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Research article

# Dye sensitized solar cells: Meta-analysis of effect sensitizer-type on photovoltaic efficiency

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ABSTRACT

Since Dye-Sensitized Solar Cells (DSSCs) was created, a versatile and cost-effective alternative among photovoltaic technology options for power generation and energy transition to combat climate change have emerged. The theoretical and experimental knowledge of DSSCs have increased in regard to their operation in the last three decades of development; it includes the device's components, as well as the most recent innovations in their application and forms of activation. In this work paper, we presented a meta-study of photovoltaic characterization parameters, 329 scientific reports of DSSCs were considered to compare three types of sensitizers (Organometallics, non-metal organic dyes and, natural dyes). The objective of this study is to compare DSSCs performance when using three different sensitizers. In general, the best reported results related to DSSCs are based on organic and organometallic sensitizers. DSSCs based on organometallic compounds have an average efficiency of approximately 9.1 %, which displays the best average result; the maximum efficiency value recorded for DSSCs sensitized to organometallic compounds is 13.0 %. DSSCs based on synthetic organic sensitizers without the presence of metals in their structure, the average efficiency is approximately 7.1 % and the maximum efficiency values is 15.2 % (DSSCs utilize the co-photosensitization system and dye pre-adsorption treatment). DSSCs based on natural sensitizers indicated an average efficiency value about 0.5 % and the maximum efficiency value recorded is 2.3 %.

## 1. Introduction

Currently, one of the main sources of greenhouse gas emissions is related to the transformation of energy in the different types of industrial, agricultural and urban activities (e.g., transporting, housing, heating, cooling) [1–3]. The last report of the Mauna Load Observatory indicated that the $CO_2$ concentration in the atmosphere was 422.72 ppm, a higher value of 140 ppm than the pre-industrial era [4]. Most of natural resources that are used to supply this energy demand, are fossil by nature. The world's leading economies (China and the United States) are located in the top of the list as the world's leading energy consumers [5,6].

At present, the negative effect on the compounds of the atmosphere that are generated during chemical transformation processes, based upon the combustion reactions of fossil resources, it is already known and accepted by most of the scientific community. This type of process is mainly associated with atmospheric pollution of water and soil; moreover, in the last decades, it is connected with the global impact phenomena (such as global warming), which is causing environmental deterioration, resource depletion, soil erosion,

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endangered species, and affecting the human beings' health [7–9]. The last report from the Intergovernmental Panel on Climate Change (IPCC) stressed that it is "indisputable that human activities are causing climate change". The recent IPCC report exposed that, the global average surface temperature increases 1.0 °C above the pre-industrial level, and it is likely to reach 1.5 °C between 2030 and 2052, they forecast an increase of 2 °C by 2100 [10]. This growth trend is accompanied by an increase in the consumption of different resources of the planet (water, farmland, and energy).

If we consider the last IPCC report to maintain a dependent globalized world in all aspects of energy with fossil resources, it becomes less and less viable; not only its scarcity but also its great demand, that increases every decade. The search for renewable energy sources and the implementation of new sustainable technologies is a priority to ensure the survival of the next generations. Therefore, the large part of the research is focused on devising new routes to use renewable energies and create a reliable and accessible system to aim a sustainable energy transition from both, an economic and an environmental perspective.

Renewable energies are characterized by having the potential to operate in cycles that can exceed several human generations (their primary source of energy is the sun); additionally, they do not produce greenhouse gases. In 2021 the renewable energy (all types) represented the 12.6 % of the total final energy consumption in the entire world [11]. In the last two decades, among all the processes of conversion of solar energy into renewable electricity, the photovoltaic (PV) technology has received the most attention from specialized research centers around the world as a real alternative within the energy mix required to decarbonize the global energy matrix. Among PV technologies, DSSCs have emerged as a versatile and economical alternative for power generation. The theoretical and experimental knowledge of DSSCs have increased in regards to their operation in the last three decades of development, it includes the device's components, as well as the most recent innovations in their application and forms of activation [12,13]. The photoconversion efficiency of DSSC has progressed from 7.1 % [14] to 15.2 % [15]. The progress in the DSSC efficiency is combined with a breakthrough in reducing the manufacturing costs and the development in different application areas. Among of all photovoltaic technologies, DSSCs are one of the technologies with the highest cost/benefit ratio. Furthermore, they have the great versatility of being able to develop applications from traditional electricity generation, through the automotive industry, at home, (specifically interiors), military applications and electronic devices [16,17].

