

Artigo

Organic Photovoltaics

Ragoussi, M.-E.; Torres, T.*

Rev. Virtual Quim., 2015, 7 (1), 112-125. Data de publicação na Web: 1 de novembro de 2014<http://www.uff.br/rvq>**Materiais Orgânicos Fotovoltaicos**

Resumo: Focamos a discussão desta revisão na descrição e princípios de funcionamento de células solares orgânicas e híbridas (sensibilizadas por corante), e abrangendo os fatores de importância na pesquisa para a otimização dos dispositivos, assim como o estado da arte em ambos os campos.

Palavras-chave: Células solares orgânicas sensibilizadas por corantes; polímeros eficientes de conversão de energia; corantes orgânicos; materiais de transporte com cavidade.

Abstract

We focus the discussion of this review in the description and operating principles of organic and hybrid (dye-sensitized) solar cells, and go through the factors of importance in the research towards the optimization of the devices, as well as the state-of-the-art in both fields.

Keywords: Organic and Dye-Sensitized Solar Cells; Power conversion efficiencies
Polymers; Organic Dyes; Hole-transporting materials.

* Universidad Autónoma de Madrid, Departamento de Química Orgánica, Cantoblanco, 28049, Madrid, Spain.

✉ tomas.torres@uam.es

DOI: [10.5935/1984-6835.20150007](https://doi.org/10.5935/1984-6835.20150007)

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Maria-Eleni Ragoussi, Tomás Torres*

Universidad Autónoma de Madrid, Departamento de Química Orgánica, Cantoblanco, 28049, Madrid, Spain. IMDEA-Nanociencia, c/Faraday 9, Campus de Cantoblanco, 28049 Madrid, Spain.

* tomas.torres@uam.es

Recebido em 1 de novembro de 2014. Aceito para publicação em 1 de novembro de 2014

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1. Introduction

Solar energy is probably the most promising answer to the constantly growing energy crisis. In an effort to secure sufficient supplies to meet the world electricity demands, and also to lower the carbon footprint, echoed in the extensive amounts of CO₂ emissions from the combustion of fossil fuels, significant research efforts are being dedicated on the development of sustainable photovoltaics.

Solar energy conversion applications consist of three different technologies: Photovoltaics (PV), providing direct conversion of sunlight into electricity, concentrating solar power systems (CSP), with indirect conversion, and solar thermal collectors for heating and cooling (SHC), employing the sun's thermal energy. Within the area of photovoltaics, crystalline silicon devices are the most widespread derivatives that currently dominate the markets.¹ These inorganic systems come in three different

forms, namely, monocrystalline, multi-crystalline and amorphous, and they are characterized by their reliable efficiency and lifetime as well as their reduced cost. In fact, lately reported efficiencies have reached levels in the order of 25%.² Alternatively, inorganic thin film devices have shown remarkable evolution with modules based on polycrystalline absorber materials, such as cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) achieving impressive performances.³ Recently, a device based on indium gallium phosphide (InGaP) yielded an unprecedented 37%.² However, resource scarcity of the required materials causes a significant limitation to this technology.

In a different outlook, organic (OPVs) and dye-sensitized (DSSCs) solar cells are emerging photovoltaic technologies that have made tremendous progress in recent years and exhibit a rising potential for future commercialization. In this tutorial review, we describe the key features and discuss the present state of the art in OPVs and DSSCs,

together with some important developments and perspectives of these innovative solar energy conversion systems.

2. All-Organic Solar Cells

Organic semiconductors differ from the above-mentioned inorganic derivatives, in that they are cheap, light and flexible, and they can also be processed in order to modulate their physicochemical properties.⁴ This renders them very attractive for solar energy applications and thereupon, wide attention has been addressed to the advancement of organic photovoltaics (OPVs).

