ-type OSCs have shown significant potential to emerge as a competitive alternative to conventional photovoltaic technologies [43, 88, 92].

The operation of a BHJ solar cell involves four main steps (**Fig. 3b**): (1) light absorption, where electron-donor molecules absorb photons incident on the active layer;

(2) formation of tightly bound excitons in the donor material; (3) dissociation of these excitons at the interface between the donor (D) and electron acceptor (A) materials in an electronic charge transfer state, resulting in free electrons and holes; and (4) charge transport taking place in an electronic charge separation state, where the electrons are conducted through the acceptor material to the cathode, while the holes are transported through the donor material to the anode. Once the electrons and holes reach their respective electrodes, an electric current is generated in the external circuit [43, 93–95].

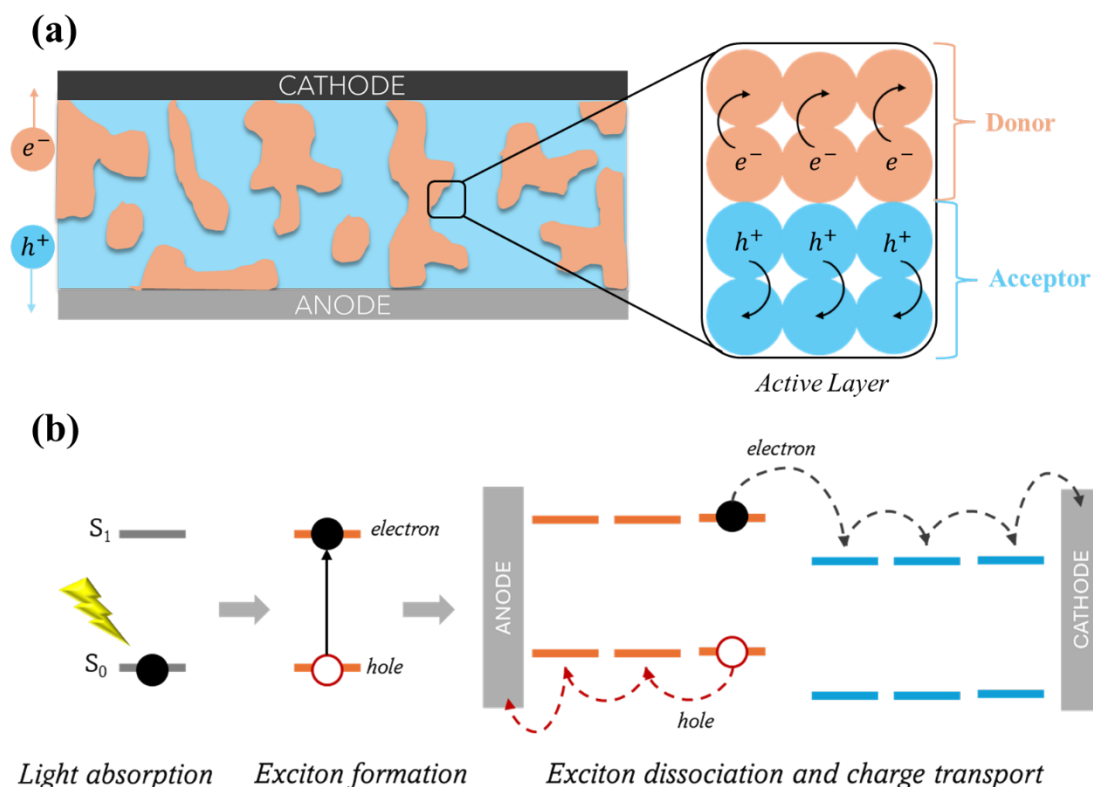


Fig. 3. (a) Active layer of a bulk heterojunction (BHJ) organic solar cell; (b) Diagram illustrating the operating mechanism of a BHJ cell, highlighting the processes of light absorption, exciton generation, charge dissociation at the donor/acceptor interface, and charge transport to the electrodes.

To achieve high power conversion efficiency (*PCE*) in BHJ solar cells, the active layer must have a sufficiently broad absorption spectrum in the wavelength range between 250 nm (4.96 eV) and 3000 nm (0.413 eV) [96] of the solar spectrum to maximize the capture of photons from sunlight. Additionally, the active layer should present appropriate energy levels in the highest occupied molecular orbitals (HOMO) and the lowest

unoccupied molecular orbitals (LUMO) for both the donor and acceptor materials. After photon absorption, an electron is excited from the donor's HOMO to its LUMO and then transferred to the acceptor's LUMO, which has a lower energy level (**Fig. 3b**) [43, 92]. For this process to be efficient, an appropriate energy offset between the donor's LUMO and the acceptor's LUMO, typically in the range of 0.1–1.4 eV, is crucial to overcome the Coulomb attraction and ensure exciton dissociation into free charges [43, 97]. Furthermore, the efficiency of a solar cell is directly influenced by the open-circuit voltage (V_{OC}), which is linearly related to the energy difference between the donor's HOMO and the acceptor's LUMO [92, 98]. Thus, the more significant this difference, the higher the theoretically-predicted value of V_{OC} . However, the overall device efficiency also depends on minimizing energy losses through processes such as charge recombination and internal resistance, to achieve optimized performance [98]. The active layer must also exhibit good charge mobility, which promotes efficient exciton separation and facilitates the effective transfer of electrical charges [24, 87, 99–102].

Dye-sensitized solar cell (DSSC)

DSSCs have become a promising alternative for photovoltaic solar energy generation [89, 90, 103, 104]. This is due to the exceptionally low-cost materials, mechanical flexibility, ease of fabrication and assembly, and environmentally friendly nature [105–108]. The basic working principle of a dye-sensitized solar cell (**Fig. 4a**) involves a photosensitive dye adsorbed onto the surface of a semiconductor material, typically titanium dioxide (TiO_2) or Zinc Oxide (ZnO) [109–111]. When sunlight strikes the device, photons are absorbed by the dye, promoting electrons from the ground state to an excited state. These excited electrons are quickly injected into the conduction band of the semiconductor. In contrast, the dye, which has lost an electron, is regenerated by an electrolyte in the cell, usually composed of the I_3^-/I^- redox couple [112–115]. The semiconductor transports the injected electrons to the conducting electrode, known as the photoanode, generating an electric current. Simultaneously, the electrolyte completes the cycle by transferring electrons to regenerate the dye, thus closing the circuit. This process, shown in **Fig. 4b**, efficiently converts sunlight into electricity, with the dye absorbing light and generating electrical charges [89, 90, 116, 117].

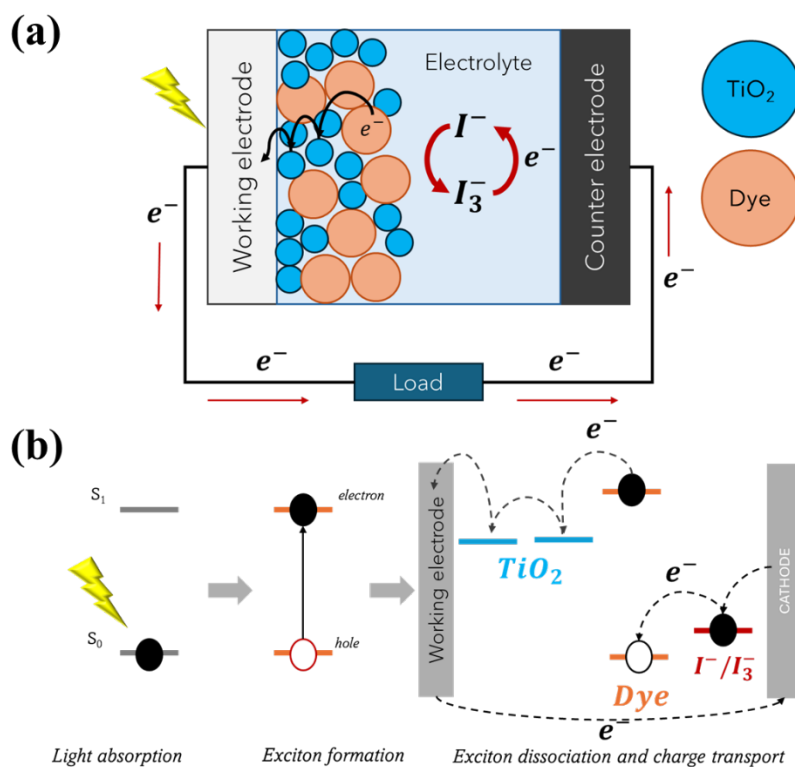


Fig. 4. (a) Operation diagram of the operation of a dye-sensitized solar cell (DSSC) and; (b) Energy level diagram, highlighting the processes of light absorption by the dye, electron injection into the semiconductor, and dye regeneration by the electrolyte.

DFT-based methods for evaluating organic photovoltaic efficiency

Although BHJ-type OSCs and DSSCs are emerging photovoltaic technologies with distinct architectures and mechanisms, both share the need for precise characterization of optoelectronic properties to optimize performance. For example, for BHJs the energy alignment at the donor-acceptor interface is essential for efficient charge separation [73, 118], whereas in DSSCs, dye properties such as light-harvesting efficiency and regeneration potential are critical for device operation [79, 119]. DFT can assist in developing materials for organic photovoltaic devices because it provides an efficient and cost-effective way to assess critical properties [24, 25, 70, 71, 120–124]. Through accurate DFT calculations, it is possible to predict and optimize critical characteristics of OPVs, such as light absorption and HOMO-LUMO energy levels, which determine the energy conversion efficiency of the devices [118, 125]. DFT enables correlating

molecular structure with electronic properties, such as HOMO and LUMO energy levels and energy gaps, which are essential parameters for the performance of photovoltaic devices [126–129]. Combined with time-dependent (TD)DFT, it is possible to compute excitation energies, oscillator strengths, and absorption characteristics and explore the structure of the involved excited states, thus producing atomistic data on the optical properties of materials [129–131]. This approach can provide rapid material screening and fine-tuning of properties, reducing the need for extensive experimentation and saving resources. Additionally, (TD)DFT provides detailed insights into the electronic structure and behavior of materials at the molecular level, guiding the selection of promising candidates and accelerating the innovation process in photovoltaic devices.

Although DFT and TDDFT have achieved widespread success in describing electronic and structural properties, their limitations remain significant, motivating the development of various exchange-correlation functionals [132–134]. Selecting the appropriate functional is critical for accurately capturing specific system properties, as not all functionals incorporate essential effects, such as long-range ones. For instance, hybrid functionals, while popular, often struggle to adequately describe long-range effects, which are essential for accurately describing the typical charge-transfer excited states of OSCs [71, 135–137].

TDDFT, widely employed to study excited states, has additional limitations, particularly in predicting the properties of excited states with strong charge-transfer character or having a sizeable electronic correlation. Alternative methods, such as *ab initio* wave functions, can offer greater accuracy in these cases [138–140]. For instance, the *ab initio* method ADC(2) (algebraic diagrammatic construction through second order) has shown notable capabilities in describing excited states. However, like other *ab initio* methods, it remains limited to smaller systems due to their high computational cost [24, 85, 139]. Additionally, they have limitations in describing the energies of molecular orbitals that are Hartree-Fock-type, which does not include electronic correlation effects [141–144]. To overcome these limitations, strategies that combine DFT with *ab initio* methods and the use of long-range or meta-GGA functionals present promising avenues for improving the description of optoelectronic properties in complex systems [71, 145, 146].

To theoretically assess the performance of OSCs, it is essential to examine different properties that directly impact their efficiency. Among the key parameters for measuring the efficiency of these devices, the power conversion efficiency (*PCE*) quantifies the device's ability to convert incident solar energy into electricity. The *PCE* is influenced by the short-circuit current (J_{sc}), the open-circuit voltage (V_{OC}), and the fill factor (*FF*). The latter reflects the quality of the cell by indicating internal losses and the efficiency of charge transport [43, 79, 147]. The device's ability to absorb light across different wavelengths is also crucial to maximize J_{sc} and enhances overall performance [43]. Another critical factor is charge mobility, given that high transport and low recombination rates ensure the efficient motion of electrons and holes, contributing to a more significant current generation [148, 149]

Understanding the relationship between the frontier orbital energy levels in donor-acceptor systems is essential because they directly affect the parameters that determine device efficiency. The frontier molecular orbitals, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), play a central role in light absorption and charge transfer processes in organic photovoltaic devices, as the energy difference between these levels affects electronic excitation and the efficient conversion of solar energy into electricity. A schematic diagram of the energy levels of a typical donor-acceptor system is shown in

Fig. 5. After photon absorption by the donor material, an exciton is formed. However, due to the low dielectric constant of organic materials, it is difficult to dissociate the strongly electrostatic bound exciton into free charges under normal (ambient) conditions. To overcome this binding energy, acceptor molecules with appropriately aligned HOMO and LUMO levels are required to produce the driving force for the rapid transfer of electrons from the donor to the acceptor. In this way, both the donor and the acceptor can contribute to the absorption spectrum of the solar cell, enhancing its efficiency in light capture and free charge generation.

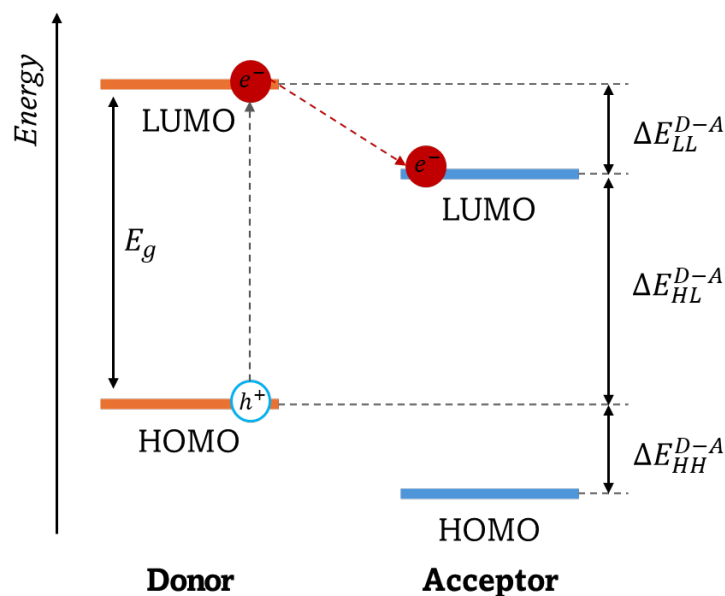


Fig. 5. Energy level diagram of a donor-acceptor system. Upon incidence of light, a hole (h^+) is produced in the ground state and an electron (e^-) is excited. The $e^- - h^+$ pair is an exciton. The energy differences on the right are discussed on the text.

