

## Organic and Organic-Inorganic Solar Cells: From Bulk Heterojunction to Perovskite Solar Cells

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### Article Info

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### Abstract

Due to the negative impact on the environment using fossil fuels, photovoltaic (PV) technology has become a new alternative for renewable energy in the last two decades. Although inorganic solar cells have dominated in the PV field, metal-free organic compounds have introduced a new challenge because of their great properties that include: i) high light-harvesting ranges, ii) optical- and electrochemical properties can be easily tuned by decorating their structure through a several synthetic approaches, and iii) their technology has high flexibility and low manufacturing cost. In this short review, we depicted our work in the synthesis of organic compounds and their applications in the PV field, specifically in bulk heterojunction solar cells (BHJSCs), dye-sensitized solar cells (DSSCs) and organic-inorganic perovskites solar cells (O-IPSCs).

**Keywords:** Fossil fuels; Photo excitation; Greenhouse gases; Photovoltaic.

### Introduction

Global warming, as a direct consequence of the emission of greenhouse gases, is one of the greatest threats to the health of humans and ecosystems in our planet, being one of the most important difficulties to overcome by the scientific community. Looking for new alternatives (environmentally friendly, price-effective and efficient) researchers are devoting great attention into the PV technology. The sun continuously releases a tremendous amount of energy in the form of electromagnetic radiation and this almost limitless source of energy is available at no cost [1]. PV solar cells (PVSCs) [2] can convert sunlight into storable energy. One may think that this is a new technology, but it has been there for almost 2 centuries. The PV effect was first observed by Becquerel AE in 1839 [3]. PV technology is based on the creation of an electron-hole pair upon photon absorption in cells composed of two different layers (p-type and n-type) of semiconductor materials. In these cells, absorption of a photon by the n-type material provides enough energy to move an electron from one layer to the other, leading to the generation of electrical power [4].

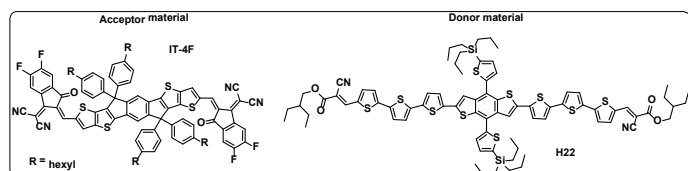
Currently, inorganic solar cells based on materials such as silicon, cadmium telluride, or copper indium germanium selenide exhibit relatively high solar energy conversion efficiencies above 20%, and dominate commercially available PV technologies [2,5,6]. However, inorganic solar cells present some limitations such as rigidity, weight and high manufacturing costs compared to those based on organic-inorganic materials, so many alternative materials are under investigation. In this regard, organic and hybrid inorganic-organic solar cells (OSCs and O-ISCs) are promising sources of renewable energy.

This short review will focus on the application of different synthetic materials developed by our groups and their applications in PV devices, specifically in the field of

BHJSCs, DSSCs and perovskite solar cells (PSCs). We will survey the relevant aspects on energy requirements, design, synthesis, electrochemical and optoelectronic characterization of the new materials for each application.

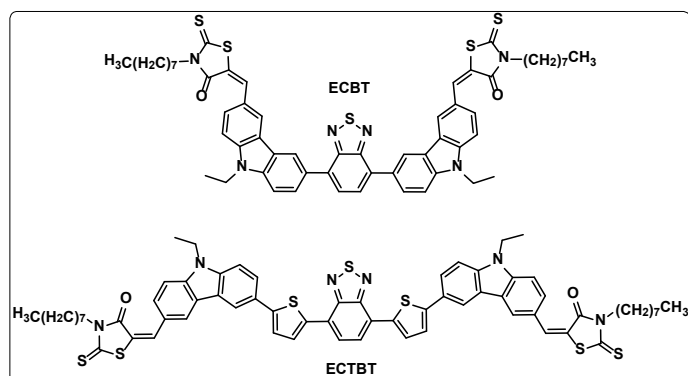
## Organic Photovoltaics (OPVs)