Initial studies in the field of OPVs involved the so-called single-layer systems, which consisted of a single organic semiconductor in the active layer. The performance of these architectures was quite poor, due to extensive charge recombination, since the electrical field provided by the asymmetric work functions of the electrodes did not provide the necessary driving force for charge separation (exciton dissociation).⁵ A major breakthrough came with Tang's pioneering study in building a two-component donor:acceptor heterojunction architecture, consisting of a copper phthalocyanine (donor) and a perylene derivative (acceptor).⁶ The success of this system laid on the efficient dissociation of excitons that occurred through a rapid charge transfer process at the interface of the two components, leading to holes in the HOMO (highest occupied molecular orbital) of the donor material and electrons in the LUMO (lowest unoccupied molecular orbital) of the acceptor. A record, for the time, power conversion efficiency (PCE) of 1% was reported.

The device structure of bilayer configurations consists of a heterogeneous junction of the donor and the acceptor

component. This photoactive layer is sandwiched between a modified ITO (Indium Tin Oxide) bottom anode, and a low-work function metal cathode, such as Al, to collect holes and electrons (Figure 1). Their function follows four basic steps, as shown in Figure 1: light absorption promotes an electron from the HOMO to the LUMO of the donor material, generating an exciton. The exciton is then diffused towards the donor-acceptor junction, where dissociation takes place, after which the separated electrons and holes are collected at the external electrodes.⁷ The main difference with inorganic semiconductors is that upon light illumination organic compounds form excitons whose dissociation into free carriers needs to take place at the donor-acceptor interface, whereas inorganic materials form free electrons and holes. Fine-tuning of the LUMO orbitals of both donor and acceptor involved molecules is essential for this process to take place.

The donor-acceptor interface can be obtained in two sorts of configurations: planar heterojunction (PHJ), with two successively deposited films of the donor and the acceptor, or bulk heterojunction (BHJ), where a unique blended film of donors and acceptors is present (Figure 1).

The great advantage of BHJ in comparison to PHJ is the interpenetrated networks of the components all along the active layer, resulting in a dramatic increase of the contact area and, hence, more efficient charge separation.⁵

Various factors, such as molecular orbital levels, charge carrier mobility, light-harvesting abilities, thickness and morphology of the layers and molecular diffusion length, control the performance of this type of devices. The field has attracted vivid interest in the last decade and the rational design of new materials, able to improve some specific requirements of OPVs, has led to PCEs above 10%.⁸