Overall, the design of new donor molecules or materials for OSCs seeks to optimize three key parameters: light harvesting, hole mobility, and *PCE*. Light harvesting is characterized by the bandgap (E_g), absorption spectrum width, and molecular absorption coefficient [150, 151]. Controlling the bandgap is essential to fine-tune these properties [152, 153]. The HOMO-LUMO gap defined in Eq. (1) as the energy difference between the HOMO and LUMO is a fundamental measure of light absorption efficiency in organic materials.

$$E_g = E_{HOMO} - E_{LUMO} \quad (1)$$

A detailed understanding of HOMO-LUMO energy levels, as well as the energy differences between HOMO and HOMO-1 (ΔE_{HOMO}) and LUMO and LUMO+1 (ΔE_{LUMO}) of donor materials is thus essential for refining the design of photovoltaic materials, enabling fine adjustments that directly impact exciton dissociation efficiency and charge transport in devices. Small energy differences between in ΔE_{HOMO} and ΔE_{LUMO} indicate that nearby molecular orbitals can also contribute to exciton formation

and dissociation, as well as to hole and electron transport [152, 153]. In donor molecules with low ΔE_{HOMO} and ΔE_{LUMO} , defined by Eqs. (2) and (3) below, this additional contribution can enhance device efficiency.

$$\Delta E_{HOMO} = E_{HOMO} - E_{HOMO-1} \quad (2)$$

$$\Delta E_{LUMO} = E_{LUMO+1} - E_{LUMO} \quad (3)$$

The alignment of energy levels at donor (D)–acceptor (A) heterojunctions plays a crucial role in the mechanisms of charge generation and recombination in BHJ devices [154, 155]. The energy of the charge transfer state at the donor-acceptor (D/A) interface can be well approximated by the energy difference between the HOMO of the donor and the LUMO of the acceptor, ΔE_{HL}^{D-A} , defined by Eq. (4) below. This difference is widely used to estimate the driving force required for exciton dissociation at the D/A interface, a crucial process for the efficiency of photovoltaic devices. The alignment of the frontier molecular orbital levels at the donor-acceptor interface can be evaluated by the energy difference between the LUMO levels of the donor and acceptor, ΔE_{LL}^{D-A} , defined in Eq. (5). This parameter measures the degree of alignment between the LUMOs, directly influencing the photoelectric efficiency. Excessively high values of ΔE_{LL}^{D-A} indicate significant energy losses at the D/A interface, impairing device performance [24, 152].

$$\Delta E_{HL}^{D-A} = E_{LUMO}^A - E_{HOMO}^D \quad (4)$$

$$\Delta E_{LL}^{D-A} = E_{LUMO}^D - E_{LUMO}^A \quad (5)$$

There are also other relations between frontier orbitals in donor and acceptor materials. The energy difference between the HOMO of the donor and acceptor, ΔE_{HH}^{D-A} , defined in Eq. (6), quantify the alignment between the HOMOs of the molecules. A small difference in HOMO energy levels is advantageous for achieving a high open-circuit voltage (V_{OC}), significantly contributing to the overall performance of solar cells. On the

other hand, a larger HOMO offset facilitates more efficient charge separation; as this offset increases, the device's ability to effectively separate charges also improves, which is essential for maintaining high efficiency [156]. Wang and collaborators [157] emphasize that finding the optimal balance in this offset is crucial. A HOMO offset close to 0 eV can result in superior performance in OSCs, characterized by a high open-circuit voltage and an elevated fill factor, suggesting that charge separation reaches its maximum potential when the HOMO offset is carefully optimized [157, 158]. This quantity is relevant for understanding charge transfer and recombination processes at the D/A interface, and it is also a determining factor in optimizing materials for photovoltaic devices [159].

$$\Delta E_{HH}^{D-A} = E_{HOMO}^A - E_{HOMO}^D \quad (6)$$

The behavior of excitons in donor materials is crucial for understanding charge separation efficiency. In donor materials, electronic excitation by light generates an exciton strongly bound by a Coulombic (i.e., electrostatic) attraction. The exciton binding energy (E_{bind}) is defined as the difference between the fundamental gap (E_{fund}) and the optical gap (E_{opt}), which quantifies this binding energy of the exciton:

$$E_{bind} = E_{fund} - E_{opt} \quad (7)$$

In OSCs, due to the low dielectric constants of organic photoactive materials, E_{bind} can reach values of several tenths of an eV [160–165], making exciton dissociation into free charges extremely challenging in pure materials [166]. Thus, the lower the value of E_{bind} , the more easily the exciton can dissociate. Exciton dissociation into free holes and electrons at donor/acceptor (D/A) interfaces is driven by the energy level offsets between donor and acceptor materials, allowing the excitons to overcome the E_{bind} . Experimental and theoretical studies frequently report E_{bind} values ranging from 0.3 to 1.0 eV in typical materials used in BHJ solar cells and dye sensitizers in DSSCs [163, 167–171]. The fundamental gap, E_{fund} , plays an essential role in calculating the exciton

binding energy E_{bind} , as it reflects the energy difference between the adiabatic ionization potential (IP_a) and the adiabatic electron affinity (EA_a) [168]. The ionization potential is determined by the total energy difference between the ground state and the $N - 1$ electronic state, while the electron affinity is given by the energy difference between the N electron ground state and the $N + 1$ electronic state. IP_a and EA_a are computed using the adiabatic approach, which optimizes the geometries of the cation and anion separately. The fundamental gap E_{fund} is then given by the energy difference:

$$E_{fund} = IP_{(a)} - EA_{(a)} \quad (8)$$

The optical gap E_{opt} of a molecule corresponds to the energy of the lowest allowed electronic transition single photon absorption, often from the ground state S_0 to the first excited state S_1 . In this context, the optical gap E_{opt} is the energy difference between the optimized structures of the S_1 and S_0 states, representing the fundamental transition that directly influences the material's light absorption efficiency:

$$E_{opt} = E_{S_1} - E_{S_0} \quad (9)$$

To evaluate the performance of organic photovoltaic devices, calculating the PCE is essential, as it provides a direct measure of the device's ability to convert solar energy into electricity [14]. The equation for calculating the PCE is given by:

$$PCE = \frac{J_{sc} V_{oc} FF}{P_{in}} \quad (10)$$

The open-circuit voltage V_{oc} is an indicator of the material quality in organic solar cells. It represents the maximum voltage a solar cell can generate in the absence of current flow in the external circuit, corresponding to the energy difference between the energy levels of electrons and holes in the photoactive material under illumination [98,

172–174]. A high V_{oc} value suggests that the solar cell has efficient charge transport properties, resulting from an efficient alignment between the donor and acceptor energy levels. This alignment, due to a larger energy difference between the energy levels of electrons and holes, significantly reduces the probability of charge recombination, contributing to greater efficiency in charge transport and electric current generation [98, 175–177]. In a BHJ device, V_{oc} is determined by the energy difference between the HOMO of the donor and the LUMO of the acceptor, according to the largely used empirical Scharber equation [88, 178, 179]

$$V_{oc} = \frac{1}{e} (|E_{HOMO}^D - E_{LUMO}^{PCBM}|) - 0.3 \text{ V} \quad (11)$$

where e represents the elementary charge, $E_{LUMO}^{PCBM} = -3.80 \text{ eV}$ [180] is the energy of the LUMO orbital of the typical acceptor material PC₆₁BM, and 0.3 V is an empirical correction accounting for transport losses to the electrodes [179]. For evaluating donor materials in DSSCs, the open-circuit voltage V_{oc} is calculated from the energy difference between the LUMO of the dye and the conduction band edge of the typical semiconductor TiO_2 in these systems as follows:

$$V_{oc} = \frac{1}{e} (|E_{LUMO}^{Dye} - E_{CB}^{TiO_2}|) \quad (12)$$

where $E_{CB}^{TiO_2}$ is the conduction band edge of TiO_2 equal to -4.0 eV [181]. Another important parameter for determining the PCE is the fill factor (FF), which can be approximated as a function of the open-circuit voltage V_{oc} , temperature T , and the Boltzmann constant k_B using the following expression:

$$FF = \frac{\frac{eV_{oc}}{k_B T} - \ln\left(\frac{eV_{oc}}{k_B T} + 0.72\right)}{\frac{eV_{oc}}{k_B T} + 1} \quad (13)$$

The short-circuit current, J_{SC} , in a solar cell is a significant parameter that reflects the device's ability to generate current under solar illumination [182, 183]. It depends on factors such as light absorption by the donor material, the efficiency of electron-hole pair generation, charge collection efficiency, and the overlap between the material's absorption spectrum and the solar spectrum [184]. The greater this overlap and the more efficient the charge collection and transport processes, the higher the J_{SC} value. To compute J_{SC} , the external quantum efficiency (EQE) is integrated multiplied by the photon flux from the AM1.5 solar spectrum [185] over the relevant wavelength range [186]:

$$J_{SC} = e \int_{\lambda_{min}}^{\lambda_{max}} EQE(\lambda) \times photons(\lambda) d\lambda \quad (14)$$

This integration provides an accurate estimate of the generated current, offering a direct measure of the photocurrent performance of the solar cell and aiding in the optimization of materials and architectures to maximize device efficiency. In Eq. (14), λ_{min} and λ_{max} are the lower and upper wavelength limits of sunlight, respectively, under AM1.5 conditions. The AM1.5 spectrum is a standard reference for the spectral distribution of solar radiation. It refers to the global irradiance on a horizontal surface under a zenith angle of $\theta = 48.2^\circ$, representing typical sunlight conditions when it reaches the Earth's surface, with a total irradiance of 1000 W.m^{-2} [174, 185]. EQE is defined as the step function Θ , equal to 0% for photon energies below the optical band gap E_{opt} of the donor material and to 65% for photon energies above this threshold,

$$EQE = 0.65 \times \Theta(\hbar\omega - E_{opt}) \quad (15)$$

where $\hbar\omega$ is the energy of the incident photon. In addition to the EQE , which assesses the proportion of photons converted into electric current, the light harvesting efficiency (LHE) quantifies the material's ability to absorb incident photons:

$$LHE = 1 - 10^{-f} \quad (16)$$

where f represents the optical oscillator strength at the wavelength of maximum absorption λ_{max} . The LHE in DSSCs is directly related to J_{SC} because it represents the initial stage of light capture and absorption by the photosensitive dye, which is essential for generating electrical current in the device [79]. The LHE in DSSCs is related to J_{SC} through the following integral equation [79, 187],

$$J_{SC} = \int_{\lambda_{min}}^{\lambda_{max}} LHE(\lambda) \phi_{inject} \eta_{collect} d\lambda \quad (17)$$

where ϕ_{inject} is the electron injection efficiency and $\eta_{collect}$ represents the charge collection efficiency. $\eta_{collect}$ is considered constant and does not vary with the type of sensitizer used in the same DSSC device [79].

Driving Forces

In a solar cell, after light absorption by the active material, charge separation occurs at the donor-acceptor interface. The driving force for this dissociation is crucial to overcome the Coulombic attraction between the electron and hole in the exciton, thus allowing charges to be effectively separated [188–190]. The efficiency of this charge separation process is directly related to the solar cell's ability to generate electric current, as only dissociated free charges contribute to the current flow [191, 192]. Therefore, calculating the driving force for charge separation provides valuable insight into the device's efficiency potential, enabling the identification and enhancement of key parameters to maximize $PCEs$ and optimize the overall performance of the solar cell. One way to develop devices with high J_{SC} values is related to the driving force for charge separation in OSCs. This driving force plays a crucial role in overcoming the exciton binding energy, enabling the efficient dissociation of electron-hole pairs at the donor/acceptor interface. This process generates a larger number of free charges available for transport and collection at the electrodes, which directly contributes to an increase in J_{SC} [193]. In BHJ cells, the Gibbs free energy for the generation of separated charges,

which involves the transition from an initial singlet excited state, usually the S_1 , with energy E_{opt} , to a final separated charge state with energy E_{CS} , is given by [189, 194]

$$\Delta G_{separation} = E_{opt} - E_{CS} \quad (18)$$

In this equation, E_{CS} is the energy difference between the LUMO of the acceptor and the HOMO of the donor, which we defined above as ΔE_{HL}^{D-A} [189].

Eq. (14) for J_{SC} shows that another strategy to increase its values involves enhancing the electron injection efficiency ϕ_{inject} , which is directly related to the injection driving force (ΔG_{inject}). For DSSCs, the charge separation process can be evaluated by calculating the electron injection driving force, ΔG_{inject} , according to the equation [122, 195, 196]:

$$\Delta G_{inject} = E_{dye}^* - E_{CB}^{TiO_2} = (E_{dye} - E_{\lambda_{max}}) - E_{CB}^{TiO_2} \quad (19)$$

where $E_{CB}^{TiO_2}$ represents the value of the TiO_2 conduction band (-4.0 eV in vacuum), E_{dye}^* is the oxidation potential of the dye, which can be approximated by its respective E_{HOMO} , and $E_{\lambda_{max}}$ is the energy of the vertical transition associated with the maximum wavelength (λ_{max}).

Dye regeneration is a fundamental step in the operation of a DSSC, as it enables the replenishment of electrons transferred to the semiconductor, thereby maintaining the energy conversion cycle and ensuring device efficiency. Therefore, it is crucial to assess the effectiveness of this regeneration process through the regeneration driving force $\Delta G_{regenerate}$ defined as [79, 122, 195]

$$\Delta G_{regenerate} = E_{redox}^{I^-/I_3^-} - E_{dye} \quad (20)$$

where $E_{redox}^{I^-/I_3^-}$ represents the redox potential of the commonly used I^-/I_3^- electrolyte, with a value of -4.8 eV in vacuum. High values of both ΔG_{inject} and $\Delta G_{regenerate}$ enhance charge transfer efficiency between the semiconductor conduction band and the electrolyte, thus promoting effective electron injection and dye regeneration processes [79, 197].

In DSSCs, the dye is regenerated from its oxidized state within a few hundred picoseconds[198] Thus, it is essential to compute the recombination driving force to evaluate the dye regeneration process. The free energy of the recombination rate can be determined by the following expression [79, 199]:

$$\Delta G_{recombination} = E_{CB}^{TiO_2} - E_{dye} = E_{CB}^{TiO_2} - E_{HOMO} \quad (21)$$

The optimal performance of a DSSC is often characterized by a low $\Delta G_{recombination}$ value, suggesting a controlled and less spontaneous electron recombination process, which is favorable for maintaining effective charge separation.