Currently, OPVs are based on two types of electron donor materials: polymers and small molecules [7,8]. Organic solar cells based on BHJ configurations have attracted considerable interest due to their easy fabrication, relatively low cost and flexibility [9-11]. In BHJ configurations, electron-donating conjugated compounds and electron-accepting (fullerene or non-fullerene) derivatives are mixed together to form a continuous interpenetrating micro-heterogeneous network with a large interfacial area for efficient exciton dissociation [12]. Over the last few years, a significant increase in the power conversion efficiencies (PCEs), exceeding 13% [13,14], has been achieved by devices based on polymer donors. On the other hand, small molecule donor based OPVs (SM-OPVs) have achieved PCEs above 10% [15]. Small-molecule donors offer several advantages over polymeric materials, such as easy purification, well-defined molar masses and molecular structures, high solubility and good batch-to-batch reproducibility [8]. Comprehensive reviews based on small molecules for BHJSCs have been reported by Hou [16] and Mishra [8]. The chemical structures of the compounds that have been used to achieve the highest PCE values are shown in figure 1.



**Figure 1.** Structure of the small molecules used in BHJSCs. A PCE value of 13.1% was achieved when IT-4F was used as the electron acceptor [13], whereas a PCE value of 10.29% has been obtained using H22 as the electron acceptor [15].

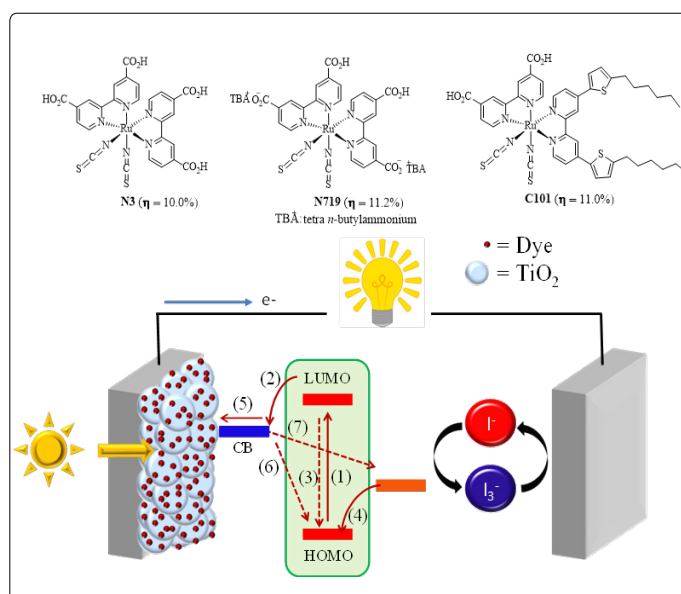
We have contributed in this type of solar cells by designing and synthesizing new small molecules, which were used as the electron donor materials in BHJSCs. Our strategy was to use donor-acceptor-donor (D-A-D) backbone structures ECBT and ECTBT [17] (Figure 2).



**Figure 2.** Structure of the small molecules used as the electron donor materials in BHJSCs. PCE values of 1.45% and 3.26% were achieved for ECBT and ECTBT BHJ-based devices, respectively [17].

## Dye-Sensitized Solar Cells

The concept of treating semiconductors with dyes was introduced in late 1960s mainly due to their spectra responses, which were mostly in the ultraviolet region resulting in low conversion efficiencies [18-21]. Although, these cells appeared as promising renewable energy resource, it was not considered until 1991 when O'regan B and co-workers reported the first efficient DSSC device that was fabricated by using a ruthenium-based dye anchored to the nanoporous TiO<sub>2</sub> surface, which showed a high PCE ranging from 7.1 to 7.9% [22]. Hereafter, the initial synthesis of new dyes for DSSC applications were based on ruthenium with different ligands (i.e. N3, N719 and C101 dyes, see figure 3), followed by the use of metal-free dyes [23-25]. The record efficiency for DSSC of 14.3% was reported in 2015 using organ silicon dye and a co-sensitizer based on triphenylamine with carboxylic units as anchor group [26].