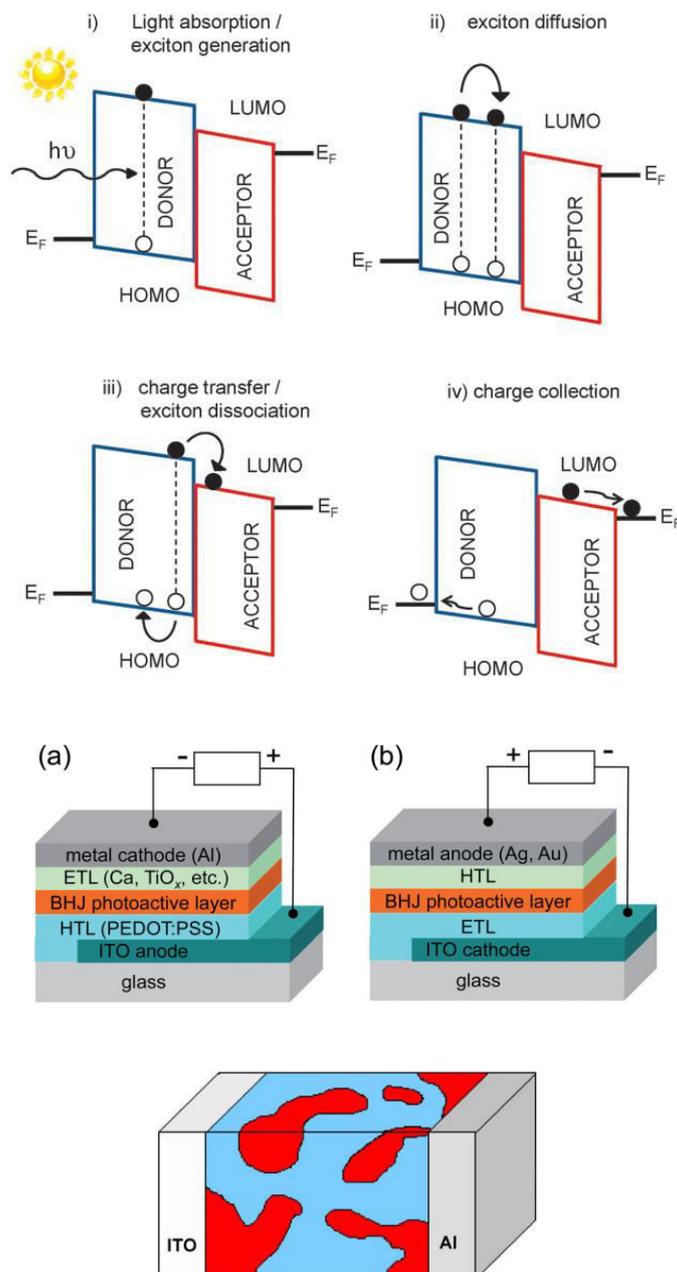


Figure 1. (upper part) Operating principles and (middle part) device structure of an organic photovoltaic system [Reproduced from references 16b and 8 respectively with permission of The Royal Society of Chemistry]. (lower part) A bulk heterojunction active layer between a transparent ITO and an Al electrode [Reprinted from reference 7, Copyright (2004), with permission from Elsevier]

(i) Polymer OPVs

In polymer-based photovoltaics, the BHJ configuration is typically adopted.⁹ The morphology of the blend at the nanoscale is

critical for performance optimization. In this respect, spin casting of organic solutions of the hole-transport semiconducting polymers and the acceptor molecules is usually applied. In this family of OPVs, the polymer plays normally the electron-donor role, and a

fullerene the electron-acceptor.¹⁰ Fullerenes are recognized as the ideal electron acceptor, promoting ultrafast charge separation and long exciton diffusion length.¹¹ A vast number of fullerene as well as other acceptor materials have been prepared and evaluated in OPV devices,¹² but the most widely used is phenyl-C61-butyric acid methyl ester (PCBM), which is considered as a benchmark *n*-type structure for OPVs (Figure 2).¹³ On the other hand, research on *p*-conjugated polymers has been mainly dedicated to tuning their energy levels in order to have a good control on the band gap of the polymer, which is a key issue to modulate light harvesting properties. Engineering of the HOMO and LUMO levels also allows their appropriate matching with the respective levels of the fullerene, essential for efficient charge transfer. Low bandgap polymers can be obtained by several approaches, such as fusion of aromatic rings for enlargement of the π -system, construction of donor-acceptor (D-A)

alternating backbones or attachment of strong electron-withdrawing substituents.⁸ A variety of soluble electroactive derivatives such as fluorene, thiophene, cyclopentadithiophene and carbazole have been used as the electron rich units, with benzothiadiazole and thienopyrazine as the electron poor units.⁴ Among the hundreds of polymers synthesized in the last decade, the best performing ones have been thieno[3,4-*b*]thiophene-based structures, presenting optimally low bandgaps and efficiencies reaching 7–9%, with the most successful derivative being polythieno[3,4-*b*]thiophene-co-benzo-dithiophene (**PTB7**) (Figure 2).¹⁴ As well, contrary to HOMO-LUMO level prediction (its bandgap does not match the optimal 1.5-1.7 eV theoretical limits), polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (**PCDTBT**) has attained high performances in the order of 7.5 % (Figure 2).¹⁵

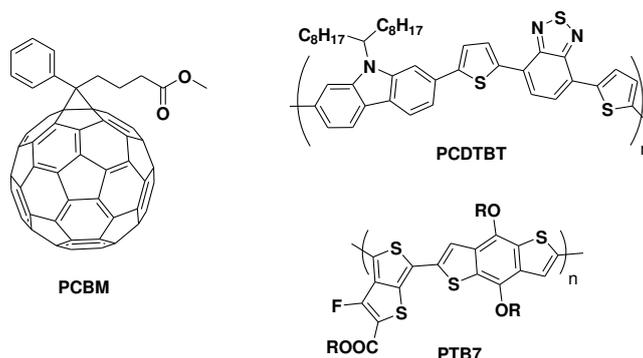


Figure 2. Structures of fullerene-acceptor **PCBM** and polymers **PCDTBT** and **PTB7** used in successful OPV devices