Reorganization energy

The reorganization energy (λ) in the framework of Marcus theory of electron transfer is a critical parameter for correlating efficiency and J_{SC} in photovoltaic devices such as BHJ solar cells and DSSCs [79, 200]. In these devices, λ represents the energetic cost associated with geometric relaxation during the charge transfer process and is inversely proportional to the mobility of charge carriers [201–203]. In DSSCs, λ is related to the process in which an electron is transferred from the dye to the semiconductor after photon absorption [79]. In contrast, in BHJ solar cells, the reorganization energy is associated with charge transfer at the donor-acceptor interface [201]. For the electron-donor materials used in the active layers of organic solar cells, higher hole mobility compared to electron mobility is particularly important, as it contributes to efficient charge transport and, consequently, to the optimized performance of the device [79].

The reorganization energy can be divided into two main components: internal reorganization (λ_{int}) and external reorganization (λ_{ext}) [203]. The internal component λ_{int} , usually the most significant, is related to structural changes and energy level shifts in the molecules involved in the charge transfer process. In contrast, λ_{ext} is associated with environmental variations, such as the polarization of the surrounding medium during the charge transfer process [203]. Since λ_{ext} is estimated to be significantly smaller than λ_{int} , its contribution is often considered negligible [201, 204]. Therefore, it is common to assume that $\lambda \approx \lambda_{int}$, which simplifies the analyses and calculations of the reorganization energy. The total reorganization energy can be calculated from equation (22), where λ_h is the reorganization energy for holes and λ_e is reorganization energy for electrons,

$$\lambda_{total} = \lambda_h + \lambda_e \quad (22)$$

where λ_h is obtained from the following equations:

$$\lambda_h = \lambda_h^{(1)} + \lambda_h^{(2)} \quad (22)$$

$$\lambda_h^{(1)} = E^{(1)}(M) - E^{(0)}(M) \quad (23)$$

$$\lambda_h^{(2)} = E^{(1)}(M^+) - E^{(0)}(M^+) \quad (24)$$

The terms in Eqs. (22) to (24) are defined in the diagram depicted in

Fig. 6. M and M^+ represent the neutral and positively charged species (containing the hole), respectively. $E^{(0)}(M)$ and $E^{(0)}(M^+)$ are the energies of the neutral and cationic states in their respective minimum-energy geometries. $E^{(1)}(M^+)$ and $E^{(1)}(M)$ correspond to the energy of the cationic state in the geometry of the neutral molecule and the energy of the neutral state in the geometry of the cationic molecule, respectively. ΔE is the

adiabatic ionization energy, while $\lambda_h^{(1)}$ and $\lambda_h^{(2)}$ are the geometric relaxation energies for the neutral and cationic states, respectively.

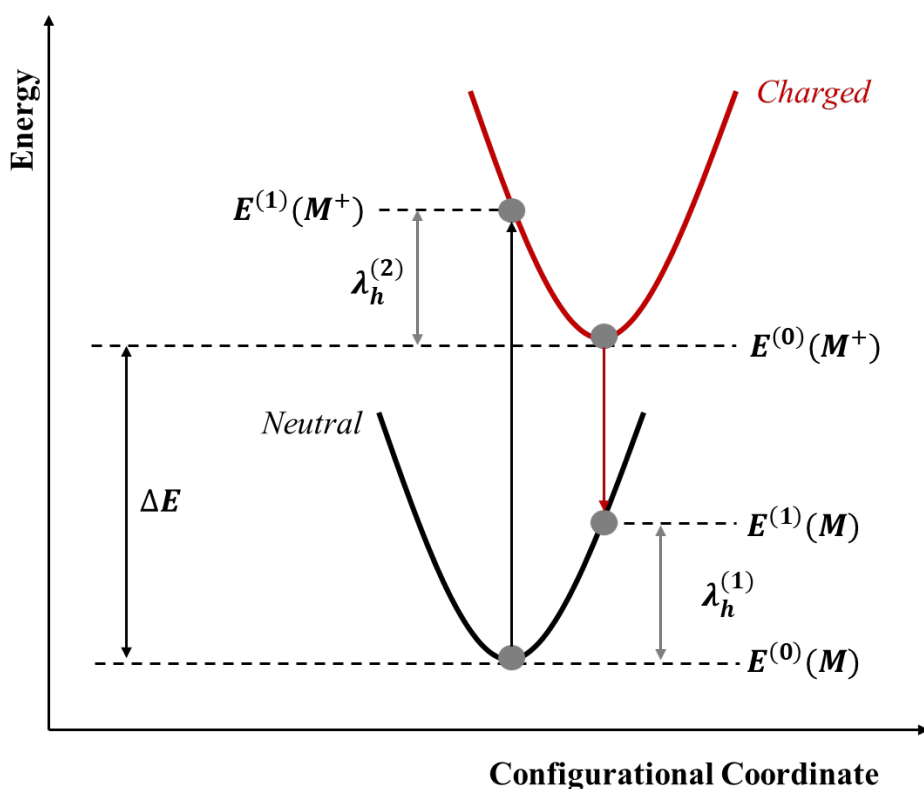


Fig. 6. Schematic representation of the potential energy surfaces for neutral and positively charged structures [201]. ΔE is the energy of adiabatic ionization, $E^{(0)}M$ and $E^{(0)}M^+$ are the energy of neutral and cationic states in the lower energy geometry, $E^{(1)}M$ and $E^{(1)}M^+$ the energy of cationic state in the geometry of the neutral molecule and the energy of neutral molecule in the geometry of the cationic molecule, and $\lambda_h^{(1)}$ and $\lambda_h^{(2)}$ are the energies of the geometric relaxation of the neutral and cationic states (reorganization energies), respectively.

The reorganization energy for electrons λ_e is obtained from similar equations:

$$\lambda_e = \lambda_e^{(1)} + \lambda_e^{(2)} \quad (25)$$

$$\lambda_e^{(1)} = E^{(1)}(M) - E^{(0)}(M) \quad (26)$$

$$\lambda_e^{(2)} = E^{(1)}(M^-) - E^{(0)}(M^-) \quad (27)$$

The hole transfer rate is inversely related to the reorganization energy involved in the process. Therefore, the higher the reorganization energy, the lower the hole mobility of the material. In general, reducing λ enhances charge transfer efficiency, allowing a larger proportion of photogenerated carriers to contribute to the photocurrent [79, 201]. For this reason, computing the reorganization energy is essential for optimizing the performance of devices such as BHJ and DSSC, providing insights for the development of materials that affords faster charge transport rates thus improved photovoltaic performance.

Global Reactivity Descriptors for Photovoltaics

Global reactivity descriptors are important quantities for understanding the electronic properties and predicting the reactive behavior of materials used in organic solar cells. These parameters enable the evaluation of stability and energy alignment between donor and acceptor components, which are critical factors for the efficiency of these devices. Ionization energy, electron affinity, chemical potential, hardness, and electronegativity values provide insights into charge transfer capabilities and exciton separation at the donor-acceptor interface. Electrophilicity values help identifying materials that can improve photoelectric efficiency. The analysis of these descriptors calculated using DFT can contribute to the rational design of new materials with optimized properties for high-performance photovoltaic devices.

Chemical hardness (η) is a parameter that reflects the stability of a compound and its resistance to electron exchange with the environment. Calculated by Eq. (28), chemical hardness is determined by the adiabatic ionization potential (IP) and the adiabatic electron affinity (EA), defined above. In general, the higher the chemical hardness of a compound, the greater its stability, indicating lower reactivity and higher resistance to electronic changes of its molecular state [205–207]. Chemical hardness is directly related to the

conversion efficiency in DSSCs and BHJs because lower chemical hardness tends to result in higher conversion efficiency [208–211].

$$\eta = \frac{1}{2}(IP - EA) \quad (28)$$

Electrophilicity (ω), measures the tendency of a compound to accept electrons, and it is defined by Eq. (29). This index quantifies the energy stabilization of a system as it absorbs the maximum electron flow from a donor. Higher electrophilicity indicates a greater capacity for electron acceptance, reflecting the compound's reactivity in electron-transfer processes [210–212].

$$\omega = \frac{(IP + EA)^2}{4(IP - EA)} \quad (29)$$

A donor material for applications in a BHJ or DSSC is expected to exhibit a high electron-donating capacity along with a high electron-accepting capacity. The electron-donating power (ω^-) and electron-accepting power (ω^+) are useful parameters described by Eqs. (30) and (31) [213], which evaluate a molecule's ability to donate and accept electrons, respectively. A lower ω^- value indicates a higher electron-donating capacity, while a higher ω^+ value reflects a better ability to accept electrons [208, 211, 214].

$$\omega^+ = \frac{(IP + 3EA)^2}{16(IP - EA)} \quad (29)$$

$$\omega^- = \frac{(3IP + EA)^2}{16(IP - EA)} \quad (30)$$

Electronegativity (χ) [206, 215], defined as the ability of a compound to attract electrons, can be calculated by Eq. (31). In OSCs, compounds with high electronegativity values tend to attract electrons more strongly, which can increase charge recombination rates. This effect reduces the number of free charges for generating electrical current, negatively impacting the solar cell's efficiency. In dyes in DSSCs, an increase in dye electronegativity is associated with a reduction in the open-circuit voltage (V_{OC}). The absolute electronegativity of the dye plays a crucial role in modulating electron diffusion, directly influencing the charge recombination mechanism through the dye [216].

$$\chi = \frac{(IP + EA)}{2} \quad (31)$$

Using Koopmann's theorem [217–219] these descriptors can be computed using HOMO and LUMO values. Koopmans' theorem establishes approximately the HOMO and LUMO energy values from the ionization potential (IP) and electron affinity (EA) in molecular systems according to the following expressions: $IP = -E_{HOMO}$ and $EA = -E_{LUMO}$. This implies that, in electronic structure calculations, the energies of the frontier orbitals can be directly used to estimate these properties. In a recent study [24], we showed that the using adiabatic IP and EA values provides an accurate description of electronic properties, as they account for the optimized geometries of ionic states, enabling a more realistic representation of electron loss and gain processes in the investigated systems.

In D-A-D systems based on diketopyrrolopyrrole (DPP) [24], it allowed the assessment of material stability, reactivity, and charge transfer capability, providing critical insights into HOMO-LUMO energy levels, charge separation efficiency, and potential applications in photovoltaic devices. Arunkumar and collaborators [76] investigated a series of D- π -A dyes based on tetrahydroquinoline, highlighting the relationship between chemical hardness and increased intramolecular charge transfer character. They identified two dyes with superior hole and electron transport properties, demonstrating their potential applicability in photovoltaic devices.

In summary, achieving high efficiency in DSSCs and BHJs OSCs requires optimizing several fundamental parameters related to charge separation, electron injection, dye regeneration, and reduction of charge recombination rates. When considered together, these theoretical evaluations provide a comprehensive understanding of the factors influencing efficiency in these OSCs, providing a solid foundation for targeted improvements in material design and device architecture. By focusing on these properties, researchers can adjust the balance of internal processes within OSCs more precisely, promoting significant advancements in performance and long-term stability for next-generation photovoltaic devices.

The importance of a judicious choice of the exchange-correlation functional in DFT for obtaining accurate values of HOMO and LUMO for computing optoelectronic properties

Selecting the appropriate exchange-correlation functional and basis set directly impacts the accuracy of the frontier orbital values, used to compute the optoelectronic properties of organic materials for OPVs according to the formulae above.

Hybrid functionals such as B3LYP [220] are widely used in organic systems due to their good balance between accuracy and computational cost, providing reliable results for general electronic properties [25, 221–226]. However, the selection of hybrid functionals should be approached with caution, as they may underestimate the spatial separation between frontier orbitals and may describe poorly charge transfer effects [227–231]. Overall, E_{HOMO} values predicted by hybrid functionals are more accurate than those obtained with pure functionals, which depend exclusively on the local or semi-local electron densities and are relatively sensitive to the fraction of Hartree-Fock (HF) exchange [229, 232]. Functionals with higher HF exchange fractions usually yield more accurate E_{HOMO} values, which are particularly relevant for systems where orbital localization and charge separation are critical for photovoltaic performance [229, 233].

Although higher HF exchange fractions improve the accuracy of HOMO levels, they frequently overestimate LUMO energies and, consequently, widen the HOMO-LUMO gap. Moreover, as highlighted by Zhang and collaborators [229], generalized gradient approximation (GGA) functionals have a smaller systematic error in predicting HOMO-LUMO gaps, despite inaccuracies in the absolute values of orbital levels. Including a significant fraction of HF exchange in long-range functionals, such as in CAM-B3LYP, further degrades the accuracy of E_{LUMO} values, leading to predictions that can significantly diverge from experimental data [229, 233, 234].

Khan and collaborators recently studied seven donor molecules based on benzo[1,2-b:4,5-b']dithiophene (BDT) with an A- π -D- π -A configuration, using DFT and TDDFT methods. The analysis of maximum absorption wavelengths identified the CAM-B3LYP functional as the most accurate, outperforming ω B97XD, B3LYP, and MPW1PW91 [73]. In a similar study, Bora and collaborators designed five new donor- π -acceptor- π -donor (D- π -A- π -D)-type conjugated acceptors, employing quinacridone as the donor, thiophene as the π bridge component, and five distinct central acceptor units. By correlating the calculated HOMO and LUMO energies, the gap energy E_g , and absorption wavelength values (λ_{max}) with experimental data, they found that the HSEH1PBE functional, using the 6-31G(d) basis set, showed the best agreement with experimental results compared to B3LYP, B3PW91, B3LYP-D3, CAM-B3LYP, PBEPBE, and ω B97XD [235].

Moudou and colleagues [236] recently reported that the B3LYP functional (20% HF exchange) provided results close to experimental values compared to the CAM-B3LYP, B3PW91, ω B97XD e MPW1PW91 functionals for six push-pull (D- π -A) molecules containing the MTPA core with different π -spacers. The results showed good agreement with the experimental data, highlighting a reduction in E_g for the thiophene and benzothiazole spacers. The B3LYP functional is widely used in the study of dye-sensitized solar cells (DSSC), offering good performance [25, 237–239]. A series of quinoxaline-based chromophores was investigated by Shafiq *et al.*, aiming to evaluate the efficiency of different functionals, including MPW1PW91, CAM-B3LYP, M06, and M06-2X, in predicting UV-vis properties. For the MTHR molecule, the MPW1PW91

functional (25% HF exchange) showed the best agreement with experimental data. The results highlighted MTH1 as a promising chromophore, achieving a *PCE* of 17.85% and V_{OC} of 1.285 V [128]. Haider and collaborators [240] evaluated modifications in the terminal groups of pyrene-based dyes, investigating the reference molecule with various functionals, including B3LYP, CAM-B3LYP, MPW1PW91, and ω B97XD. Based on the maximum absorption wavelength, the ω B97XD functional showed the best agreement with experimental values. Using DFT calculations, several properties were determined, such as frontier molecular orbital (FMO) energies, optical properties, LHE, FF, V_{OC} , among others.