**Figure 3.** Chemical structure of the ruthenium dyes (top) and schematic diagram of a DSSC (bottom).

In a typical DSSC device, light is absorbed by the dye molecules, which are anchored to the TiO<sub>2</sub> exciting electrons from the higher occupied molecular orbital (HOMO) to lower unoccupied molecular orbital (LUMO) (see figure 3, step 1). The photo excitation of the dye molecules results in an excited singlet state called exciton in which the electrons are linked to their corresponding holes by electrostatic Coulomb force [27]. The electrons from the excited state of the dye are then injected into the conduction band of the TiO<sub>2</sub> ( $E = \sim 3.90$  eV vs vacuum) (step 2), this process competes kinetically with the state excited decay, which has a negative impact on the overall conversion efficiencies (step 3). The dye is restored to its ground state by an oxidation-reduction process with the electrolyte redox couple (step 4), which is also reduced by electron transfer from platinum counter electrode (step 5). The process of regeneration of the dye is competing with the electronic recombination between the semiconductor and the dye (step 6) as well as between the semiconductor and the redox couple system (step 7) [28].

The organic dyes that are one of the most important components of these cells, should meet certain requirements for an efficient electron transfer to the conduction band of the  $\text{TiO}_2$  and hence result in efficient power conversion. These requirements are namely: i) dye should be a stable electron donor compound with a broad absorption spectrum absorbing light in the visible range; ii) the oxidation potential of the donor moiety should be lower than the  $\text{I}^-/\text{I}_3^-$  redox couple, ensuring an efficient dye regeneration as well as a stabilized charge-separated state; iii) there must be a strong interaction between  $\text{TiO}_2$  and the LUMO level localized near the anchoring group of the dye, ensuring good electronic coupling [29,30].

The interest on metal-free organic sensitizers has grown in recent years, as they offer several advantages over other sensitizers. Among these advantages are the higher molar absorption coefficients due to intramolecular  $\pi$ - $\pi^*$  transitions, easy modification due to relatively short synthetic routes and tunable electrochemical properties [31]. Different organic materials have showed great properties for DSSC applications, and taking a look at their structures, generally they are based on a donor moiety linked covalently to an acceptor moiety [32-34]. Several synthetic strategies have been studied to improve the optoelectronic properties of organic dyes, which can be summarized in: i) the use of bulky co-donor systems to block the approach of the electrolyte redox couple to the semiconductor surface avoiding the electronic recombinant processes [35]; ii) the development of novel anchoring units with better optical- and electrochemical properties as well as higher stability in comparison with the conventional carboxylic-based acceptor [36,37] and iii) the improvement of the light harvesting in the red region of the visible spectrum through the  $\pi$ -conjugation increase [38].

Following these strategies, we studied the changes in the optical and electrochemical properties upon the incorporation of different highly conjugated donor and co-donor systems linked to anchoring units' as cyanoacrylic acid, rhodanine-3-acetic acid and acceptor systems without carboxylic groups with strong absorption in the visible range. Among the highly conjugated donor, *ex* TTF is one of the most studied systems due to its wide absorption spectrum, low oxidation potential and easy functionalization [39]. In 2014, we reported the synthesis of *ex*TTF-based dyes endowed with a rhodanine 3-acetic acid unit as the acceptors and their further DSSC application, finding that the driving force for dye regeneration was negatively affected, because the difference between the first oxidation potential (HOMO) of the dyes and the  $\text{I}^-/\text{I}_3^-$  redox couple was very small, resulting in a low PCE ranging from 0.68-1.59% [40]. The replacement of the anchoring unit based on rhodanine 3-acetic acid by cyanoacrylic acid resulted in a HOMO stabilization, which increased the driving force for dye regeneration (see figure 4) [41].