(ii) Small molecule OPVs

An attractive approach looking to overcome the limitations of polymers in BHJs (synthesis, purification, and inherent electronic properties) has been their replacement by small conjugated molecules. In this context, numerous oligomers, dendrimers, porphyrins, phthalocyanines and other organic dyes, have been used as molecular donors blended with fullerene

derivatives.¹⁶ As opposed to their plastic analogues, solution processed BHJs of small conjugated molecules are characterized by poor charge transport capabilities, and for this reason co-evaporation methods (vacuum deposition) are commonly applied, even though a number of thriving solution processed examples have lately appeared in the literature.¹⁷ Intense research in the field has resulted in efficiencies approximating those of the successful polymer devices. The most promising results have been obtained

by

the use of oligothiophenes, and in particular with the use of **1** or **DR3TBDTT** as the molecular donor in solution-processed devices (Figure 3). Specifically, solar cells fabricated with the architecture ITO/PEDOT:PSS/**1**:PC₇₁BM/Ca/Al, showed PCE

values of 7%,¹⁸ and those with ITO/PEDOT:PSS/**DR3TBDTT**:PC₇₁BM/LiF/A

l gave 8.12%.¹⁹ These analogues are characterized by their low bandgap and intense absorption bands between 500–700 nm.

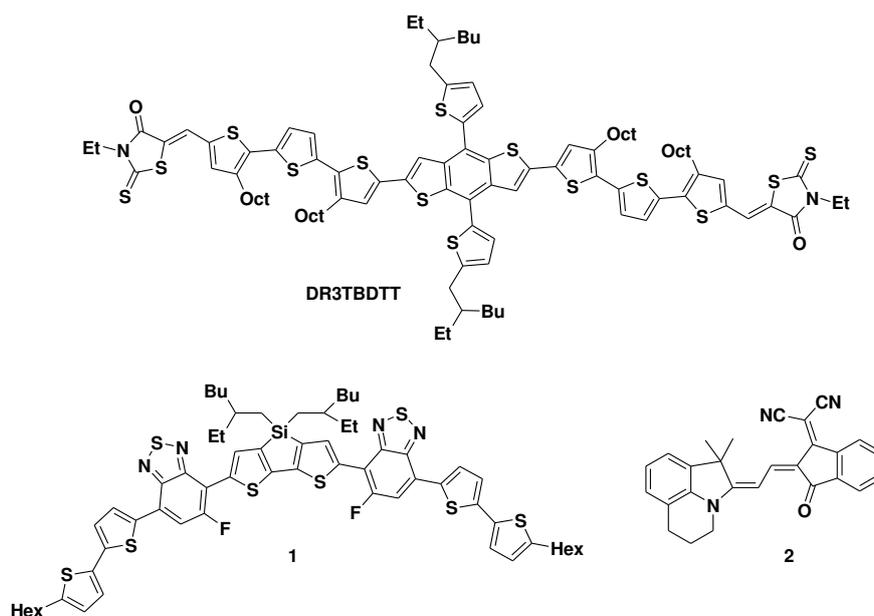


Figure 3. Structures of the most efficient small molecules used in OPV devices

Among other organic dyes, intriguing results were recently observed with a merocyanine as the molecular donor in small-molecule OPVs (Figure 3, compound **2**).²⁰ In fact, 6% efficiency was reported in a vacuum-deposited single-junction configuration. Remarkably, notwithstanding the great success of porphyrins in dye-sensitized solar cells, (discussed in Section 3) this class of compounds has not been as triumphant in OPVs due to their reduced absorption in the red region of the visible spectrum and the lower charge-carrier mobility and exciton-diffusion length of the evaporated films.^{21b}