We recently investigated the design and application in BHJ and DSSC OSCs of nine star-shaped molecules with a triazine (Tr) core built with thiophene (Th), phenyl (Ph), and carbazole (Cz) fragments. For the Tr-Th and Tr-Cz systems, we used TDDFT to calculate excited-state electronics properties, using the B3LYP, PBE, M06-2X, CAM-B3LYP, ω B97XD, and LC-wPBE functionals. We found that the B3LYP frontier molecular orbital energy values agreed with available experimental data and similar systems containing the triazine core. Although the PBE functional also yielded good results, with deviations of approximately 11% for HOMO and LUMO energy values in the Tr-Cz system, B3LYP provided a more balanced combination of accuracy and computational cost. Despite the low fraction of HF exchange, which is relevant for systems having significant charge transfer effects, as in semiconductor polymers, the B3LYP functional remains widely used, with a large body of recent studies showing satisfactory results for calculating optoelectronic properties in donor and acceptor materials for organic photovoltaic devices [241, 242]. Many investigations have shown that, although B3LYP may underestimate some electronic properties of conjugated organic systems, it still offers good relative accuracy in predicting HOMO and LUMO energy levels and optical gaps. Its simplicity, along with a good balance between computational cost and accuracy, make B3LYP a popular choice in research focused on designing and optimizing materials for OSCs [25, 241–246].

Finally, it is important to highlight the recommendations of Bursch and collaborators [228], which guide the selection of the functional based on the chemical

system and the specific task, rather than on popularity alone. First, it is advisable always to include a dispersion correction to improve accuracy in intermolecular interactions. Additionally, it is recommended to assess cost-effective combinations, considering the use of (m)GGA-type functionals, which, although less precise than hybrids, offer lower computational costs. Hybrid functionals are preferred for accuracy, but their use should be balanced against computational demand. Verifying consistency across different classes of functionals—such as comparing a hybrid with an (m)GGA—is also suggested, especially in comparative analyses. In critical cases, it may be useful to test hybrids that include different fractions of HF exchange to ensure that the results accurately reflect the properties of the system under study.

The choice of basis set is a crucial factor for the accuracy of optoelectronic property calculations and should consider the type of system studied, the required precision, and computational cost. Basis sets such as 6-31G(d,p) [225, 247, 248] or 6-311G(d,p) [242, 246, 249, 250] are widely used for medium-sized organic molecules, as they balance cost and accuracy, making them suitable for fundamental electronic properties like HOMO-LUMO energy levels. For systems requiring higher accuracy, especially in large conjugated structures, basis sets like Def2-SVP [25, 251–253] or Def2-TZVP [253–255] are recommended due to their detailed descriptions of electronic interactions and orbitals. Thus, the selection should balance available computational resources with the level of detail required by the study.

On the importance of the DFT HOMO and LUMO value for computing the OPV properties: the triazine molecule as an illustrative case

The relationship between *PCE* in OSCs and HOMO-LUMO energy levels is directly associated with fundamental processes such as charge separation, electron, and hole transport, and charge recombination. The alignment between donor and acceptor HOMO and LUMO energy levels, for instance, plays a crucial role in determining the open-circuit voltage (V_{OC}), a key parameter for achieving good *PCE* values.

We recently investigated [25] the influence of the choice of functional on the determination of the HOMO and LUMO energy levels in donor-acceptor (D-A) systems with a triazine (Tr) nucleus. We investigated nine star molecules with this nucleus, finding *PCE* values close to 30% due to a favorable alignment of the energy levels. The calculations employed the B3LYP, PBE, M06-2X, CAM-B3LYP, wB97XD, and LC-wPBE functionals, to analyze their impact on the optoelectronic properties of the systems.

The literature indicates that, for conjugated D-A systems containing a triazine nucleus, the HOMO and LUMO energy values typically vary between -5.0 and -6.0 eV (HOMO) and between -1.5 and -3.5 eV (LUMO) [255-258]. In our work, we found that the B3LYP functional produced the smallest deviations compared to the experimental data, with only 0.6% deviation for the HOMO and 37.4% for the LUMO. The PBE functional also presented good results, with deviations close to 11%, but the B3LYP stood out for providing a more balanced combination of accuracy and computational cost.

The analysis of the HOMO and LUMO levels showed a significant influence on the optoelectronic properties of the systems, in particular on the band gap energy (E_g). The wB97XD E_g values were significantly higher, around 7.6 eV, in contrast to the B3LYP results, around 3.9 eV. Although the corresponding exciton binding energy (E_{bind}) did not show substantial variations between the two functionals, the parameters related to the driving force showed a significant dependence on the HOMO and LUMO energy levels.

In addition, parameters such as V_{OC} and *PCE* were also shown to be strongly influenced by the frontier orbitals. For the systems containing a triazine core, the wB97XD functional resulted in a maximum *PCE* value of 10.58% for a BHJ and 10.26% for a DSSC. On the other hand, the B3LYP functional led to a maximum *PCE* of 32.39%, evidencing that the precision in the alignment of the HOMO and LUMO levels can drastically affect the optoelectronic properties of OPVs.

Systems with optimized HOMO-LUMO levels favored charge transport by reducing recombination rates and improving electron and hole mobility. In triazine-based systems, substituents such as carbazole stabilized these energy levels, positively impacting photovoltaic performance. These results emphasize the importance of adjusting computational methods and molecular design to optimize energy level alignment and improve the efficiency of photovoltaic devices.

Conclusion

This work systematically presented the main processes involved in producing an electric current in BHJ solar cells and DSSCs. We discussed these processes in detail and presented several simple equations for computing relevant practical properties of these devices using DFT. We also discussed the limitations of this approach, mainly related to the choice of the exchange-correlation functional.

By providing reliable and accurate predictions, DFT-based methods can accelerate the screening of promising materials, significantly reducing the time and costs associated with laboratory experiments. Furthermore, DFT can facilitate the rational design of donor and acceptor materials, allowing for precise tuning of their electronic and structural properties to maximize performance. This approach has been essential in addressing challenges such as exciton dissociation, charge recombination, and device stability, leading to significant advancements in the field. Although significant advances have been made in understanding the relationship between electronic properties and the efficiency of organic photovoltaic devices, challenges remain, including the need for a comprehensive evaluation of functionals and basis sets suitable for different chemical systems. In this context, we emphasize the importance of selecting computational methodologies appropriate to the specific problem, striving to balance computational cost and accuracy.

References

1. Smets AHM, Jäger Klaus, Isabella Olindo, et al (2016) Solar energy: the physics and engineering of photovoltaic conversion, technologies and systems. UIT Cambridge Ltd., Cambridge
2. Herzog A V, Lipman TE, Kammen DM Renewable Energy Sources. In: Perspectives and Overview of Life Support Systems and Sustainable Development. <https://www.eolss.net/sample-chapters/c08/E3-03-27.pdf> . Accessed 15 Dec 2024
3. Energy Institute (2024) Statistical Review of World Energy. <https://www.energyinst.org/statistical-review> . Accessed 15 Dec 2024
4. Ferruzzi G, Delcea C, Barberi A, et al (2023) Concentrating Solar Power: The State of the Art, Research Gaps and Future Perspectives. *Energies (Basel)* 16:1–39. <https://doi.org/10.3390/en16248082>
5. Pazheri FR, Othman MF, Malik NH (2014) A review on global renewable electricity scenario. *Renewable and Sustainable Energy Reviews* 31:835–845. <https://doi.org/10.1016/j.rser.2013.12.020>
6. Lyu X, Ruan T, Wang W, Cai X (2024) A bibliometric evaluation and visualization of global solar power generation research: productivity, contributors and hot topics. *Environmental Science and Pollution Research* 31:8274–8290. <https://doi.org/10.1007/s11356-023-31715-x>
7. Thirugnanasambandam M, Iniyan S, Goic R (2010) A review of solar thermal technologies. *Renewable and Sustainable Energy Reviews* 14:312–322. <https://doi.org/10.1016/j.rser.2009.07.014>
8. Subtil Lacerda J, Van Den Bergh JCJM (2016) Diversity in solar photovoltaic energy: Implications for innovation and policy. *Renewable and Sustainable Energy Reviews* 54:331–340. <https://doi.org/10.1016/j.rser.2015.10.032>
9. Sampaio PGV, González MOA (2017) Photovoltaic solar energy: Conceptual framework. *Renewable and Sustainable Energy Reviews* 74:590–601. <https://doi.org/10.1016/j.rser.2017.02.081>

10. Green MA (2000) Photovoltaics: technology overview. *Energy Policy* 28:989–998. <https://doi.org/10.1063/1.1697243>
11. Sano M, Pope M, Kallmann H (1965) Electroluminescence and band gap in anthracene. *J Chem Phys* 43:2920–2921. <https://doi.org/10.1063/1.1697243>
12. Pope M, Kallmann HP, Magnante P (1963) Electroluminescence in organic crystals. *J Chem Phys* 38:2042–2043. <https://doi.org/10.1063/1.1733929>
13. Helfrich W, Schneider WG (1965) Recombination Radiation in Anthracene Crystals. *Phys Rev Lett* 14:229–231. <https://doi.org/10.1103/PhysRevLett.14.229>
14. Ostroverkhova O (2016) Organic Optoelectronic Materials: Mechanisms and Applications. *Chem Rev* 116:13279–13412. <https://doi.org/10.1021/acs.chemrev.6b00127>
15. Köhler A, Bässler H (2015) *Electronic Processes in Organic Semiconductors*, First Edition. Wiley-VCH, Weinheim, Germany
16. Douglass Plenum DH, York N, M Varma by C, et al (1959) Electrical Conductivity in Doped Polyacetylene. *Phys Rev Lett* 39:415. <https://doi.org/10.1103/PhysRevLett.39.1098>
17. Chiang CK, Park YW, Heeger AJ, et al (1978) Conducting polymers: Halogen doped polyacetylene. *J Chem Phys* 69:5098–5104. <https://doi.org/10.1063/1.436503>
18. Hideki Shirakawa B, Louis EJ, Macdiarmid AG, et al (1977) Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)_x. *J Chem Soc Chem Commun* 578–580. <https://doi.org/10.1039/C39770000578>
19. Borges I, Aquino AJA, Köhn A, et al (2013) Ab initio modeling of excitonic and Charge-transfer states in organic semiconductors: The PTB1/PCBM low band gap system. *J Am Chem Soc* 135:18252–18255. <https://doi.org/10.1021/ja4081925>
20. Gupta N, Nagar MR, Anamika, et al (2022) Triazine and Thiophene-Containing Conjugated Polymer Network Emitter-Based Solution-Processable Stable Blue

- Organic LEDs. *ACS Appl Polym Mater* 5:130–140.
<https://doi.org/10.1021/acsapm.2c01337>
21. Rasool A, Zahid S, Ans M, et al (2022) Bithieno Thiophene-Based Small Molecules for Application as Donor Materials for Organic Solar Cells and Hole Transport Materials for Perovskite Solar Cells. *ACS Omega* 7:844–862.
<https://doi.org/10.1021/acsomega.1c05504>
 22. Zhou H, Yang L, You W (2012) Rational design of high performance conjugated polymers for organic solar cells. *Macromolecules* 45:607–632.
<https://doi.org/10.1021/ma201648t>
 23. Sun D, Si C, Wang T, Zysman-Colman E (2022) 1,3,5-Triazine-Functionalized Thermally Activated Delayed Fluorescence Emitters for Organic Light-Emitting Diodes. *Adv Photonics Res* 3:1-54. <https://doi.org/10.1002/adpr.202200203>
 24. Rosa NMP, Borges I (2024) Photophysical properties of donor (D)–acceptor (A)–donor (D) diketopyrrolopyrrole (A) systems as donors for applications to organic electronic devices. *J Comput Chem* 45:2885–2898.
<https://doi.org/10.1002/jcc.27492>
 25. Rosa NMP, Borges I (2024) Star-Shaped Molecules with a Triazine Core: (TD)DFT Investigation of Charge Transfer and Photovoltaic Properties of Organic Solar Cells. *Brazilian Journal of Physics* 54:252.
<https://doi.org/10.1007/s13538-024-01636-2>
 26. Kaur N, Singh M, Pathak D, et al (2014) Organic materials for photovoltaic applications: Review and mechanism. *Synth Met* 190:20–26.
<https://doi.org/10.1016/j.synthmet.2014.01.022>
 27. Oni AM, Mohsin ASM, Rahman MM, Hossain Bhuian MB (2024) A comprehensive evaluation of solar cell technologies, associated loss mechanisms, and efficiency enhancement strategies for photovoltaic cells. *Energy Reports* 11:3345–3366. <https://doi.org/10.1016/j.egy.2024.03.007>
 28. Zhu L, Zhang M, Xu J, et al (2022) Single-junction organic solar cells with over 19% efficiency enabled by a refined double-fibril network morphology. *Nat Mater* 21:656–663. <https://doi.org/10.1038/s41563-022-01244-y>

29. Wang J, Zheng Z, Zu Y, et al (2021) A Tandem Organic Photovoltaic Cell with 19.6% Efficiency Enabled by Light Distribution Control. *Advanced Materials* 33:1-9. <https://doi.org/10.1002/adma.202102787>
30. Chong K, Xu X, Meng H, et al (2022) Realizing 19.05% Efficiency Polymer Solar Cells by Progressively Improving Charge Extraction and Suppressing Charge Recombination. *Advanced Materials* 34:1-11. <https://doi.org/10.1002/adma.202109516>
31. Zhang KN, Du XY, Yan L, et al (2024) Organic Photovoltaic Stability: Understanding the Role of Engineering Exciton and Charge Carrier Dynamics from Recent Progress. *Small Methods* 8:1-29. <https://doi.org/10.1002/smtd.202300397>
32. Li C, Zhou J, Song J, et al (2021) Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells. *Nat Energy* 6:605–613. <https://doi.org/10.1038/s41560-021-00820-x>
33. Cui Y, Xu Y, Yao H, et al (2021) Single-Junction Organic Photovoltaic Cell with 19% Efficiency. *Advanced Materials* 33:1-8. <https://doi.org/10.1002/adma.202102420>
34. Zheng Z, Wang J, Bi P, et al (2022) Tandem Organic Solar Cell with 20.2% Efficiency. *Joule* 6:171–184. <https://doi.org/10.1016/j.joule.2021.12.017>
35. Cusumano P, Arnone C, Giambra MA, Parisi A (2020) Donor/acceptor heterojunction organic solar cells. *Electronics (Switzerland)* 9:1-8. <https://doi.org/10.3390/electronics9010070>
36. Malk FH, Abdul Karem AAH, Al – Tememe EH (2022) Organic Solar Cells: Short Review. *MINAR International Journal of Applied Sciences and Technology* 4:174–181. <https://doi.org/10.47832/2717-8234.13.16>
37. Clarke TM, Durrant JR (2010) Charge photogeneration in organic solar cells. *Chem Rev* 110:6736–6767. <https://doi.org/10.1021/cr900271s>
38. Balzer D, Kassal I (2024) Delocalisation enables efficient charge generation in organic photovoltaics, even with little to no energetic offset. *Chem Sci.* 15:4779-4789. <https://doi.org/10.1039/d3sc05409h>