Efforts in the field of DSSCs have been directed at studying different types of sensitizers, obtaining a fundamental understanding of the principles of operation by modifying their electrical and optical properties, as well as advanced characterization techniques. Sensitizer candidates should accomplish the following requirements: (i) A wide range of electromagnetic radiation absorption in the visible range of the spectrum, preferably extending to the near-infrared. (ii) Reduced phenomena of deactivation of its excited state by emission of light or heat. (iii) Irreversible adsorption (chemisorption) on the semiconductor surface. (iv) Strong electron coupling between the excited state of the sensitizer and the valence band of the semiconductor. (v) Chemical stability in both the basal and excited states. (vi) Reduction potential sufficiently greater (greater than 0.15–0.20 V) than the edge of the semiconductor conduction band. Ease of injection into the conduction band. (vii) Oxidation potential sufficiently lower (greater than 0.20–0.30 V) than the redox potential of the redox-pair mediator. Easily regeneration of the sensitizer at its baseline state [18]. Efforts in the synthesis of sensitizers for DSSC can be classified into two broad areas: (i) Ruthenium(II)-polypyridyl (N3, N719, Z907) functional complexes with conversion efficiencies in the range 7.0–11.4 % [19]. (ii) Metal-free organic compounds in different types of configurations report conversion efficiencies in a wide range of 0.5–14 % depending on the type of organic sensitizer (synthetic or natural) used in the DSSC [19–21] and, (iii) natural dyes obtained from extracts of some plants and fruits with average efficiencies lower than 3 %.

In the first section, we covered introductory concepts of DSSCs operation, then, in the second section, we presented a meta-study of photovoltaic characterization parameters from 329 scientific reports of DSSCs to compare three types of sensitizers.

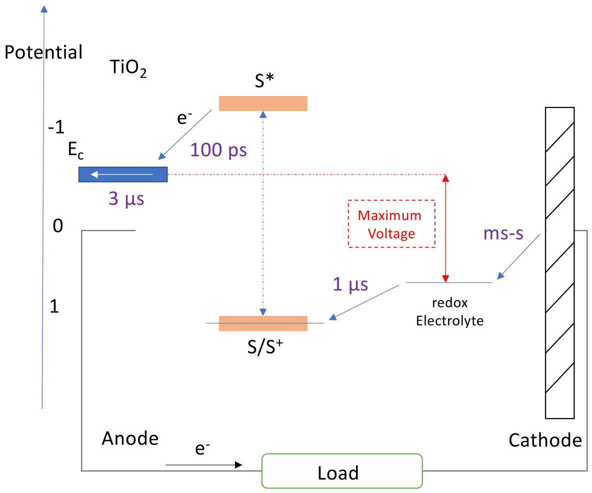


**Fig. 1.** (a) General scheme of the energetic levels in the DSSCs. Inside figure, the timescales to charge the transport process it is shown in purple color.

### 1.1. DSSCs operations

The components of DSSCs are: (i) Electrical contact, a window glass coated with a thin film of a transparent conductive oxide (TCO, e.g. Tin-doped indium oxide (ITO)). (ii) Photoelectrode, a meso-porous thin film of a semiconductor, being $TiO_2$ the most commonly used. (iii) Sensitizer, monolayer of an organic synthetic, or natural compound with a high molar absorptivity coefficient value in the visible range of the electromagnetic spectrum. (iv) Redox electrolyte: the most commonly used includes pair ($3I^-/I_3^-$) or pair ($Co^{3+}/Co^{2+}$). (v) Counter-electrode: TCO with a thin film of a conductor (platinum, gold, carbon). Fig. 1 shows the general scheme of DSSCs.

The principle of operation of a DSSC is according to these physical-chemical reactions:

$$TiO_2 \,/\, S + h\nu \leftrightarrow TiO_2/S^{*}_{LUMO} \tag{1}$$

$$TiO_2 \,/\, S^{*}_{LUMO} \rightarrow TiO_2\left(e^-_{CB}\right) / \, S^+ \tag{2}$$