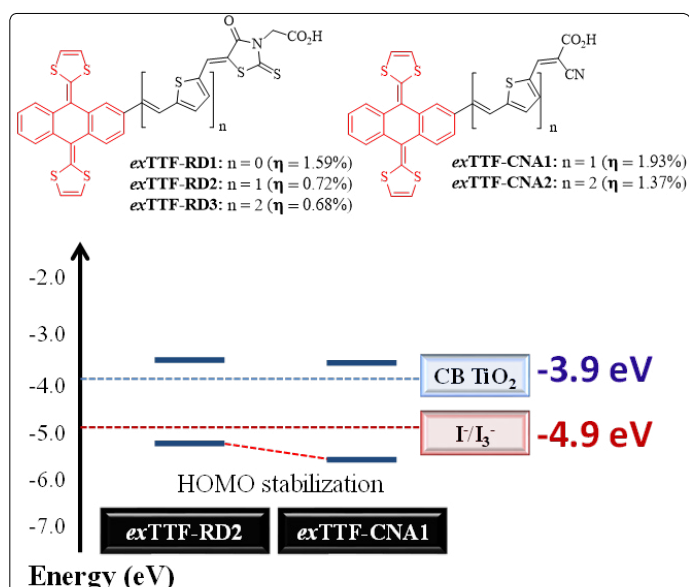


Figure 4. Schematic energy diagram of *ex*TTF-based dyes.

Considering the low oxidation potentials of the *ex*TTF-based dyes that led to low conversion efficiencies in a typical DSSC device, even though such dyes showed a great absorption property in the visible range, the design of new efficient donors with co-donor systems for increasing molar absorptivity coefficients in the visible range was necessary. In 2015, we reported organic dyes based on two units of triphenylamine (TPA) as co-donor-donor (co-DD) with different  $\pi$ -spacers linked to cyanoacrylic acid as anchoring unit to the  $\text{TiO}_2$  (Figure 5) [42]. The devices fabricated with these dyes showed good PCE values ranging from 2.26-5.67% whereas the ruthenium-(N719) based devices displayed a PCE value of 6.31%.

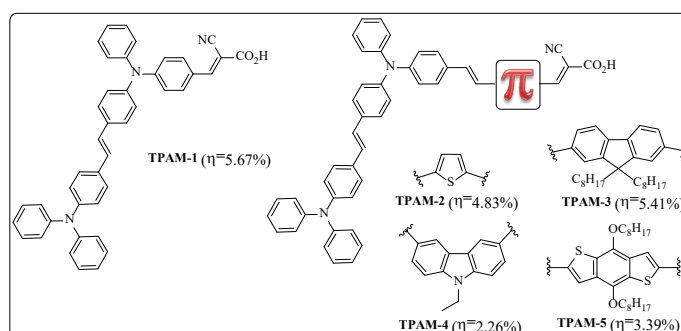


Figure 5. Chemical structure of dyes TPAM (1-5) based on co-DD.

Different electron acceptors using a carboxylic acid (COOH) anchoring groups for binding to the  $\text{TiO}_2$  have been reported [43-46]. However, it was demonstrated that COOH dissociates on the  $\text{TiO}_2$  surface after long irradiation times, increasing the liability of these molecules [47]. Because of this, it is important the development of novel anchoring units that are able to bind strongly to the  $\text{TiO}_2$  [48-50]. Insuasty et al. [36] Reported the synthesis of *push-pull* systems covalently attached to the 2-(1,1-dicyanomethylene) rhodanine (DCRD) that can also work as an efficient anchoring unit to the  $\text{TiO}_2$  without the presence of the COOH group [37]. Echeverry et al. [51] developed triphenylamine-based dyes (DCR 1-5) using DCRD as efficient anchoring unit, which showed moderate conversion efficiency values. Among these dyes, a device

made with DCR-2 (Figure 6a) exhibited the best PV performance with a short-circuit photocurrent density ( $J_{sc}$ ) value of 7.76 mA/cm<sup>2</sup>, an open-circuit voltage ( $V_{oc}$ ) value of 0.621 V, and a fill factor (FF) of 0.682, corresponding to an overall PCE value of 3.78%. We [52] also reported the synthesis of different triphenylamine-based dyes linked to 3-methylquinoxaline-2(1H)one (MQ) as anchoring unit carboxylic acid-free, however the poor electron-acceptor character of MQ was reflected with low photoconversion efficiencies (Figure 6a).