39. Firdaus Y, Le Corre VM, Karuthedath S, et al (2020) Long-range exciton diffusion in molecular non-fullerene acceptors. *Nat Commun* 11:1-10. <https://doi.org/10.1038/s41467-020-19029-9>
40. Solak EK, Irmak E (2023) Advances in organic photovoltaic cells: a comprehensive review of materials, technologies, and performance. *RSC Adv* 13:12244–12269. <https://doi.org/10.1039/d3ra01454a>
41. Schlenker CW, Thompson ME (2012) Current challenges in organic photovoltaic solar energy conversion. *Top Curr Chem* 312:175–212. https://doi.org/10.1007/128_2011_219
42. Reese MO, Nardes AM, Rupert BL, et al (2010) Photoinduced degradation of polymer and polymer-fullerene active layers: Experiment and theory. *Adv Funct Mater* 20:3476–3483. <https://doi.org/10.1002/adfm.201001079>
43. Rafique S, Abdullah SM, Sulaiman K, Iwamoto M (2018) Fundamentals of bulk heterojunction organic solar cells: An overview of stability/degradation issues and strategies for improvement. *Renewable and Sustainable Energy Reviews* 84:43–53. <https://doi.org/10.1016/j.rser.2017.12.008>
44. Liu Q, Jiang Y, Jin K, et al (2020) 18% Efficiency organic solar cells. *Sci Bull (Beijing)* 65:272–275. <https://doi.org/10.1016/j.scib.2020.01.001>
45. Jing J, Dong S, Zhang K, et al (2022) Semitransparent Organic Solar Cells with Efficiency Surpassing 15%. *Adv Energy Mater* 12:1-11. <https://doi.org/10.1002/aenm.202200453>
46. Cui Y, Xu Y, Yao H, et al (2021) Single-Junction Organic Photovoltaic Cell with 19% Efficiency. *Advanced Materials* 33:1-8. <https://doi.org/10.1002/adma.202102420>
47. Xu S, Zhang Y, Sun Y, et al (2025) An Unprecedented Efficiency with Approaching 21% Enabled by Additive-Assisted Layer-by-Layer Processing in Organic Solar Cells. *Nanomicro Lett* 17:37. <https://doi.org/10.1007/s40820-024-01529-8>

48. Chen C, Wang L, Xia W, et al (2024) Molecular interaction induced dual fibrils towards organic solar cells with certified efficiency over 20%. *Nat Commun* 15:1-10. <https://doi.org/10.1038/s41467-024-51359-w>
49. Green MA, Dunlop ED, Hohl-Ebinger J, et al (2020) Solar cell efficiency tables (Version 55). *Progress in Photovoltaics: Research and Applications* 28:3–15. <https://doi.org/10.1002/pip.3228>
50. Green MA, Dunlop ED, Yoshita M, et al (2024) Solar cell efficiency tables (Version 64). *Progress in Photovoltaics: Research and Applications* 32:425–441. <https://doi.org/10.1002/pip.3831>
51. Green M, Dunlop E, Hohl-Ebinger J, et al (2021) Solar cell efficiency tables (version 57). *Progress in Photovoltaics: Research and Applications* 29:3–15. <https://doi.org/10.1002/pip.3371>
52. Green MA, Emery K, Hishikawa Y, et al (2015) Solar cell efficiency tables (Version 45). *Progress in Photovoltaics: Research and Applications* 23:1–9. <https://doi.org/10.1002/pip.2573>
53. Green MA, Emery K, Hishikawa Y, et al (2017) Solar cell efficiency tables (version 49). *Progress in Photovoltaics: Research and Applications* 25:3–13. <https://doi.org/10.1002/pip.2855>
54. Green MA, Hishikawa Y, Dunlop ED, et al (2018) Solar cell efficiency tables (version 51). *Progress in Photovoltaics: Research and Applications* 26:3–12. <https://doi.org/10.1002/pip.2978>
55. Green MA, Dunlop ED, Hohl-Ebinger J, et al (2022) Solar cell efficiency tables (version 59). *Progress in Photovoltaics: Research and Applications* 30:3–12. <https://doi.org/10.1002/pip.3506>
56. Green MA, Hishikawa Y, Dunlop ED, et al (2019) Solar cell efficiency tables (Version 53). *Progress in Photovoltaics: Research and Applications* 27:3–12. <https://doi.org/10.1002/pip.3102>
57. Green MA, Dunlop ED, Yoshita M, et al (2024) Solar cell efficiency tables (Version 63). *Progress in Photovoltaics: Research and Applications* 32:3–13. <https://doi.org/10.1002/pip.3750>

58. Green MA, Dunlop ED, Siefer G, et al (2023) Solar cell efficiency tables (Version 61). *Progress in Photovoltaics: Research and Applications* 31:3–16. <https://doi.org/10.1002/pip.3646>
59. Green MA, Emery K, Hishikawa Y, et al (2013) Solar cell efficiency tables (version 41). *Progress in Photovoltaics: Research and Applications* 21:1–11. <https://doi.org/10.1002/pip.2352>
60. Green MA, Emery K, Hishikawa Y, et al (2014) Solar cell efficiency tables (version 43). *Progress in Photovoltaics: Research and Applications* 22:1–9. <https://doi.org/10.1002/pip.2452>
61. Green MA, Emery K, Hishikawa Y, Warta W (2011) Solar cell efficiency tables (version 37). *Progress in Photovoltaics: Research and Applications* 19:84–92. <https://doi.org/10.1002/pip.1088>
62. Green MA, Emery K, Hishikawa Y, et al (2016) Solar cell efficiency tables (version 47). *Progress in Photovoltaics: Research and Applications* 24:3–11. <https://doi.org/10.1002/pip.2728>
63. Green MA, Emery K, Hishikawa Y, et al (2012) Solar cell efficiency tables (version 39). *Progress in Photovoltaics: Research and Applications* 20:12–20. <https://doi.org/10.1002/pip.2163>
64. Green MA, Emery K, Hishikawa Y, Warta W (2010) Solar cell efficiency tables (version 35). *Progress in Photovoltaics: Research and Applications* 18:144–150. <https://doi.org/10.1002/pip.974>
65. Green MA, Emery K, Hishikawa Y, Warta W (2009) Solar cell efficiency tables (Version 33). *Progress in Photovoltaics: Research and Applications* 17:85–94. <https://doi.org/10.1002/pip.880>
66. Green MA, Emery K, King DL, et al (2007) Solar cell efficiency tables (version 29). *Progress in Photovoltaics: Research and Applications* 15:35–40. <https://doi.org/10.1002/pip.741>
67. Green MA, Emery K, Hishikawa Y, Warta W (2008) Solar cell efficiency tables (version 31). *Progress in Photovoltaics: Research and Applications* 16:61–67. <https://doi.org/10.1002/pip.808>

68. Green MA, Dunlop ED, Yoshita M, et al (2024) Solar Cell Efficiency Tables (Version 65). Progress in Photovoltaics: Research and Applications. <https://doi.org/10.1002/pip.3867>
69. Hösel M, Søndergaard RR, Jørgensen M, Krebs FC (2014) Failure modes and fast repair procedures in high voltage organic solar cell installations. Adv Energy Mater 4:1-7. <https://doi.org/10.1002/aenm.201301625>
70. Modesto-Costa L, Borges I, Aquino AJA, Lischka H (2018) Electronic structure theory gives insights into the higher efficiency of the PTB electron-donor polymers for organic photovoltaics in comparison with prototypical P3HT. Journal of Chemical Physics 149:1–7. <https://doi.org/10.1063/1.5054919>
71. Borges I, Uhl E, Modesto-Costa L, et al (2016) Insight into the Excited State Electronic and Structural Properties of the Organic Photovoltaic Donor Polymer Poly(thieno[3,4-b]thiophene benzodithiophene) by Means of ab Initio and Density Functional Theory. Journal of Physical Chemistry C 120:21818–21826. <https://doi.org/10.1021/acs.jpcc.6b07689>
72. Sharma SJ, Sekar N (2024) Exploring charge transfer effects on linear, non-linear optical, and dye-sensitized solar cell properties: A DFT and TD-DFT investigation of carbazole and aniline-based dyes. Int J Quantum Chem 124:1-22. <https://doi.org/10.1002/qua.27419>
73. Usman Khan M, Shafiq F, Ramzan Saeed Ashraf Janjua M, et al (2024) Predicting benzodithiophene based donor materials with enhanced 19.09% PCE, open-circuit voltage and optoelectronic attributes for solar cell applications: Photochemical insights from DFT. J Photochem Photobiol A Chem 446:1-16. <https://doi.org/10.1016/j.jphotochem.2023.115115>
74. Pourebrahimi S, Pirooz M (2024) Exploring the optoelectronic properties of Flavylum cations as acceptors in organic solar Cells: DFT/TD-DFT investigations. Solar Energy 275:1–11. <https://doi.org/10.1016/j.solener.2024.112617>
75. Mejbel HK, Al-Badry LF (2024) Tuning the optoelectronic properties for small organic compounds as organic solar cell applications. Optoelectron Lett 20:412–417. <https://doi.org/10.1007/s11801-024-3165-7>

76. Arunkumar A, Ju XH (2024) Computational method on highly efficient D- π -A- π -D-based different molecular acceptors for organic solar cells applications and non-linear optical behaviour. *Spectrochim Acta A Mol Biomol Spectrosc* 317:1-15. <https://doi.org/10.1016/j.saa.2024.124391>
77. Sadiq S, Khera RA, Tawfeek AM, et al (2024) Theoretical investigation of substituted end groups in thiophene-phenyl-thiophene (TPT) derivatives for high efficiency organic solar cells. *J Phys Org Chem* 37:1-15. <https://doi.org/10.1002/poc.4607>
78. Le Bahers T, Labat F, Pauporté T, et al (2011) Theoretical procedure for optimizing dye-sensitized solar cells: From electronic structure to photovoltaic efficiency. *J Am Chem Soc* 133:8005–8013. <https://doi.org/10.1021/ja201944g>
79. Conradie J (2024) Effective dyes for DSSCs—Important experimental and calculated parameters. *Energy Nexus* 13:1-15. <https://doi.org/10.1016/j.nexus.2024.100282>
80. Bernède JC (2008) Organic Photovoltaic Cells: History, Principle and Techniques. *J Chil Chem Soc* 53:1549-1564. <https://doi.org/10.4067/S0717-97072008000300001>
81. Moliton A, Nunzi JM (2006) How to model the behaviour of organic photovoltaic cells. *Polym Int* 55:583–600. <https://doi.org/10.1002/pi.2038>
82. Ramoroka ME, Yussuf ST, Nwambaekwe KC, et al (2024) Advances in Organic Photovoltaic Cells: Fine-Tuning of the Photovoltaic Processes. *Solar RRL* 8:1-29. <https://doi.org/10.1002/solr.202300982>
83. Nelson J (2002) Organic photovoltaic films. *Curr Opin Solid State Mater Sci* 6:87–95. [https://doi.org/10.1016/S1359-0286\(02\)00006-2](https://doi.org/10.1016/S1359-0286(02)00006-2)
84. Sampaio PGV, González MOA (2022) A review on organic photovoltaic cell. *Int J Energy Res* 46:17813–17828 <https://doi.org/10.1002/er.8456>
85. Borges I, Guimarães RMPO, Monteiro-de-Castro G, et al (2023) A comprehensive analysis of charge transfer effects on donor-pyrene (bridge)-acceptor systems using different substituents. *J Comput Chem* 44:2424–2436. <https://doi.org/10.1002/jcc.27208>

86. Liu H, Geng Y, Xiao Z, et al (2024) The Development of Quinoxaline-Based Electron Acceptors for High Performance Organic Solar Cells. *Advanced Materials*. 36:1-35. <https://doi.org/10.1002/adma.202404660>
87. Zhou D, Wang Y, Yang S, et al (2024) Recent Advances of Benzodithiophene-Based Donor Materials for Organic Solar Cells. *Small* 20:1-67. <https://doi.org/10.1002/sml.202306854>
88. Scharber MC, Sariciftci NS (2013) Efficiency of bulk-heterojunction organic solar cells. *Prog Polym Sci* 38:1929–1940. <https://doi.org/10.1016/j.progpolymsci.2013.05.001>
89. Grätzel M (2003) Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4:145–153. [https://doi.org/10.1016/S1389-5567\(03\)00026-1](https://doi.org/10.1016/S1389-5567(03)00026-1)
90. Hagfeldt A, Boschloo G, Sun L, et al (2010) Dye-sensitized solar cells. *Chem Rev* 110:6595–6663. <https://doi.org/10.1021/cr900356p>
91. Jean R (2009) Molecular bulk heterojunctions: An emerging approach to organic solar cells. *Acc Chem Res* 42:1719–1730. <https://doi.org/10.1021/ar900041b>
92. Lu L, Zheng T, Wu Q, et al (2015) Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem Rev* 115:12666–12731. <https://doi.org/10.1021/acs.chemrev.5b00098>
93. Deibel C, Dyakonov V (2010) Polymer-fullerene bulk heterojunction solar cells. *Reports on Progress in Physics* 73:1-40. <https://doi.org/10.1088/0034-4885/73/9/096401>
94. Facchetti A (2013) Polymer donor-polymer acceptor (all-polymer) solar cells. *Materials Today* 16:123–132. <https://doi.org/10.1016/j.mattod.2013.04.005>
95. Dou L, You J, Hong Z, et al (2013) 25th anniversary article: A decade of organic/polymeric photovoltaic research. *Advanced Materials* 25:6642–6671. <https://doi.org/10.1002/adma.201302563>
96. Meftah M, Damé L, Bolsée D, et al (2018) SOLAR-ISS: A new reference spectrum based on SOLAR/SOLSPEC observations. *Astron Astrophys* 611:1-14. <https://doi.org/10.1051/0004-6361/201731316>