$$TiO_2\left(e^-_{CB}\right) / \, TCO \rightarrow TiO_2 \,/\, TCO(e^-) \tag{3}$$

$$TiO_2 \,/\, S^+ + 3I^- \rightarrow [I_3]^- + TiO_2 \,/\, S \tag{4}$$

$$(e^-) + Pt \rightarrow Pt(e^-) \tag{5}$$

$$Pt(e^-) + [I_3]^- \rightarrow 3I^- \tag{6}$$

Where S represents the sensitizer molecule, CB represents the conduction band of $TiO_2$. In the first stage, S absorbs visible radiation; next, there is an energetic transition from the HOMO orbital to the LUMO orbital of the S (eq. (1)). Then, the photo-generated electrons are transferred to the semiconductor conduction band, oxidizing the ($S^+$) sensitizer (eq. (2)) with a timescale 100 ps. Afterwards, the electron migrates through $TiO_2$ to the TCO and the electron can exit to the external circuit to perform electrical work (eq. (3)) with a timescale 3 μs. The sensitizer is reduced to its initial state and $I^-$ is oxidized to $I_3^-$ (eq. (4)) in a timescale 1 μs. The ($e^-$) enters the solar cell again through the counter-electrode (Pt electrode) (eq. (5)). Finally, the redox pair regeneration occurs after receiving the ($e^-$) from the counter-electrode (eq. (6)) in a timescale between ms-s [22]; thus, the photovoltaic cycle is closed and the DSSC can start it again. The potential difference between the HOMO orbital of the sensitizer and the conduction band of the semiconductor determines the thermodynamic viability of the photo-generated electron injection process from the sensitizer to the semiconductor. The maximum voltage value obtained from a DSSC is attributed to the potential difference between the conduction band of $TiO_2$ and the redox potential of the electrolyte used to regenerate the sensitizer (Fig. 1). The redox pair typically used as an electrolyte is the pair ($I^-/I_3^-$) that exhibits a redox potential of 0.536 V versus the standard potential of hydrogen. In principle, it is possible to increase the maximum voltage value by using an electrolyte with a more positive redox potential value [23]. The redox-pair Cobalt$^{(3+/2+)}$ tris(1, 10-phenanthroline) ($[Co(phen)3]^{3+/2+}$)) with a redox potential of 0.2 V more positive redox pair ($I^-/I_3^-$) is used as an alternative redox-pair. Aside from the energetic requirements, entropic factors are associated with the proper functioning of the DSSC. Some authors argue that the greater number of available delocalized within the semiconductor, in comparison with the lower number of states within the sensitizer molecule may be associated with an increase in the entropy of the charge injection process from the

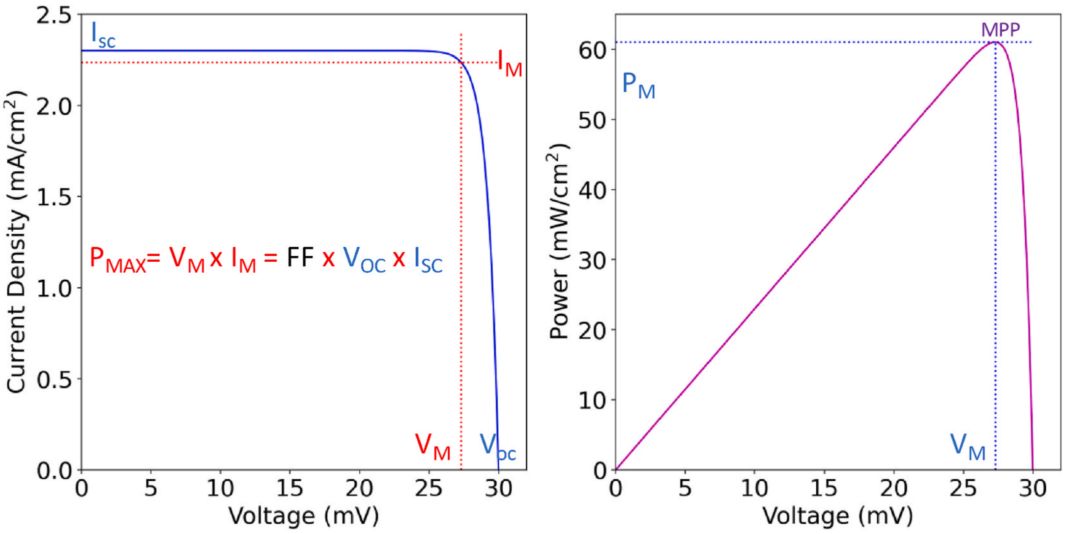


**Fig. 2.** (a) I-V curve and (b) P-V curve of a solar cell simulation using eq. (7). Inside figure: $V_{OC}$ = Open circuit voltage. $J_{SC}$ = Short circuit current. $I_M$ = Current of maximum power. $V_M$ = Voltage of maximum power. MPP = Maximum power point.

sensitizer; this factor makes possible the charge separation process [24]. Another influential aspect that affects the DSSCs operation is related to the competition of different physicochemical processes altered by time. The kinetic aspects of these phenomena determine the rates of excitation and electron transfer within the device and the rates of the recombination processes that act on the device's performance [25].

### 1.2. DSSCs characterization

The solar cells performance is tested by carrying out current measurements (I) as a function of the bias voltage (V) under illumination. This methodology allows to obtain the IV-curve of the solar cell. This type of characterization can be executed by specialized centers or in research laboratories under standard conditions: 25°C, total irradiance of 1000 W/$m^2$ according to the standard (EC standard 60904-3) [26]. The I-V curve under illumination is given by the following ratio:

$$I = I_{ph} - I_s - \left[ e^{\left(\frac{q\nu}{kT}\right)} - 1 \right] \tag{7}$$

Where $I_{ph}$ is the of the photocurrent generated under irradiation. $I_s$ is the diode saturation current, $V$ the bias voltage, $q$ the charge of the electron, $k$ the Boltzmann constant, and $T$ the absolute temperature. Under illumination, curve IV (eq. (7)) yields several important parameters (see Fig. 2(a)).