It is noteworthy that one of the most uprisng molecules in the area of OPVs is subphthalocyanines (SubPcs).²¹ Studies have revealed that this phthalocyanine analogue can be used favorably both as the molecular

donor as well as the acceptor subcomponent of the device. In fact, SubPc **3**:C70 architectures have achieved 5.4% efficiencies,²² while fullerene-free systems, consisting of subnaphthalocyanine (SubNc) **5** as the donor and hexachlorinated SubPc **4** as the acceptor recently accomplished outstanding PCEs of 6.4% (Figure 4).²³ These are the so-called “all SubPc based-devices”, where the phthalocyanine analogue plays both donor (electron-rich SubPc **3** and SubNc **5**) and acceptor (electro-deficient SubPc **4**) roles. Interestingly, when **3** and **5** were used both as acceptors in a three-layer architecture with an α -sexithiophene (α -6T – compound **6**, Figure 4) as the donor, a record (in fullerene-free systems) 8.4% efficiency was observed.²⁴

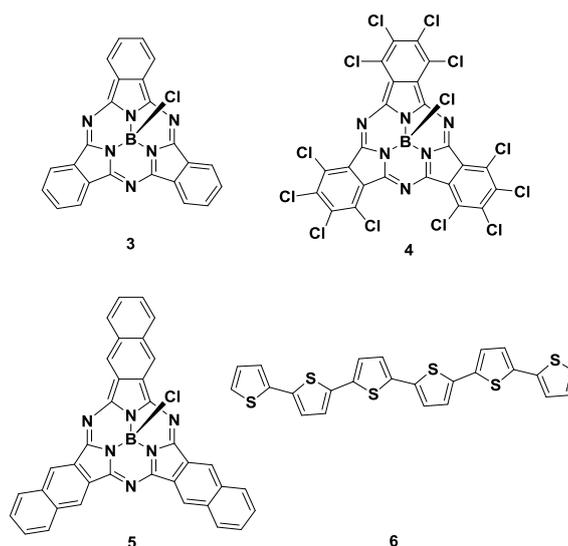


Figure 4. Donor and acceptor subphthalocyanine analogues and **a-6T** donor for OPVs

(iii) Multijunction (tandem) Solar Cells

The performance of single-junction OPVs has some limitations associated to the fact that only a small fraction of the solar

flux can be harvested by a single-layer BHJ. Organic semiconductors have, in general, low charge-carrier mobilities, which means that the thickness of the active layer must be restricted, and thus, only part of the incident light at the absorption maximum is absorbed. These limitations can be met by multi-junction configurations, consisting of multiple active layers with the same or different absorption characteristics, in a way that broader light-harvesting can be accomplished.

Polymers as well as small organic

molecules have been employed in multi-junction architectures.²⁵ In fact, in most cases, both the single- as well as the tandem-junction architectures are constructed, with the latter yielding usually enhanced performance.

In polymer tandem devices, the record is held by low bandgap analogue poly[2,7-

(5,5-bis-(3,7-dimethyloctyl)-5H dithieno[3,2-b:20,30-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)] (**PDTP-DFBT** – Figure 5), which, in a single-junction mode gave a 7.9% PCE, while in a tandem-mode, in conjunction with a P3HT:Indene-C60Bisadduct(ICBA), the performance grew to 10.6%.²⁶ When two identical PDTP-DFBT:PC₇₁BM sub-cells were used, instead, to construct a tandem device, the reported performance was 10.2% (Figure 5).²⁷