97. Mayer AC, Scully SR, Hardin BE, et al (2007) Polymer-based solar cells. 10:28-33. [https://doi.org/10.1016/S1369-7021\(07\)70276-6](https://doi.org/10.1016/S1369-7021(07)70276-6)
98. Qi B, Wang J (2012) Open-circuit voltage in organic solar cells. *J Mater Chem* 22:24315–24325. <https://doi.org/10.1039/c2jm33719c>
99. Cui C, Li Y (2019) High-performance conjugated polymer donor materials for polymer solar cells with narrow-bandgap nonfullerene acceptors. *Energy Environ Sci* 12:3225–3246. <https://doi.org/10.1039/C9EE02531F>
100. Yang H, Cui C, Li Y (2021) Effects of Heteroatom Substitution on the Photovoltaic Performance of Donor Materials in Organic Solar Cells. *Acc Mater Res* 2:986–997. <https://doi.org/10.1021/accountsmr.1c00119>
101. He K, Kumar P, Yuan Y, et al (2021) A Wide Bandgap Polymer Donor Composed of Benzodithiophene and Oxime-Substituted Thiophene for High-Performance Organic Solar Cells. *ACS Appl Mater Interfaces* 13:26441–26450. <https://doi.org/10.1021/acsami.1c02442>
102. An C, Zheng Z, Hou J (2020) Recent progress in wide bandgap conjugated polymer donors for high-performance nonfullerene organic photovoltaics. *Chemical Communications* 56:4750–4760. <https://doi.org/10.1039/d0cc01038c>
103. Fakharuddin A, Jose R, Brown TM, et al (2014) A perspective on the production of dye-sensitized solar modules. *Energy Environ Sci* 7:3952–3981. <https://doi.org/10.1039/C4EE01724B>
104. Ashok A, Mathew SE, Shivaram SB, et al (2018) Cost effective natural photosensitizer from upcycled jackfruit rags for dye sensitized solar cells. *Journal of Science: Advanced Materials and Devices* 3:213–220. <https://doi.org/10.1016/j.jsamd.2018.04.006>
105. Avilés-Betanzos R, Oskam G, Pourjafari D (2023) Low-Temperature Fabrication of Flexible Dye-Sensitized Solar Cells: Influence of Electrolyte Solution on Performance under Solar and Indoor Illumination. *Energies (Basel)* 16:1–35. <https://doi.org/10.3390/en16155617>

106. Li G, Sheng L, Li T, et al (2019) Engineering flexible dye-sensitized solar cells for portable electronics. *Solar Energy* 177:80–98.
<https://doi.org/10.1016/j.solener.2018.11.017>
107. Hendi AA, Alanazi MM, Alharbi W, et al (2023) Dye-sensitized solar cells constructed using titanium oxide nanoparticles and green dyes as photosensitizers. *J King Saud Univ Sci* 35:1–7.
<https://doi.org/10.1016/j.jksus.2023.102555>
108. Alessa H, Wijyantha KGU (2024) A very simple flexible tandem dye-sensitized solar cell. *Journal of Umm Al-Qura University for Applied Sciences* 1–9.
<https://doi.org/10.1007/s43994-024-00136-y>
109. Shakeel Ahmad M, Pandey AK, Abd Rahim N (2017) Advancements in the development of TiO₂ photoanodes and its fabrication methods for dye sensitized solar cell (DSSC) applications. A review. *Renewable and Sustainable Energy Reviews* 77:89–108. <https://doi.org/10.1016/j.rser.2017.03.129>
110. Jamalullail N, Mohamad IS, Norizan MN, et al (2017) Recent improvements on TiO₂ and ZnO nanostructure photoanode for dye sensitized solar cells: A brief review. *EPJ Web Conf* 162:1–5. <https://doi.org/10.1051/epjconf/201716201045>
111. Kannan S (2018) A REVIEW ON TITANIUM DIOXIDE FOR DYE SENSITIZED SOLAR CELLS APPLICATION. *Int J Curr Adv Res* 7:10575–10579. <https://doi.org/10.24327/ijcar.2018.10579.1797>
112. Shaban S, Pradhan S, Pandey SS (2023) Fabrication and Characterization of Bifacial Dye-Sensitized Solar Cells Utilizing Indoline Dye with Iodine- and Cobalt-Based Redox Electrolytes. *Physica Status Solidi (A) Applications and Materials Science* 220:1–7. <https://doi.org/10.1002/pssa.202300241>
113. Jeon J, Park YC, Han SS, et al (2014) Rapid dye regeneration mechanism of dye-sensitized solar cells. *Journal of Physical Chemistry Letters* 5:4285–4290.
<https://doi.org/10.1021/jz502197b>
114. Yan W, Xiang F, Ou J, et al (2024) Highly efficient dye-sensitized solar cells achieved by matching energy levels between pseudohalogen redox couples and organic donor- π -acceptor cyanoacrylic acid dyes. *Electrochim Acta* 473:1–10.
<https://doi.org/10.1016/j.electacta.2023.143522>

115. Hailu YM, Nguyen MT, Jiang JC (2020) Theoretical study on the interaction of iodide electrolyte/organic dye with the TiO₂ surface in dye-sensitized solar cells. *Physical Chemistry Chemical Physics* 22:26410–26418. <https://doi.org/10.1039/d0cp02532a>
116. Andualem A, Demiss S (2018) Review on Dye-Sensitized Solar Cells (DSSCs). *Journal of Heterocyclics* 1:29–34. <https://doi.org/10.33805/2639-6734.103>
117. Grätzel M (2005) Solar energy conversion by dye-sensitized photovoltaic cells. *Inorg Chem* 44:6841–6851. <https://doi.org/10.1021/ic0508371>
118. Setsoafia DDY, Ram KS, Mehdizadeh-Rad H, et al (2022) DFT and TD-DFT Calculations of Orbital Energies and Photovoltaic Properties of Small Molecule Donor and Acceptor Materials Used in Organic Solar Cells. *J Renew Mater* 10:2553–2567. <https://doi.org/10.32604/jrm.2022.020967>
119. Bouzzine SM, Abdelaaziz A, Hamidi M, et al (2024) Computational investigation of geometrical and optoelectronic properties of isolated and adsorbed organic bi-anchoring dyes-based different donors on TiO₂ surfaces. *Mater Sci Semicond Process* 174:1-14. <https://doi.org/10.1016/j.mssp.2024.108189>
120. Pourebrahimi S, Pirooz M (2024) Exploring the optoelectronic properties of Flavylum cations as acceptors in organic solar Cells: DFT/TD-DFT investigations. *Solar Energy* 275:1-11. <https://doi.org/10.1016/j.solener.2024.112617>
121. El Mouhi R, Slimi A, Fitri A, et al (2022) DFT, DFTB and TD-DFT theoretical investigations of π -conjugated molecules based on thieno[2,3-b] indole for dye-sensitized solar cell applications. *Physica B Condens Matter* 636:1–13. <https://doi.org/10.1016/j.physb.2022.413850>
122. Xu Z, Li Y, Zhang W, et al (2019) DFT/TD-DFT study of novel T shaped phenothiazine-based organic dyes for dye-sensitized solar cells applications. *Spectrochim Acta A Mol Biomol Spectrosc* 212:272–280. <https://doi.org/10.1016/j.saa.2019.01.002>
123. El-Meligy AB, Koga N, Iuchi S, et al (2018) DFT/TD-DFT calculations of the electronic and optical properties of bis-N,N-dimethylaniline-based dyes for use in

- dye-sensitized solar cells. *J Photochem Photobiol A Chem* 367:332–346.
<https://doi.org/10.1016/j.jphotochem.2018.08.036>
124. AL-Temimei FA, Omran Alkhayatt AH (2020) A DFT/TD-DFT investigation on the efficiency of new dyes based on ethyl red dye as a dye-sensitized solar cell light-absorbing material. *Optik (Stuttg)* 208:1–7.
<https://doi.org/10.1016/j.ijleo.2019.163920>
125. Khlaifia D, Chemek M, Alimi K (2020) DFT/TDDFT approach: an incredible success story in prediction of organic materials properties for photovoltaic application. *Moroccan Journal of Chemistry* 8:683–699.
<https://doi.org/10.48317/IMIST.PRSM/morjchem-v8i3.18518>
126. Shi H, Liang Y, Hou B, et al (2025) Theoretical study of the photovoltaic properties of dye-sensitized solar cells with novel D-A- π -A-type benzothiazole molecules as auxiliary acceptors. *Chem Phys* 591:1-11.
<https://doi.org/10.1016/j.chemphys.2024.112562>
127. Asghar MA, Jabbar A, Nadeem S, et al (2025) Photovoltaic response promoted via intramolecular charge transfer in triphenylpyridine core with small acceptors: A DFT/TD-DFT study. *Mater Sci Semicond Process* 186:1-14.
<https://doi.org/10.1016/j.mssp.2024.109086>
128. Shafiq I, Nasrullah S, Zafar M, et al (2024) Structural Modeling of Fluorinated Quinoxaline Core-Based Chromophores for Efficient Photovoltaic Materials: A DFT Study. *J Phys Org Chem*. 1-16. <https://doi.org/10.1002/poc.4663>
129. Gara R, Morales-García Á, Arfaoui Y, Illas F (2025) Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) Studies of Porphyrin Adsorption on Graphene: Insights on the Effect of Substituents and Central Metal on Adsorption Energies. *J Comput Chem* 46:1-10. <https://doi.org/10.1002/jcc.27526>
130. Kamalinalahad S, Vessally E, Noormohammadbeigi M (2025) Improving the efficiency of organic solar cells using non-fullerene acceptor for molecular engineering of IDT-based chromophores. *J Photochem Photobiol A Chem* 462:..
<https://doi.org/10.1016/j.jphotochem.2024.116185>
131. Li J, Wang L, Gao H, et al (2025) Enhancing optoelectronic performance of organic solar cells: Alkoxy substitution of central cores and π -bridge units in fully

- non-fused ring electron acceptors. *J Mol Liq* 417:1-11.
<https://doi.org/10.1016/j.molliq.2024.126681>
132. Makkar P, Ghosh NN (2021) A review on the use of DFT for the prediction of the properties of nanomaterials. *RSC Adv* 11:27897–27924.
<https://doi.org/10.1039/D1RA04876G>
133. Oh Y, Song S, Bae J (2024) A Review of Bandgap Engineering and Prediction in 2D Material Heterostructures: A DFT Perspective. *Int J Mol Sci* 25:1-27.
<https://doi.org/10.3390/ijms252313104>
134. De Angelis F (2014) Modeling materials and processes in hybrid/organic photovoltaics: From dye-sensitized to perovskite solar cells. *Acc Chem Res* 47:3349–3360. <https://doi.org/10.1021/ar500089n>
135. Dreuw A, Plötner J, Wormit M, et al (2010) An Additive Long-range Potential to Correct for the Charge-transfer Failure of Time-dependent Density Functional Theory. *Progress in Physical Chemistry Volume 3: Modern and Universal First-principles Methods for Many-electron Systems in Chemistry and Physics*, edited by Franz Michael Dolg, München: Oldenbourg Wissenschaftsverlag, 2010, pp. 21-34. <https://doi.org/10.1524/9783486711639.21>
136. Marmolejo-Valencia AF, Mata-Pinzón Z, Amador-Bedolla C (2021) Charge-transfer electronic states in organic solar cells: A TDDFT study. *Physical Chemistry Chemical Physics* 23:16806–16815.
<https://doi.org/10.1039/d1cp00723h>
137. Ribeiro RB, Varella MT do N (2024) Excited state properties of an A-D-A non-fullerene electron acceptor: a LC-TD-DFTB study. *Physical Chemistry Chemical Physics* 26:12993–13005. <https://doi.org/10.1039/d3cp06166c>
138. Pershin A, Szalay PG (2015) Improving the Accuracy of the Charge Transfer Integrals Obtained by Coupled Cluster Theory, MBPT(2), and TDDFT. *J Chem Theory Comput* 11:5705–5711. <https://doi.org/10.1021/acs.jctc.5b00837>
139. Trofimov AB, Stelter G, Schirmer J (2002) Electron excitation energies using a consistent third-order propagator approach: Comparison with full configuration interaction and coupled cluster results. *Journal of Chemical Physics* 117:6402–6410. <https://doi.org/10.1063/1.1504708>

140. Dreuw A, Head-Gordon M (2005) Single-reference ab initio methods for the calculation of excited states of large molecules. *Chem Rev* 105:4009–4037. <https://doi.org/10.1021/cr0505627>
141. Corzo HH (2023) Chapter 1 - The importance of correlation in the molecular orbital picture. In: Kaya S, von Szentpály L, Serdaroğlu G, Guo L (eds) *Chemical Reactivity*. Elsevier, pp 1–26. <https://doi.org/10.1016/B978-0-32-390257-1.00007-3>.
142. Onishi T (2018) Hartree-Fock Method. In: *Quantum Computational Chemistry: Modelling and Calculation for Functional Materials*. Springer Singapore, Singapore, pp 27–39. https://doi.org/10.1007/978-981-10-5933-9_3
143. Dreuw A, Papapostolou A, Dempwolff AL (2023) Algebraic Diagrammatic Construction Schemes Employing the Intermediate State Formalism: Theory, Capabilities, and Interpretation. *Journal of Physical Chemistry A* 127:6635–6646. <https://doi.org/10.1021/acs.jpca.3c02761>
144. Hodecker M, Dempwolff AL, Rehn DR, Dreuw A (2019) Algebraic-diagrammatic construction scheme for the polarization propagator including ground-state coupled-cluster amplitudes. I. Excitation energies. *Journal of Chemical Physics* 150:174104. <https://doi.org/10.1063/1.5081663>
145. Mester D, Kállay M (2022) Charge-Transfer Excitations within Density Functional Theory: How Accurate Are the Most Recommended Approaches? *J Chem Theory Comput* 18:1646–1662. <https://doi.org/10.1021/acs.jctc.1c01307>
146. Li H, Nieman R, Aquino AJA, et al (2014) Comparison of LC-TDDFT and ADC(2) methods in computations of bright and charge transfer states in stacked oligothiophenes. *J Chem Theory Comput* 10:3280–3289. <https://doi.org/10.1021/ct500072f>
147. Sikiru S, Oladosu TL, Amosa TI, et al (2022) Recent advances and impact of phase change materials on solar energy: A comprehensive review. *J Energy Storage* 53:1–20. <https://doi.org/10.1016/j.est.2022.105200>
148. Tan CH, Zhang J, Jia T, et al (2023) The Role of Device Mobility on the Charge Generation Process in Polymerized Small-Molecule Acceptor Based Organic