When the output voltage is equal to zero (V = 0) the short-circuit current ($J_{sc}$) is obtained, when the current is equal to zero (I = 0) the open-circuit voltage ($V_{oc}$) is obtained. The $V_{oc}$ value of the cell relies on the potential difference between the conduction band of $TiO_2$ and the redox pair of the redox-pair, the highest values of $V_{oc}$ are located between 0.85 and 1.05 V (details in supporting information). Fig. 2(b) shows the Power curve as a function of the Cell Voltage (PV-curve). From this curve, the point of maximum PM power of the solar cell is estimated. The maximum power of the cell corresponds to the maximum rectangular area that can be obtained under the IV-curve at the Maximum Power Voltage and Current points (red rectangle Fig. 2(b). This parameter allows to calculate the fill factor (FF) of the solar cell, which is another parameter that characterizes the performance of the cell, the FF is defined as follows:

$$FF = \frac{I_M V_M}{I_{sc} V_{sc}} \tag{8}$$

Where $I_M$ and $V_M$ represent the current and voltage at the point of maximum power PM (see Fig. 2(b). A suitable *FF* (eq. (8)) value presents values between 0.7 and 0.90 range. A higher fill factor indicates a more efficient and optimized device [27]. Finally, another parameter that characterizes the solar cell is the conversion efficiency (η). This parameter is determined by dividing the maximum

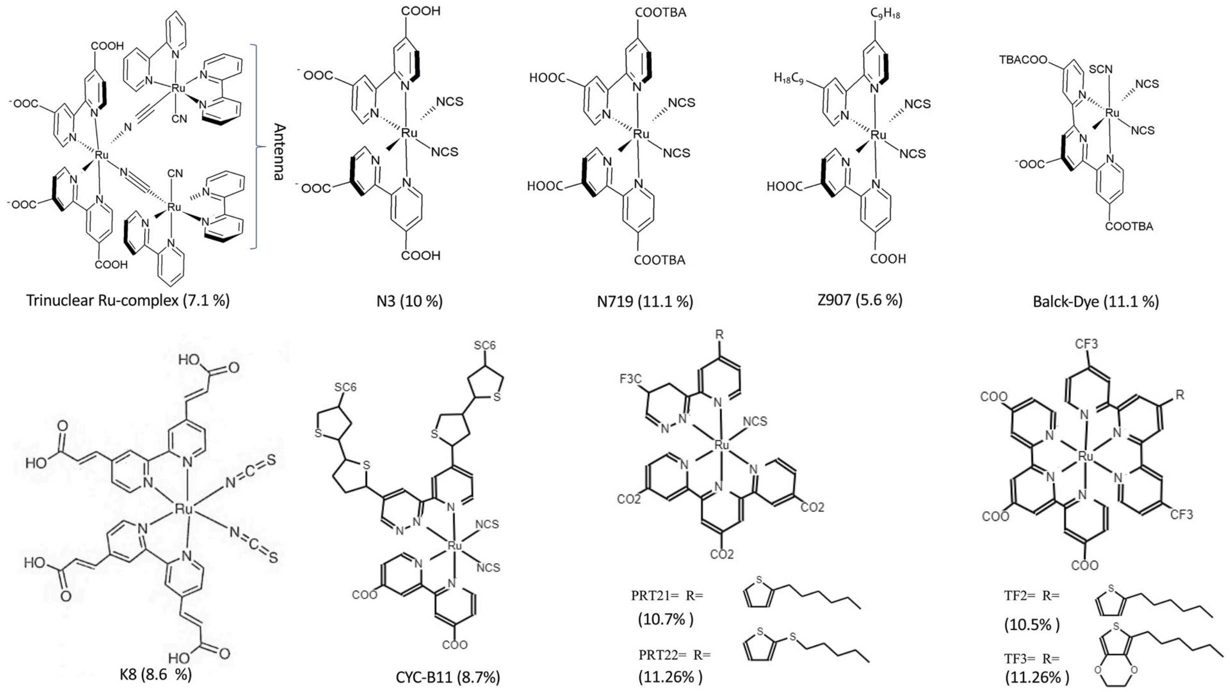


**Fig. 3.** Trinuclear Ruthenium complex reported by Grätzel in the first DSSC and chemical structure of some Ruthenium complexes reported as sensitizers in DSSCs. (Inside figure TBA = terbutyl alcohol).

power generated by the cell into the power of the incident radiation that can be calculated through the following relationship:

$$\eta = \frac{I_M v_M}{W_{incident}} \tag{9}$$

The theoretical limit of a traditional solar cell conversion efficiency (eq. (9)) is close to 30 %. However, the record efficiency of this type of cell is 15.2 % currently. In the following sections, we present a meta-study, in which more than 329 reports of DSSCs were considered to compare the IV-curve parameters that incorporate three types of dyes: (i) Organometallics, (ii) non-metal organic dyes and, (iii) natural dyes.