Although, several organic dyes with promising results for DSSCs have been studied, there is still a need to design novel compounds with high light-harvesting abilities in the visible spectrum to improve the current densities of the devices [28]. The use of perylene-tetracarboxylic dianhydride in optoelectronic devices has increased in the last decades [53], because of their strong absorption in the visible region with high molar extinction coefficients ( $\epsilon=30,000-90,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), high photo-stability and electron-drawing ability [54,55]. Echeverry et al. [56] reported the synthesis, structural and electronic properties of two novel dyes based on perylene imides PI-1 and PI-2 as well as their application in DSSCs (Figure 6b). DSSC devices based on PI-1 and PI-2 showed low conversion efficiencies of 1.0 and 1.3%, respectively. These low PCE values were associated with the weak driving force for the electron injection from the dyes to the conduction band of the TiO<sub>2</sub>. Although, the use of perylene-based dyes led to low efficiencies, these values were higher than 1.0%, very similar to other PCEs perylene-based DDSSCs [57].

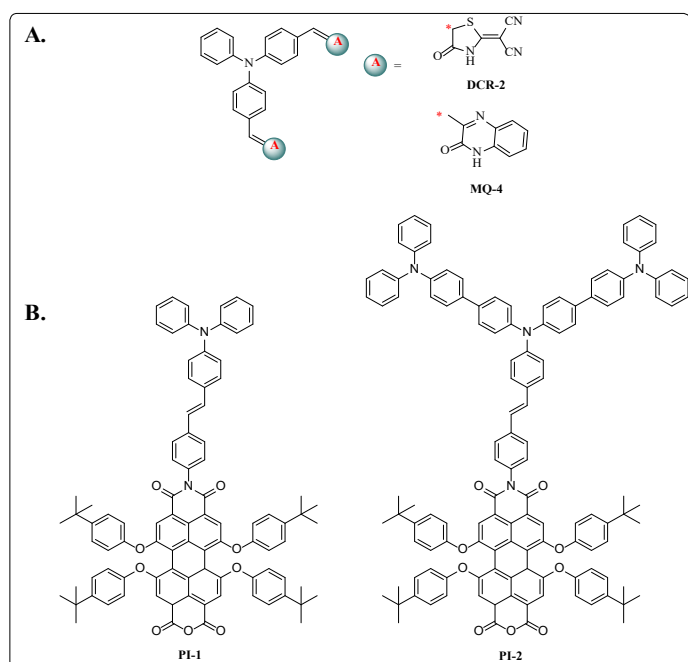


Figure 6. Structure of the dyes with different anchoring units used for DSSC applications.

DSSCs continue being a promising energy resource for the future, due to their high PCE, low manufacturing cost and eco-friendly nature. Currently, the synthesis of new organic dyes and the manipulation of either photo anode or counter electrode continue being a hot topic, improving the efficiencies of these devices. We have used different strategies for improving the device PCEs, being the introduction of co-DD systems and DCRD as anchoring group the better ones.

## Organic-Inorganic Hybrid Perovskite Solar Cells

The unique properties of O-IPSCs make them promising candidates for developing next-generation PVs that would compete with silicon solar cells [58,59]. O-IPSCs have shown a remarkable PCE increase from 3.8% in 2009 to 23.3% in 2018 [60,61]. Among the different perovskite configurations [62,63], the inverted planar structure with a configuration: substrate transparent electrode (ITO or FTO)/hole transporting layer (HTL)/perovskite/electron transporting layer (ETL)/metal electrode has gained great attention due to its simple structure, low temperature processing and negligible hysteric behavior [64]. The most used ETL in this inverted configurations is the [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PC<sub>61</sub>BM), besides PC<sub>61</sub>BM, other studies have shown that single or double fullerene layers (PC<sub>61</sub>BM/C<sub>60</sub>, ICBA/C<sub>60</sub>, C<sub>60</sub>/bis-C<sub>60</sub>), can also work as ETLs in O-IPSCs (Figure 7) [65-68]. Comprehensive reviews about fullerenes used in O-IPSCs has been reported by Castro et al. [63] and Gatti et al. [69]. However, the influence of the functional groups on the fullerene-based O-IPSCs is still being under investigation.