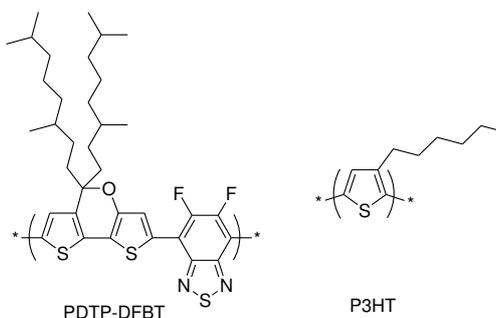


Figure 5. Structures of polymers **PDTP-DFBT** and **P3HT**, used in Tandem OPVs

3. Dye-Sensitized Solar Cells

Dye-Sensitized Solar Cells (DSSCs) were introduced by O'Regan and Gratzel in the 1990s²⁸ and brought a revolution in the area of photovoltaics.²⁹ The last decade has seen a tremendous evolution in the field and DSSC technologies exhibit a bright alternative to the standard silicon photovoltaics,³⁰ with the obtained efficiencies recently reaching 13%.³¹

The function of a DSSC is based on photoinduced electron injection from the excited state of an organic chromophore into the conduction band of a nanocrystalline metal oxide film, typically

TiO₂. In detail, the process begins by photoexcitation of the organic dye, upon which it injects an electron to the TiO₂. The oxidized dye is then regenerated by electron donation from the redox couple of the electrolyte (Figure 6). An external circuit is responsible for diffusing the injected electrons from the TiO₂ to the counterelectrode. Other than the productive phenomena, there are also competing processes that take place, namely, the recombination of the injected electrons with the oxidized dye or the redox couple (see processes 2 and 3 in Figure 6), and the relaxation of the excited dye to its ground state by a non-radiative decay process (process 1 in Figure 6).

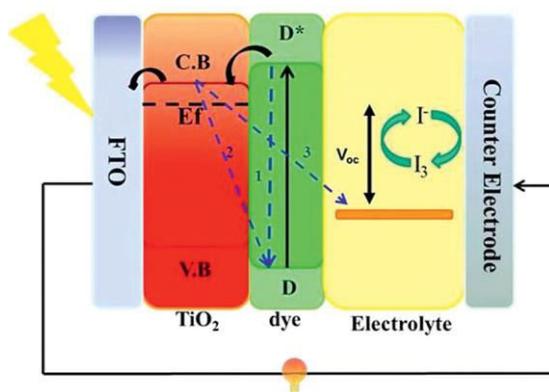


Figure 6. Operating principles of Dye-Sensitized Solar Cells. [Reprinted from reference 33b, Copyright (2013), with permission from Wiley]

Dye-Sensitized Solar Cells are defined by their low production costs and interesting technical features, including transparency, ease of processing and stability. Tailoring the physicochemical properties of the three main components of the cell (organic dye, nanocrystalline semiconductor and redox couple in the electrolyte) is of paramount importance for optimizing the performance of the devices.³²

The selected organic dye should fulfill certain requirements: it is necessary to possess appropriate HOMO and LUMO levels for dye regeneration and charge injection into the TiO₂. In addition, a

suitable anchoring group is required to attach to the semiconducting material, and, lastly, high extinction coefficients and absorption in the visible and NIR region are also important for efficient light-harvesting.³³ A vast amount of organic sensitizers have been tested in this respect, with the best performances being achieved with Ru-polypyridyl dyes,^{34,35} and porphyrins (Por)^{31,36} (Figure 7). The strong overlap of their absorption with the terrestrial solar spectrum together with their synthetic versatility, accountable for engineering the molecular properties, makes them ideal sensitizers for DSSCs.

At present, the record in DSSCs is held by M. Grätzel *et al.* with a “push-pull” porphyrin dye (**SM315**) that exhibits panchromatic response (Figure 7).³¹ An

outstanding 13% power conversion efficiency (PCE) was reported for this porphyrin-based device. As for Ru-polypyridyl dyes, the best performance has been achieved with **CYC-B11**, reaching an excellent 11.5% PCE (Figure 7).³⁵