## 2. Sensitization in DSSCs

### 2.1. Ruthenium complex

Since the first report made by O'Reagan and Grätzel, in which a polynuclear ruthenium complex was used as a sensitizer, these sensitizers have presented a great evolution. The first compound reported as a photosensitizer of DSSCs contained 3 Ruthenium centers (Fig. 3), in these two bipyridine ruthenium complexes (highlighted in blue) were linked to the central ruthenium complex through cyanide bonds. The central ruthenium bipyridine complex (highlighted in green) was anchored to the $TiO_2$ surface via one-carboxylate group bonds. Fig. 3 shows the chemical structures of main Ruthenium complex used as sensitizers in the manufacture of DSSCs [28]. The trinuclear Ru-Complex (Fig. 3) presented two absorption bands in the visible range; the antenna complexes absorbed the higher energy visible radiation and transferred it to the anchoring complex by means of Metal-Ligand Charge Transfer (MLCT) and the lower energy visible radiation is associated with the MLCT process of the central complex. For this system Grätzel et al. reported an efficiency of 7.1 % [14]. Despite the promising result obtained with the trinuclear ruthenium complex, the two metal complexes of the "antennas" generated a great steric effect that prevents their additional modification. Next, Nazeeruddin et al. reported a maximum efficiency of 8.6 % by using K8 dye as sensitizer [29].

Consequently, Nazeeruddin et al. reported the dye N3 (cis-di(thiocyanate)bis(2,2-bipyridine-4,4dicarboxylate)ruthenium]]) as a sensitizer of a DSSC with an efficiency of 10.3 % [30]. This sensitizer only contained a ruthenium center and was structurally simpler, generating a lower steric effect during the adsorption and coupling process on the $TiO_2$ surface than the trinuclear ruthenium complex of the original DSSC. The elimination of the two ruthenium centers allowed to expand the range of possible modifications that could be made to improve the optoelectronic properties of the potential sensitizers. In 2006 Nazeeruzzin et al. reported the dye N719 (Fig. 3) where a modification of the carboxylate group counterion is added within the pyridine ring (TBA+: tebutylammonium cation), the inclusion of this new group improved the DSSC performance, it was reported an efficiency of 11.2 % [31]. Ru(II) complexes have a general formula of cis-di(thiocyanate)bis(2,2bipyridyl-4,4-dicarboxylate)-ruthenium(II), they present outstanding properties as charge transfer sensitizers and a wide range of visible light absorption. They also expose the relatively long-lived excited state; those characteristics turn a sensitizer into an attractive one for homogeneous and heterogeneous redox reactions [32]. The high efficiencies of DSSCs based on Ruthenium (II)-polypyridyl compounds can be attributed to their wide absorption range from the visible region to the near-infrared (NIR) and the Metal-Ligand Charge Transfer process, which results in high $I_{sc}$ values (18–25 $mA/cm^2$), they also have sufficient stability in their excited state to guarantee that heterogeneous charge transfer processes (towards the conduction band of $TiO_2$) can occur. Additionally, this type of compound has carboxylic groups within its structure; the carboxylate groups attached to the bipyridyl rest reduce the energy of the $p^+$ orbital of the ligand. Since the electronic transition is an MLCT charge transfer type, the excitation energy is effectively channeled towards the carboxylate group and injection of the charge carrier into the conduction band of $TiO_2$ occurs efficiently [33]. The HOMO and LUMO orbitals of the sensitizer must be spatially separated within the molecule to guarantee that MLCT process will be efficient. If the LUMO orbital is located in the vicinity of the anchoring group to the surface of the semiconductor, it will facilitate the injection process of the charge carrier towards the semiconductor; on the contrary, if the HOMO orbital is located on opposite place from the surface of the semiconductor, the recombination processes will be reduced and the regeneration process of the sensitizer will be facilitated due to the interaction with the electrolyte in solution [34]. Once the carboxylate group is added to the sensitizer that it has been fixed to the TiO2 surface, it provides stability during the charge transfer process; research about the modification of the anchoring functional group of the sensitizer to the $TiO_2$ surface is limited; most of the reports implement the carboxylate group as the anchoring group [35]. Some authors have reported that phosphonate groups as anchoring alternatives between ruthenium dye and $TiO_2$ are viable options [36]; however, the 2,2-Bipyridine-4,4-dicarboxylic acid is consider the best option to anchor Ruthenium dye on $TiO_2$ surface [37]. The chemical interaction between the carboxylic group and the $TiO_2$ surface can occur mainly through a monodentate coupling or bidentate bridge. 2. The most probable type of adsorption of the carboxyl groups is the bidentate type, in contrast to the monodentate type (or ester bond), because the negative charge is distributed over the substituent groups [38]. Mishima et al. reported a theoretical study using density functional theory (DFT) of the system cis-$[Ru(4,4'\text{-}COO\text{-}2,2'\text{-}bpy)_2(NCS)_2]/TiO_2$. They reported that the electronic injection process from the ruthenium sensitizer to the $TiO_2$ is favored from the thermodynamic point due to the strong molecular coupling between the sensitizer and the $TiO_2$, they reported that the LUMO orbital of the sensitizer was greater than the obtained for $TiO_2$ [39].