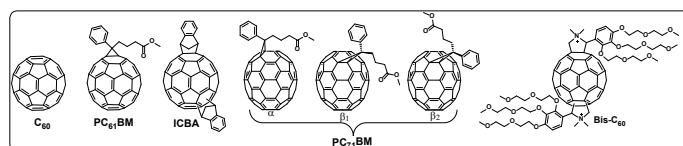


Figure 7. Chemical structure of fullerenes used in O-IPSCs.

In a first attempt to understand the role of the fullerenes in O-IPSCs, we reported the synthesis, characterization and PV applications of DMEC<sub>60</sub> and DMEC<sub>70</sub> (Figure 8). It was found that inverted O-IPSCs based on DMEC<sub>60/70</sub> as ETLs exhibited both higher PCE values and higher device-stability compared to devices based on the PC<sub>61/71</sub>BM, which was attributed to the efficient ability of these compounds to extract electrons from the perovskite layer, most-likely due to some specific interactions between the fullerenes' addends (carbonyls and amino groups) and the perovskite crystals at the interfaces, as established by infrared (IR) spectroscopy [70,71].

A great effort to improve the  $V_{oc}$  values has been devoted [72-74] and typically, fullerenes with lower LUMO energy exhibit higher  $V_{oc}$  values. It has also been found that the energy disorder in the ETL influences the  $V_{oc}$  values [75]. Taking this into consideration we investigated the effect of the C<sub>70</sub> fullerene derivatives isomeric purity when used as ETLs in O-IPSCs ( $\alpha$ -DMEC<sub>70</sub>, Figure 8) [71]. We found a considerable impact on the  $V_{oc}$  values when using a pure isomer ( $\alpha$ -DMEC<sub>70</sub>), and this remarkable effect can even reverse the expected results based solely on HOMO/LUMO energy level considerations [71,76].

Recently, we systematically studied the effect of new C<sub>60</sub> fullerene derivatives functionalized with thiophene moieties as well as with electron donating or electron withdrawing groups bromine (Br) or cyano (CN) (1-4, respectively, figure 8), when used as the ETLs in O-IPSCs [77]. The photo conversion efficiencies of O-IPSCs based on these compounds were higher than those of devices based on PC<sub>61</sub>BM, which was



associated with the better passivation ability, due to specific interactions between  $S \cdots Pb$  atoms [77]. Important facts when synthesizing new ETLs are solubility and electron mobility, which need to be balanced. Unfortunately, in most cases solubility is accompanied by lower electron mobilities [78,79]. Keeping in mind these considerations, we synthesized  $PC_{61}BEH$  (Figure 8) to be used as ETL in O-IPSCs, by changing the methyl group of the  $PC_{61}BM$  for the 2-ethylhexyl group of  $PC_{61}BEH$ , it was found that the solubility of  $PC_{61}BEH$  in chlorobenzene was increased considerably (a factor of 3) without sacrificing the electron mobility nor the HOMO/LUMO energy levels, all in all, resulting in improved overall device performance [80].

For this technology to be commercialized, the improvement of the long-term device stability needs to be addressed, one approach to overcome this issue is using hydrophobic compounds, which minimize the penetration of water into the perovskite layer in inverted O-IPSCs. In 2017, we reported for the first time, the use of a  $PC_{61}BM$ -dimer ( $D-C_{60}$ , figure 8), as an efficient ETL in inverted O-IPSCs, our idea was the use of a hydrophobic ETM to enhance the power endurance of the devices [81]. We not only improved the PCE value, but also the device stability of  $D-C_{60}$ -based devices was substantially improved, as compared to devices based on  $PC_{61}BM$ . This improved performance was attributed to synergetic effective perovskite film surface passivation and improved electron extraction, as determined by photoluminescence (PL) techniques and electrochemical impedance (EIS) [81].