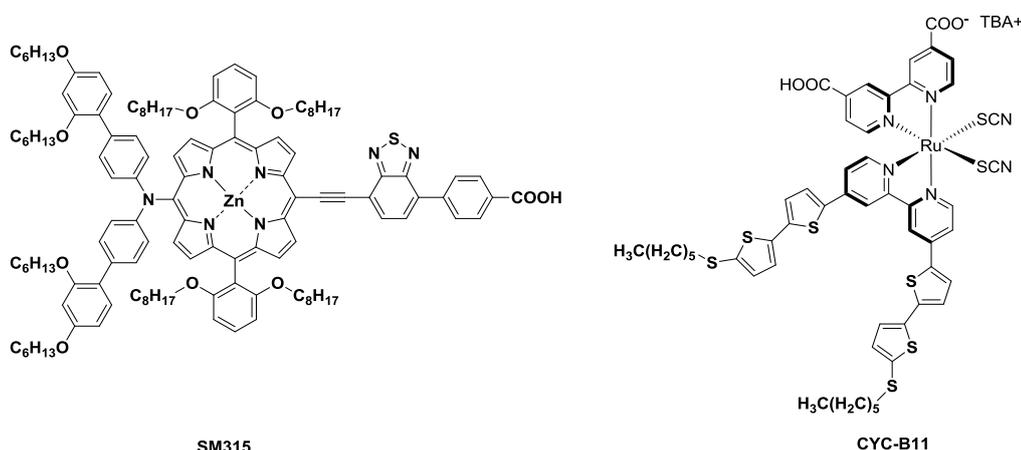


Figure 7. Structures of the most efficient porphyrin (**SM315**) and Ru-polypyridyl (**CYC-B11**) dyes used in Dye-Sensitized Solar Cells

In terms of the nanocrystalline semiconductor, it is noteworthy that the key to the breakthrough of DSSCs when they were introduced was the use of a mesoporous TiO₂ electrode;³⁷ a low-cost material that can be processed in transparent flexible films of significant interfacial area, that allows a high load of dye, and high electron mobility. Other oxides, such as ZnO,³⁸ SnO₂,³⁹ and Nb₂O₅,⁴⁰ have been tested as alternatives, but TiO₂ has overall given the best results, and it is still the most commonly used metal semiconductor.

Lastly, the third component of DSSCs that influences the device performance is the redox couple of the electrolyte. The role of the redox couple is to regenerate the oxidized dye after electron photoinjection. Usually I⁻/I₃⁻ is the preferred system, as it performs better than all other alternatives.⁴¹ However, certain disadvantages, such as its corrosive nature and complex two-electron redox chemistry, have led to other combinations being tested, including Br⁻/Br₃⁻,⁴² LiBr/Br₂⁴³ as well

as iodine- and hydroquinone-based redox couples.⁴⁴ Poor performance was, however, observed. The great breakthrough was achieved by the introduction of cobalt electrolytes. An attractive feature of these complexes is that their electronic properties and redox chemistry can be strategically engineered by varying the ligand environment. Tris(2,2'-bipyridyl)cobalt(II/III) was reported in 2010 by Feldt *et al.*,⁴⁵ and was followed by a number of other complexes, most based on 2,2'-bipyridine (bpy),⁴⁶ phenanthroline⁴⁷ and polypyridyl⁴⁸ ligands. Co-based electrolytes are now established as the most promising alternative to the standard I⁻/I₃⁻.

All the above mentioned results were obtained on liquid electrolyte-based devices. However, there is a number of engineering issues that are associated to the unfavorable properties of liquid electrolytes, and mainly their corrosiveness, leakage and volatility, which pose a major challenge in the mass production of DSSCs. In this context, great efforts are focused on the development of solid hole-transporting

materials towards the preparation of all-solid-state hybrid devices (ss-DSSCs).⁴⁹ To-date, even though tremendous progress has been seen, efficiencies of ss-DSSCs have not risen to the challenge of being at par with that of their liquid electrolyte counterparts. Several organic and inorganic materials have been proposed as hole-transporters,

with the best-performing ones being triphenylamine-based spiro-MEOTAD⁵⁰ (Figure 8) in organic-based materials, giving an overall efficiency 7.2% when paired with **Y123** dye,⁵¹ and CsSnI₃ in the inorganic analogues, reaching 10.2% in conjunction with the well-known **N719** dye (Figure 8).⁵²