Since Grätzel's first report, a series of modifications to ruthenium complexes have been made to improve photoconversion efficiency and stability [40]. Tris(2,2-bipyridyl) ruthenium (II) and its homologs are widely studied for being redox sensitizers in the excited state of the analog bis(2,2-bipyridyl) ruthenium (II). Their chemical stability and ease interfacial charge exchange with semiconductor are characteristics of these derivatives. One of the most attractive factors of these complexes is their high extinction coefficient in the visible range [41]. Different molecular design factors allow in principle to improve the response of the synthesized sensitizers; Potential modifications include structural changes to improve the characteristics of: (i) Absorption in the visible range. (ii) Increase in the absorption range to the near-infrared. (iii) Stability of the excited state of the sensitizer. (iv) Addition of ligands to improve the electron injection into the semiconductor conduction band. Various types of chemical groups *moites* in the *ortho-, meta- and para*-positions of the pyridine group have a great influence on the absorption coefficient and therefore on the photocurrent of DSSCs. Other studies suggest that modifying the target position of the sensitizer anchoring group results in lower DSSC efficiency [42]. The reduction in the modification in the *meta* position of this type of sensitizer is associated with the generation of competition reactions and steric problems during the dye adsorption process. In relation to *p*-derivatives sensitizers best efficiencies have been reported (e.g., four times more efficient than the derivatives obtained from modification in the *meta*-position and two times more efficient than *ortho*-derivatives positions [43]). Furthermore, the extension of the pi-system of the peripheral ligands (-para position of the pyridine ring) is a strategy that was reported to increase the molar extinction coefficient [44]. The incorporation of auxiliary ligands with extended π conjugation allows shifting the absorption range of the dye towards lower energy values (shift towards the