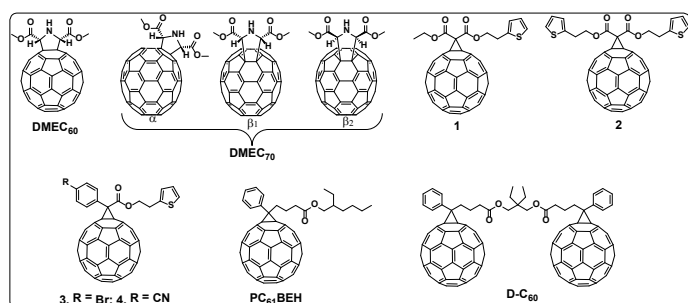


Figure 8. Structure of the fullerene derivatives synthesized in our group.

There are many hole transporting materials (HTMs) amenable for O-IPSCs fabrication [82]. However, the use of electron transporting materials (ETMs) has been limited mainly to fullerenes and their derivatives, and there was only few examples of efficient non-fullerene inverted O-IPSCs reported [83-86]. To further enhance O-IPSCs' performance, we studied the effect of two atomically-precise edge-functionalized graphene nanoribbons **hPDI2-Pyr-hPDI2** and **hPDI3-Pyr-hPDI3** (Figure 9), which outperformed  $PC_{61}BM$  when used as ETLs in O-IPSCs. These new materials provided a facile fabrication process, high electron mobility, strong light absorption, and HOMO/LUMO levels that matched those of the lead-halide perovskite active layers [87-89].

We also studied the effect of three-dimensional graphene nanostructures (**Trip-hPDI2** and **Trip-hPDI3**, (Figure 9) as the ETLs in O-IPSCs, which exhibited remarkable new properties, such as an enhancement in absorption, an ability to accept and delocalize 18 electrons into three-dimensions [90].

Devices based on largest of these compounds achieved a PCE value of 18.01%, which is one of the highest values for non-fullerene electron extracting layers in O-IPSCs [90].

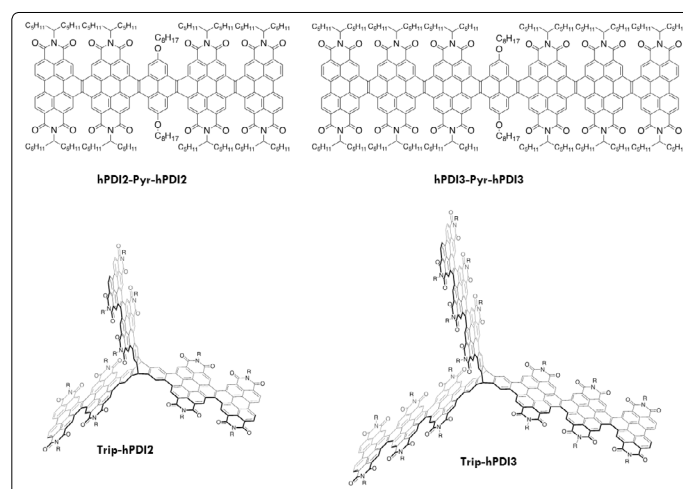


Figure 9. Structure of the non-fullerene derivatives used as efficient ETLs.

## Perspectives

Although a tremendous progress has been made toward increasing PCE values and device stability of OSCs and O-IPSCs, there are still many barriers to further overcome to compete with the inorganic-based solar cells that currently lead the market.

To address one of these barriers OSCs and O-IPSCs are being studied under drastic conditions such as long-time light-soaking conditions in the presence of air, and several research studies have been devoted to their stability under atmospheric conditions. To minimize fabrication costs, more amenable inexpensive organic materials are being studied to be used either as the electron acceptors, electron donors and ETMs or HTMs. This has called the attention of a large research community to design new efficient materials.

## Conflict of Interest

There are no conflicts to declare.

## Acknowledgments

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