- Solar Cells. *Journal of Physical Chemistry C* 127:12135–12142.
<https://doi.org/10.1021/acs.jpcc.3c02104>
149. Brédas JL, Norton JE, Cornil J, Coropceanu V (2009) Molecular understanding of organic solar cells: The challenges. *Acc Chem Res* 42:1691–1699.
<https://doi.org/10.1021/ar900099h>
150. Ragoussi ME, Torres T (2015) Organic photovoltaics. *Revista Virtual de Química* 7:112–125. <https://doi.org/10.5935/1984-6835.20150007>
151. Hedström S, Henriksson P, Wang E, et al (2014) Light-harvesting capabilities of low band gap donor-acceptor polymers. *Physical Chemistry Chemical Physics* 16:24853–24865. <https://doi.org/10.1039/c4cp03191a>
152. Sahu H, Ma H (2019) Unraveling Correlations between Molecular Properties and Device Parameters of Organic Solar Cells Using Machine Learning. *Journal of Physical Chemistry Letters* 10:7277–7284.
<https://doi.org/10.1021/acs.jpcllett.9b02772>
153. Sahu H, Rao W, Troisi A, Ma H (2018) Toward Predicting Efficiency of Organic Solar Cells via Machine Learning and Improved Descriptors. *Adv Energy Mater* 8:1–9. <https://doi.org/10.1002/aenm.201801032>
154. Li X, Zhang Q, Yu J, et al (2022) Mapping the energy level alignment at donor/acceptor interfaces in non-fullerene organic solar cells. *Nat Commun* 13:1–9. <https://doi.org/10.1038/s41467-022-29702-w>
155. Oehzelt M, Akaike K, Koch N, Heimel G (2015) Computer Modeling: Energy-level alignment at organic heterointerfaces. *Sci Adv* 1:1–8.
<https://doi.org/10.1126/sciadv.1501127>
156. Zhang J, Liu W, Zhou G, et al (2020) Accurate Determination of the Minimum HOMO Offset for Efficient Charge Generation using Organic Semiconducting Alloys. *Adv Energy Mater* 10:1–8. <https://doi.org/10.1002/aenm.201903298>
157. Wang L, Zhang C, Su Z, et al (2023) Near 0 eV HOMO offset enable high-performance nonfullerene organic solar cells with large open circuit voltage and fill factor. *J Mater Chem C* 11:6971–6980. <https://doi.org/10.1039/D3TC00547J>

158. Liu W, Zhang J, Xu S, Zhu X (2019) Efficient organic solar cells achieved at a low energy loss. *Sci Bull (Beijing)* 64:1144–1147.
<https://doi.org/10.1016/j.scib.2019.07.005>
159. Zhang J, Liu W, Zhang M, et al (2019) Revealing the Critical Role of the HOMO Alignment on Maximizing Current Extraction and Suppressing Energy Loss in Organic Solar Cells. *iScience* 19:883–893.
<https://doi.org/10.1016/j.isci.2019.08.038>
160. Kraner S, Scholz R, Plasser F, et al (2015) Exciton size and binding energy limitations in one-dimensional organic materials. *Journal of Chemical Physics* 143:1–7. <https://doi.org/10.1063/1.4938527>
161. News R, Brédas J-L, Cornil J, Heeger AJ (1996) The Exciton Binding Energy in Luminescent Conjugated Polymers. *Adv. Mater.* 8:447–452.
<https://doi.org/10.1002/adma.19960080517>
162. Shuai Z, Pati SK, Su WP, et al (1997) Binding energy of 1Bu singlet excitons in the one-dimensional extended Hubbard-Peierls model. *Phys Rev B* 55:368–371.
<https://doi.org/10.1103/PhysRevB.55.15368>
163. Sun H, Hu Z, Zhong C, et al (2016) Quantitative Estimation of Exciton Binding Energy of Polythiophene-Derived Polymers Using Polarizable Continuum Model Tuned Range-Separated Density Functional. *Journal of Physical Chemistry C* 120:8048–8055. <https://doi.org/10.1021/acs.jpcc.6b01975>
164. Knupfer M (2003) Exciton binding energies in organic semiconductors. *Appl Phys A Mater Sci Process* 77:623–626. <https://doi.org/10.1007/s00339-003-2182-9>
165. Zhu L, Yi Y, Chen L, Shuai Z (2008) Exciton Binding Energy of Electronic Polymers: A First Principles Study. *J Theor Comput Chem* 11:517–530.
<https://doi.org/10.1142/S0219633608003939>
166. Zhu L, Wei Z, Yi Y (2022) Exciton Binding Energies in Organic Photovoltaic Materials: A Theoretical Perspective. *Journal of Physical Chemistry C* 126:14–21. <https://doi.org/10.1021/acs.jpcc.1c08898>

167. Kashani S, Rech JJ, Liu T, et al (2024) Exciton Binding Energy in Organic Polymers: Experimental Considerations and Tuning Prospects. *Adv Energy Mater* 14:1–15. <https://doi.org/10.1002/aenm.202302837>
168. Bredas JL (2014) Mind the gap! *Mater Horiz* 1:17–19. <https://doi.org/10.1039/c3mh00098b>
169. Kraner S, Scholz R, Koerner C, Leo K (2015) Design Proposals for Organic Materials Exhibiting a Low Exciton Binding Energy. *Journal of Physical Chemistry C* 119:22820–22825. <https://doi.org/10.1021/acs.jpcc.5b07097>
170. Nayak PK (2013) Exciton binding energy in small organic conjugated molecule. *Synth Met* 174:42–45. <https://doi.org/10.1016/j.synthmet.2013.04.010>
171. Dkhissi A (2011) Excitons in organic semiconductors. *Synth Met* 161:1441–1443. <https://doi.org/10.1016/j.synthmet.2011.04.003>
172. Elumalai NK, Uddin A (2016) Open circuit voltage of organic solar cells: An in-depth review. *Energy Environ Sci* 9:391–410. <https://doi.org/10.1039/c5ee02871j>
173. Marinova N, Valero S, Delgado JL (2017) Organic and perovskite solar cells: Working principles, materials and interfaces. *J Colloid Interface Sci* 488:373–389. <https://doi.org/10.1016/j.jcis.2016.11.021>
174. Arno Smets, René van Swaaij, Klaus Jäger, et al (2016) *Solar energy The physics and engineering of photovoltaic conversion, technologies and systems*. UIT Cambridge.
175. Nelson J, Kirkpatrick J, Ravirajan P (2004) Factors limiting the efficiency of molecular photovoltaic devices. *Phys Rev B Condens Matter Mater Phys* 69:1–11. <https://doi.org/10.1103/PhysRevB.69.035337>
176. Vandewal K, Tvingstedt K, Gadisa A, et al (2009) On the origin of the open-circuit voltage of polymer-fullerene solar cells. *Nat Mater* 8:904–909. <https://doi.org/10.1038/nmat2548>
177. Potscavage WJ, Yoo S, Kippelen B (2008) Origin of the open-circuit voltage in multilayer heterojunction organic solar cells. *Appl Phys Lett* 93:1–4. <https://doi.org/10.1063/1.3027061>

178. Qi B, Zhou Q, Wang J (2015) Exploring the open-circuit voltage of organic solar cells under low temperature. *Sci Rep* 5:1–10. <https://doi.org/10.1038/srep11363>
179. Scharber MC, Mühlbacher D, Koppe M, et al (2006) Design rules for donors in bulk-heterojunction solar cells - Towards 10 % energy-conversion efficiency. *Advanced Materials* 18:789–794. <https://doi.org/10.1002/adma.200501717>
180. Niinomi T, Matsuo Y, Hashiguchi M, et al (2009) Penta(organo)[60]fullerenes as acceptors for organic photovoltaic cells. *J Mater Chem* 19:5804–5811. <https://doi.org/10.1039/b904485j>
181. Asbury JB, Wang Y-Q, Hao E, et al (2001) Evidences of hot excited state electron injection from sensitizer molecules to TiO₂ nanocrystalline thin films. *Res Chem Intermed* 27:393–406. <https://doi.org/10.1163/156856701104202255>
182. Padilla M, Michl B, Thaidigsmann B, et al (2014) Short-circuit current density mapping for solar cells. *Solar Energy Materials and Solar Cells* 120:282–288. <https://doi.org/10.1016/j.solmat.2013.09.019>
183. Hartnagel P, Kirchartz T (2020) Understanding the Light-Intensity Dependence of the Short-Circuit Current of Organic Solar Cells. *Adv Theory Simul* 3:1–11. <https://doi.org/10.1002/adts.202000116>
184. Lu N, Li L, Sun P, Liu M (2014) Short-circuit current model of organic solar cells. *Chem Phys Lett* 614:27–30. <https://doi.org/10.1016/j.cplett.2014.08.070>
185. (2020) ASTM Standard G173-03. Standard Tables for Reference Solar Spectrallrradiances: Direct Normal and Hemispherical on 37° Tilted Surface. In: ASTM International. <https://www.astm.org/g0173-03r20.html> . Accessed 15 Dec 2024
186. Bérubé N, Gosselin V, Gaudreau J, Côté M (2013) Designing polymers for photovoltaic applications using ab initio calculations. *Journal of Physical Chemistry C* 117:7964–7972. <https://doi.org/10.1021/jp309800f>
187. Feng J, Jiao Y, Ma W, et al (2013) First principles design of dye molecules with ullazine donor for dye sensitized solar cells. *Journal of Physical Chemistry C* 117:3772–3778. <https://doi.org/10.1021/jp310504n>

188. Han G, Yi Y (2022) Molecular Insight into Efficient Charge Generation in Low-Driving-Force Nonfullerene Organic Solar Cells. *Acc Chem Res* 55:869–877. <https://doi.org/10.1021/acs.accounts.1c00742>
189. Nakano K, Chen Y, Xiao B, et al (2019) Anatomy of the energetic driving force for charge generation in organic solar cells. *Nat Commun* 10:1–10. <https://doi.org/10.1038/s41467-019-10434-3>
190. Coffey DC, Larson BW, Hains AW, et al (2012) An optimal driving force for converting excitons into free carriers in excitonic solar cells. *Journal of Physical Chemistry C* 116:8916–8923. <https://doi.org/10.1021/jp302275z>
191. Lüer L, Wang R, Liu C, et al (2024) Maximizing Performance and Stability of Organic Solar Cells at Low Driving Force for Charge Separation. *Advanced Science* 11:1–20. <https://doi.org/10.1002/advs.202305948>
192. Ward AJ, Ruseckas A, Kareem MM, et al (2015) The impact of driving force on electron transfer rates in photovoltaic donor-acceptor blends. *Advanced Materials* 27:2496–2500. <https://doi.org/10.1002/adma.201405623>
193. Yang W, Yao Y, Guo P, et al (2018) Optimum driving energy for achieving balanced open-circuit voltage and short-circuit current density in organic bulk heterojunction solar cells. *Physical Chemistry Chemical Physics* 20:29866–29875. <https://doi.org/10.1039/c8cp05145c>
194. Liu J, Chen S, Qian D, et al (2016) Fast charge separation in a non-fullerene organic solar cell with a small driving force. *Nat Energy* 1:16089. <https://doi.org/10.1038/nenergy.2016.89>
195. Sun LL, Zhang T, Wang J, et al (2015) Exploring the influence of electron donating/withdrawing groups on hexamolybdate-based derivatives for efficient p-type dye-sensitized solar cells (DSSCs). *RSC Adv* 5:39821–39827. <https://doi.org/10.1039/c5ra05164a>
196. Xu Z, Lu X, Li Y, Wei S (2020) Theoretical analysis on heteroleptic Cu(I)-based complexes for dye-sensitized solar cells: Effect of anchors on electronic structure, spectrum, excitation, and intramolecular and interfacial electron transfer. *Molecules* 25:1-15. <https://doi.org/10.3390/molecules25163681>

197. Megala M, Rajkumar BJM (2016) Theoretical study of anthoxanthin dyes for dye sensitized solar cells (DSSCs). *J Comput Electron* 15:557–568.
<https://doi.org/10.1007/s10825-016-0791-8>
198. Benesperi I, Michaels H, Freitag M (2018) The researcher's guide to solid-state dye-sensitized solar cells. *J Mater Chem C Mater* 6:11903–11942.
<https://doi.org/10.1039/C8TC03542C>
199. Keremane KS, Abdellah IM, Naik P, et al (2020) Simple thiophene-bridged D- π -A type chromophores for DSSCs: a comprehensive study of their sensitization and co-sensitization properties. *Physical Chemistry Chemical Physics* 22:23169–23184. <https://doi.org/10.1039/d0cp02781b>
200. Zhang ZL, Zou LY, Ren AM, et al (2013) Theoretical studies on the electronic structures and optical properties of star-shaped triazatruxene/heterofluorene copolymers. *Dyes and Pigments* 96:349–363.
<https://doi.org/10.1016/j.dyepig.2012.08.020>
201. Oliveira EF, Lavarda FC (2016) Reorganization energy for hole and electron transfer of poly(3-hexylthiophene) derivatives. *Polymer (Guildf)* 99:105–111.
<https://doi.org/10.1016/j.polymer.2016.07.003>
202. Poelking Carl and Daoulas K and TA and AD (2014) Morphology and Charge Transport in P3HT: A Theorist's Perspective. In: Ludwigs S (ed) *P3HT Revisited – From Molecular Scale to Solar Cell Devices*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp 139–180. https://doi.org/10.1007/12_2014_277
203. García G, Moral M, Garzón A, et al (2012) Poly(arylenethynyl-thienoacenes) as candidates for organic semiconducting materials. A DFT insight. *Org Electron* 13:3244–3253. <https://doi.org/10.1016/j.orgel.2012.09.029>
204. Hutchison GR, Ratner MA, Marks TJ (2005) Hopping transport in conductive heterocyclic oligomers: Reorganization energies and substituent effects. *J Am Chem Soc* 127:2339–2350. <https://doi.org/10.1021/ja0461421>
205. Parr RG, Pearson RG (1983) Absolute Hardness: Companion Parameter to Absolute Electronegativity. *J Am Chem Soc* 105:7512–7516.
<https://doi.org/10.1021/ja00364a005>