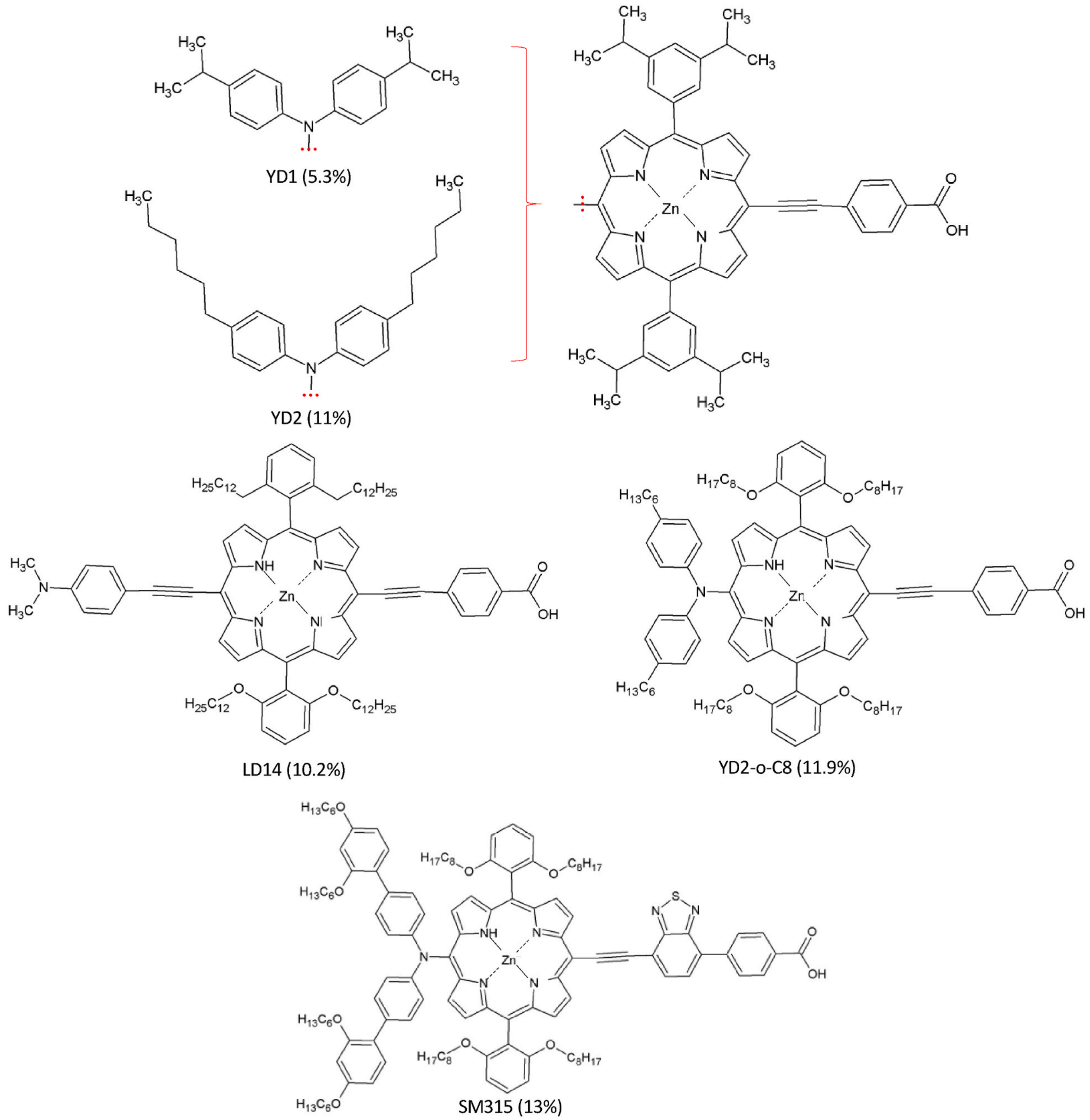


**Fig. 4.** Chemical structure of some *push-pull* porphyrins employed in DSSCs.

near-infrared) of the electromagnetic spectrum. Additionally, this type of modification can increase the value of the molar extinction coefficient of the dye [45]. Another strategy reported to improve the stability of DSSCs subjected to high temperatures has been the use of amphiphilic polypyridyl ruthenium sensitizers. When these amphiphilic sensitizers have been implemented in DSSCs, efficiencies of 8.2 % have been reported [46]. The use of thiocyanate ligands allows shifting the absorption range of the dye towards lower energy values (shift towards the near-infrared) of the electromagnetic spectrum. Notwithstanding, thiocyanate ligands are fragile parts of ruthenium sensitizers. It is a monodentate ligand and, it is easier to uncoordinated than a bidentate ligand like the bipyridine.

## 2.2. Porphyrin dyes

The porphyrins are an important group of sensitizers employed in DSSCs. The optical behavior of porphyrin is characterized by two intense absorption bands in the visible range of the electromagnetic spectrum, the Soret band between 400 and 500 nm and the Q band between 550 and 700 nm [47]. Modification of the molecular structure and the type of metal coupling to the porphyrin core allows modulation of these two bands in such a way that the panchromatic dyes are suitable as sensitizers for DSSCs [48]. Among the most important research on the study of these chemical structures is the progress of Tachibana et al. [49]. This research describes the charge transfer process between tetrakis(4-carboxyphenyl)potphyrin and $TiO_2$, revealing very fast electron injection kinetics similar to those observed in ruthenium-based cells. The presence of a dimethylaniline donor group introduced the concept of *push-pull* porphyrins. In this system, the macrocycle acts as a π-spacer between a strong electron donor group and an electron acceptor group being successful for optical absorption and collection visible radiation of larger fractions increasing the efficiency of photoconversion. Cheng-Wei et. alt., reported one of the first *push pull* porphyrins. They used dye YD1 and reported an efficiency of 5.3 % [50]. Cheng et al. reported high efficiency of photoconversion by using LD-14 dye as sensitizer, they reported an efficiency of 10.2 % [51]. After that, Grätzel et al. reported an efficiency of 11 % when incorporate YD2 dye as sensitizer [52]. Grätzel et al. reported improved the efficiency until 11.9 % when incorporate YD2-o-C8 dye as sensitizer [53]. The record of photoconversion for porphyrins sensitizers was reported by Mathew et al. they used the SM315 dye a reported an efficiency of 13 % [54]. Fig. 4 shows the chemical structures of these phthalocyanines.

The main drawback of these dyes is the tendency to porphyrin-aggregation on the $TiO_2$ surface, which leads to an automatic extinction of the absorbed photon before the electron injection into the semiconductor. To prevent the aggregation, it is common the implementation of co-adsorbents to maintain the molecules physically separated after anchoring to $TiO_2$ surface [55]. Popular co-adsorbents include chenodeoxycholic acid (CDCA) [56], hexadecylmalonic acid (HDMA) [57] and, dineohexylbis (3,3-dimethylbutyl) phosphinic acid (DNHOP) [58]. Employing long alkyl chain prevents aggregation and allows to protect $TiO_2$ from unwanted interactions with the electrolyte to make work the macrocycle core. An alternative strategy to improve the photoconversion efficiency of DSSCs is related to the redox mediator, other than the classical one (iodide/triiodide), porphyrin-based DSSCs report promising