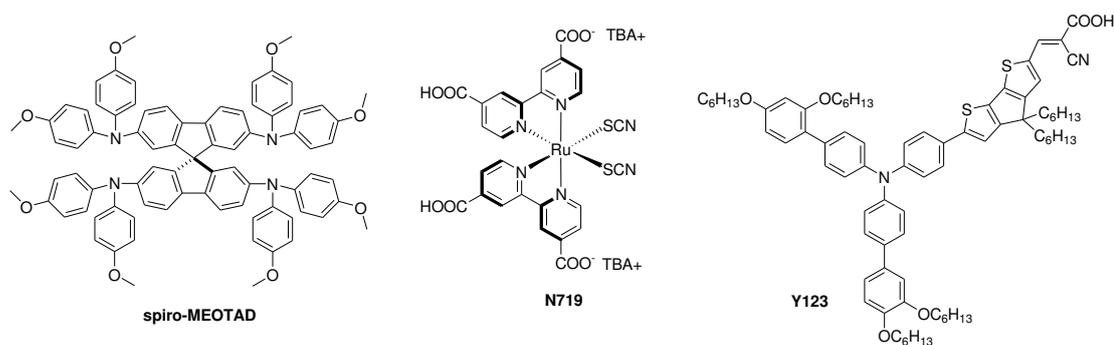


Figure 8. Structures of hole-transporting **spiro-MEOTAD** and organic dyes **N719** and **Y123**

4. Conclusions and new trends in solar cell research

Advanced solar energy technologies are widely pursued in an effort to achieve sustainable development while securing energy supplies. The areas of organic and hybrid photovoltaics have exhibited formidable progress recently, confirming the fact that they are among the most promising candidates for future energy production.

In particular, OPVs lately managed to break the symbolic 10% barrier with a tandem device, and DSSCs are on a flourishing ride, with efficiencies currently at 13% with a porphyrin-based architecture. Despite the extraordinary developments in these third-generation photovoltaics, further enhancements in the factors limiting device efficiency are required for these technologies to become more competitive. In OPVs current research focuses on the design and development of improved active materials, processing methods, and device structures.

Morphology is probably the major challenge in OPVs in an effort to reproducibly coat the active layer so as not to compromise charge separation and performance. As well, deeper understanding of photovoltaic processes and theoretical studies could accelerate the progress in the field. In terms of DSSCs, research focuses on organic sensitizers with better light-harvesting capabilities and alignment of molecular orbitals, lower tendency to aggregate, as well as higher photostability. Also intense efforts are dedicated in optimized liquid and solid electrolytes. Considering the pace of recent developments in both fields, it is quite probable that the 15% threshold is not very far from becoming reality.

Yet, one of the major breakthroughs in solar cell research came in 2009 with the introduction of perovskites as a visible-light sensitizer material.⁵³ This new class of photovoltaics has attracted extraordinary focus and has undoubtedly become the current trend in new generation solar energy applications. Perovskites are inorganic octahedral structures, represented as AMX₃ ("A" and "M" being different cations and "X" the anion that

binds to both), and it is their organohalide analogues (where X = halogen and A = aliphatic or aromatic ammonium) that have shown the most promising characteristics. These hybrid perovskites offer the advantages both of organic compounds (solution processability and synthetic versatility) and those of inorganic crystalline semiconductors (high charge mobilities and large absorption coefficients). In the last 5 years the area has met ballistic progress, going from 3.81% to over 17% efficiencies today.⁵⁴ The configuration of perovskite-based solar cells is very similar to that of DSSCs, however it is suggested that they work differently, even though their operating principles are not yet well-understood. With regard to performance, liquid-phase mesoscopic cells have reached 6%,⁵⁵ while more substantial developments have been accomplished in solid-state architectures. In particular, recently the Korean Research Institute of Chemical Technology reported a record 17.9% PCE.⁵⁶ Considering the latest achievements and the room for optimization of current state-of-the-art devices, efficiencies of 20% have been predicted.⁵⁷ For more-in-depth discussion on the various aspects of perovskite-sensitized solar cells, the reader is referred to several comprehensive reviews.^{54,58}

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