206. Pearson RG (1986) Absolute electronegativity and hardness correlated with molecular orbital theory. *Proc Natl Acad Sci USA* 83:8440–8441. <https://doi.org/10.1073/pnas.83.22.8440>
207. Idrissi A, Elfakir Z, Atir R, Bouzakraoui S (2023) Small thiophene-based molecules with favorable properties as HTMs for perovskite solar cells or as active materials in organic solar cells. *Journal of Physics and Chemistry of Solids* 181:1-7. <https://doi.org/10.1016/j.jpics.2023.111492>
208. Delgado-Montiel T, Baldenebro-López J, Soto-Rojo R, Glossman-Mitnik D (2016) Quantum chemical study of the effect of π -bridge on the optical and electronic properties of sensitizers for DSSCs incorporating dioxithiophene and thiophene units. *Theor Chem Acc* 135:1-10. <https://doi.org/10.1007/s00214-016-1989-3>
209. Arunkumar A, Deepana M, Shanavas S, et al (2019) Computational Investigation on Series of Metal-Free Sensitizers in Tetrahydroquinoline with Different π -spacer Groups for DSSCs. *ChemistrySelect* 4:4097–4104. <https://doi.org/10.1002/slct.201803961>
210. Soto-Rojo R, Baldenebro-López J, Glossman-Mitnik D (2015) Study of chemical reactivity in relation to experimental parameters of efficiency in coumarin derivatives for dye sensitized solar cells using DFT. *Physical Chemistry Chemical Physics* 17:14122–14129. <https://doi.org/10.1039/c5cp01387a>
211. Delgado-Montiel T, Baldenebro-López J, Soto-Rojo R, Glossman-Mitnik D (2020) Theoretical study of the effect of π -bridge on optical and electronic properties of carbazole-based sensitizers for DSSCs. *Molecules* 25:1-17. <https://doi.org/10.3390/molecules25163670>
212. Chattaraj PK, Roy DR (2007) Electrophilicity index. *Chem Rev* 107:46–74. <https://doi.org/10.1021/cr078014b>
213. Gázquez JL, Cedillo A, Vela A (2007) Electrodonating and electroaccepting powers. *Journal of Physical Chemistry A* 111:1966–1970. <https://doi.org/10.1021/jp065459f>
214. Afolabi SO, Semire B, Akiode OK, Idowu MA (2022) Quantum study on the optoelectronic properties and chemical reactivity of phenoxazine-based organic

- photosensitizer for solar cell purposes. *Theor Chem Acc* 141:1-14.
<https://doi.org/10.1007/s00214-022-02882-w>
215. Parr RG, Donnelly RA, Levy M, Palke WE (1977) Electronegativity: The density functional viewpoint. *J Chem Phys* 68:3801–3807.
<https://doi.org/10.1063/1.436185>
216. Constantin CP, Damaceanu MD, Mihaila M, Kusko M (2022) Open-Circuit Voltage Degradation by Dye Mulliken Electronegativity in Multi-Anchor Organic Dye-Based Dye-Sensitized Solar Cells. *ACS Appl Energy Mater* 5:7600–7616.
<https://doi.org/10.1021/acsaem.2c01059>
217. Phillips JC (1961) Generalized Koopmans' Theorem*. *Physical Review* 123:420–424. <https://doi.org/10.1103/PhysRev.123.420>
218. Tsuneda T, Song JW, Suzuki S, Hirao K (2010) On Koopmans' theorem in density functional theory. *Journal of Chemical Physics* 133:1-9.
<https://doi.org/10.1063/1.3491272>
219. Koopmans YT (1934) Uber Die Zuordnung Von Wellenfunk-Tionen Und Eigenwerten Zu Den, Einzelnen Elektronen Eines Atoms. *Physica* 1–6.
[https://doi.org/10.1016/S0031-8914\(34\)90011-2](https://doi.org/10.1016/S0031-8914(34)90011-2)
220. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652. <https://doi.org/10.1063/1.464913>
221. Khadiri A, Warad I, Abuelizz HA, et al (2024) Predicting photovoltaic parameters using DFT and TD-DFT calculations of novel triphenylamine-based organic dyes: The effect of the internal or auxiliary acceptors on photovoltaic performance for DSSC. *Solar Energy* 279:1-22.
<https://doi.org/10.1016/j.solener.2024.112832>
222. Akram W, Walayat A, Zahid WA, et al (2024) Rational Design and Engineering of Terminal Functional Groups in Dibenzothiophene-Diphenylamine Small Molecular Electron Donors for Enhanced Photovoltaic Efficiency in All-Small-Molecule Organic Solar Cells. *Adv Theory Simul* 7:1-22.
<https://doi.org/10.1002/adts.202400289>

223. Pourebrahimi S, Pirooz M (2024) Exploring the optoelectronic properties of Flavylium cations as acceptors in organic solar Cells: DFT/TD-DFT investigations. *Solar Energy* 275:1–11. <https://doi.org/10.1016/j.solener.2024.112617>
224. Khadiri A, Warad I, Abuelizz HA, et al (2024) Predicting photovoltaic parameters using DFT and TD-DFT calculations of novel triphenylamine-based organic dyes: The effect of the internal or auxiliary acceptors on photovoltaic performance for DSSC. *Solar Energy* 279:1-22. <https://doi.org/10.1016/j.solener.2024.112832>
225. Shafiq F, Mubarik A, Rafiq M, Alshehri SM (2024) Star-shaped small donor molecules based on benzotriindole for efficient organic solar cells: a DFT study. *J Mol Model* 30:1-14. <https://doi.org/10.1007/s00894-024-05870-y>
226. Bourass M, Benjelloun AT, Benzakour M, et al (2016) DFT and TD-DFT calculation of new thienopyrazine-based small molecules for organic solar cells. *Chem Cent J* 10:1-11. <https://doi.org/10.1186/s13065-016-0216-6>
227. Brédas JL (2017) Organic Electronics: Does a Plot of the HOMO-LUMO Wave Functions Provide Useful Information? *Chemistry of Materials* 29:477–478. <https://doi.org/10.1021/acs.chemmater.6b04947>
228. Bursch M, Mewes J-M, Hansen A, Grimme S (2022) Best-Practice DFT Protocols for Basic Molecular Computational Chemistry. 134:1-27. <https://doi.org/10.26434/chemrxiv-2022-n304h>
229. Zhang G, Musgrave CB (2007) Comparison of DFT methods for molecular orbital eigenvalue calculations. *Journal of Physical Chemistry A* 111:1554–1561. <https://doi.org/10.1021/jp061633o>
230. Zhou B, Hu Z, Jiang Y, et al (2018) Benchmark study of ionization potentials and electron affinities of armchair single-walled carbon nanotubes using density functional theory. *Journal of Physics Condensed Matter* 30:1-11. <https://doi.org/10.1088/1361-648X/aabd18>
231. Kronik L, Stein T, Refaely-Abramson S, Baer R (2012) Excitation gaps of finite-sized systems from optimally tuned range-separated hybrid functionals. *J Chem Theory Comput* 8:1515–1531. <https://doi.org/10.1021/ct2009363>

232. Wong BM, Hsieh TH (2010) Optoelectronic and excitonic properties of oligoacenes: Substantial improvements from range-separated time-dependent density functional theory. *J Chem Theory Comput* 6:3704–3712. <https://doi.org/10.1021/ct100529s>
233. Rostami Z, Hosseinian A, Monfared A (2018) DFT results against experimental data for electronic properties of C60 and C70 fullerene derivatives. *J Mol Graph Model* 81:60–67. <https://doi.org/10.1016/j.jmgm.2018.02.009>
234. Grüning M, Gritsenko O V., Baerends EJ (2003) Exchange-correlation energy and potential as approximate functionals of occupied and virtual Kohn-Sham orbitals: Application to dissociating H₂. *Journal of Chemical Physics* 118:7183–7192. <https://doi.org/10.1063/1.1562197>
235. Bora SR, Kalita DJ (2024) Molecular engineering of the core part of D- π -A- π -D based small acceptor molecules for efficient organic solar cells: a DFT approach. *New Journal of Chemistry* 48:10897–10909. <https://doi.org/10.1039/d4nj01629g>
236. Nait Moudou MB, EL Ouafy H, Halil L, et al (2025) Exploring the role of π -Spacers in six novel Push-Pull photovoltaic systems based on N-Methylarylamine: A theoretical DFT Investigation. *Comput Theor Chem* 1244:1-13. <https://doi.org/10.1016/j.comptc.2024.115023>
237. AL-Temime FA, Awayiz MT, Abbood HI (2024) Molecular Design and DFT Analysis of High-performance Dyes Based on Pyrene with Different Donor Parts and Their Optoelectronic Applications. *J Fluoresc.* <https://doi.org/10.1007/s10895-024-03936-x>
238. Al-Fatlawe BA, AL-Temime FA (2025) Optimizing Electronic and Photovoltaic Properties of D- π -A Organic Dyes for DSSCs Using Density Functional Theory. *J Fluoresc.* <https://doi.org/10.1007/s10895-024-04118-5>
239. Wu LN, Yin H, Li MY, et al (2019) Density functional theory analysis for the limitations of fluoranthene-fused imide based small molecule acceptor materials in photovoltaic performance. *Comput Theor Chem* 1156:37–42. <https://doi.org/10.1016/j.comptc.2019.04.005>
240. Haider MDS, Hussain R, Kanwal N, et al (2024) Evaluating metal-free pyrene-centered donor dye via terminal group to enhance PCE of organic solar cells: A

- DFT approach. *Journal of Physics and Chemistry of Solids* 192:1-13.
<https://doi.org/10.1016/j.jpcs.2024.112101>
241. Tommalieh MJ, Aljameel AI, Hussein RK, et al (2024) The Effect of Conjugated Nitrile Structures as Acceptor Moieties on the Photovoltaic Properties of Dye-Sensitized Solar Cells: DFT and TD-DFT Investigation. *Int J Mol Sci* 25:1-15.
<https://doi.org/10.3390/ijms25137138>
242. Abdali SA, AL-Temimei FA, Al-Abbas SS (2024) Design a New D- π -A Formation Dyes as Dye-sensitized Solar Cells Applications/ a DFT and TD-DFT Study. *J Fluoresc* 34:795–807. <https://doi.org/10.1007/s10895-023-03311-2>
243. Mouhi R El, Slimi A, Khattabi S El, et al (2024) Computational study of new small molecules D-A based on triphenylamines for bulk heterojunction solar cells (BHJ). *Comput Theor Chem* 1241:1-11.
<https://doi.org/10.1016/j.comptc.2024.114899>
244. Huang Y, Zhang K, Song P, et al (2024) Heterojunction Organic Solar Cells with Efficient Charge Mobility and Separation Capabilities Studied by DFT. *Chemistry – A European Journal*. 30:1-17.
<https://doi.org/10.1002/chem.202402928>
245. Praveen PA, Saravanapriya D, Bhat S V., et al (2024) Comprehensive analysis of DFT-3C methods with B3LYP and experimental data to model optoelectronic properties of tetracene. *Mater Sci Semicond Process* 173:1-8.
<https://doi.org/10.1016/j.mssp.2024.108159>
246. Kumar R, Singh A (2024) Designing of π -Bridge for Metal Free Dye-Sensitized Solar Cell and Optoelectronic Properties: An ab initio DFT Perspective. *Chemistry Select* 9:1-10. <https://doi.org/10.1002/slct.202400526>
247. Hehre WJ, Ditchfield K, Pople JA (1972) Self-consistent molecular orbital methods. XII. Further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J Chem Phys* 56:2257–2261.
<https://doi.org/10.1063/1.1677527>
248. Tommalieh MJ, Aljameel AI, Hussein RK, et al (2024) The Effect of Conjugated Nitrile Structures as Acceptor Moieties on the Photovoltaic Properties of Dye-

- Sensitized Solar Cells: DFT and TD-DFT Investigation. *Int J Mol Sci* 25:1-15.
<https://doi.org/10.3390/ijms25137138>
249. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J Chem Phys* 72:650–654. <https://doi.org/10.1063/1.438955>
250. Lopez SA, Pyzer-Knapp EO, Simm GN, et al (2016) The Harvard organic photovoltaic dataset. *Sci Data* 3:1-7. <https://doi.org/10.1038/sdata.2016.86>
251. Setsoafia DDY, Ram KS, Mehdizadeh-Rad H, et al (2023) Density Functional Theory Simulation of Optical and Photovoltaic Properties of DRTB-T Donor-Based Organic Solar Cells. *Int J Energy Res* 2023:1-12.
<https://doi.org/10.1155/2023/6696446>
252. Weigend F, Ahlrichs R (2005) Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics* 7:3297–3305.
<https://doi.org/10.1039/b508541a>
253. Qadir KW, Mohammadi MD, Abbas F, Abdullah HY (2024) Molecular engineering of BTO for superior photovoltaic efficiency: A DFT exploration. *Mater Chem Phys* 314:1-9. <https://doi.org/10.1016/j.matchemphys.2023.128866>
254. Tendongmo H, Kogge BF, Tamafo Fouegue AD, et al (2024) Theoretical screening of N-[5'-methyl-3'-isoxasolyl]-N-[(E)-1-(2-thiophene)]methylidene]amine and its isoxazole based derivatives as donor materials for bulk heterojunction organic solar cells: DFT and TD-DFT investigation. *J Mol Model* 30:1-16. <https://doi.org/10.1007/s00894-024-05978-1>
255. Jin, R. (2015) Theoretical study of the optical and charge transport properties of star-shaped molecules with 1,3,5-triazine-core derivatives as organic lightemitting and organic solar cells materials. *C. R. Chim.* 18: 954–959.
<https://doi.org/10.1016/j.crci.2015.05.021>
256. Vidya, VM, Tripathi, A, Prabhakar, C (2019) Linear, non-linear optical properties and reorganization energies of D- π -A star-shaped triazine derivatives: a DFT study. *J. Mol. Struct.* 1176:855–864.
<https://doi.org/10.1016/j.molstruc.2018.09.025>

257. Zhang, H, Zang, XF, Hong, YP, Chen, ZE (2021) Theoretical and photovoltaic investigations of 1,3,5-triazine-based photosensitizers achieving highly efficient DSSCs. *Synth. Met.* 280:1-7. <https://doi.org/10.1016/j.synthmet.2021.116882>
258. Vidya VM, Someshwar, P, Prabhakar, C. (2021) Optoelectronic and charge transport properties of D-n-A type 1,3,5-triazine derivatives: a combined experimental and DFT study. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 245:1-13. <https://doi.org/10.1016/j.saa.2020.118940>