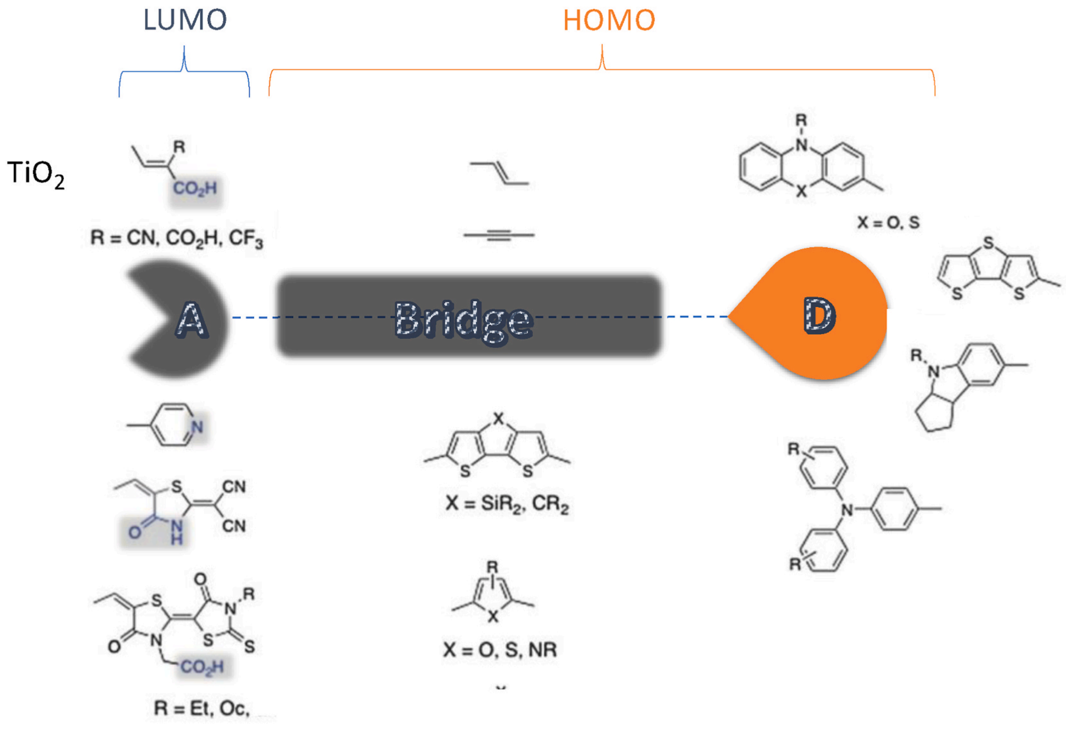


**Fig. 5.** Diagram of the A-π-D configuration with some of the main groups of each unit. Inside figure, A: (acceptor group, the anchor groups to the semiconductor surface are highlighted in grey). Bridge: (bridge - π -). D: (donor group). A diagram of the distribution of the HOMO and LUMO orbitals within the system is shown. Adapted from Ref. [20].

results, using the $Co^{2+/3+}$ tris(Bipyridyl) complex, in which reported improvements were higher than 20 % in comparison with reference [59]. Reports that have the highest percentages in their results, they employ this pair-redox inside these DSSCs structures.

### 2.3. Organic synthetic dyes

In searching for the improvement of DSSCs, different types of sensitizers have been used, ruthenium organometallic complexes and sensitizers based on metallic porphyrins have long reported the best efficiency values. Nevertheless, over the years several types of metal-free organic compounds have been developed with reported efficiencies greater than 10 %. These types of compounds offer design and synthesis advantages, high molar absorptivity coefficients, and lower manufacturing costs, if they are compared to organometallic complexes. Within this framework, regarding the manufacture of sensitizers, it has been used a wide configuration called Acceptor-Bridge-Donor (A-bridge-D, A-π-D), this configuration is developed to guarantee the charge separation and electronic injection from the sensitizer to the semiconductor [20]. Fig. 5 shows a general scheme of the A-π-D configuration with some of the main groups of each unit within system. A donor group (D) (with high negative density) is connected via a bridge (a group with conjugated π bonds) to a charge-acceptor group (A) bonded to the semiconductor.

This strategy seeks to favor the process of electronic injection to the semiconductor, ensuring adequate electronic coupling, while reducing recombination processes [23]. Donor groups include carbazoles, indoles, trialrylamines, phenoxazines, and dithianethiophenes. In addition, polyenes, thiophenes, furans, pyrroles, and benzothiadiazoles are examples as π spacer units [24]. In a sensitizer with the A-π-D configuration, the HOMO orbital is mainly located between the donor unit and the π bridge, and the LUMO orbital is distributed in the acceptor part (Fig. 5). This is one of the attractions of this type of sensitizer since the modification or change of each of the units that make up the A-π-D configuration is one of the most used strategies to control the energy levels of the excited state, thus influence the photophysical properties of the compounds [60]. Fig. 6(a) shows a schematic example of anchoring of the dye TC301 on the $TiO_2$ surface employing the A-π-D configuration [40]. Furthermore, Fig. 6(b) shows the timescale for the possible recombination process in DSSCs. The possible $e^-$-recombination process includes: (i) $e^-$-recombination from the semiconductor HOMO of the dye, (ii) $e^-$-recombination from the semiconductor to the electrolyte. (iii) electron transfer from the FTO to the electrolyte [22]. Fig. 7 shows some examples of organic dyes with A-π-D configuration. Wang et al. reported cumarin NKX-2700 as new A-π-D sensitizer to DSSCs (see Fig. 7). They reported that breakup of π-stacked aggregates might improve electron injection yield. They reported an efficiency of 8.2 % after the addition of deoxycholic acid (employed as co-adsorbent) during sensitization of $TiO_2$ [61].

After Wang et al. reported MK-dyes which have a carbazole derivative as an electron donor and a cyanoacrylic acid moiety as an electron acceptor and an anchoring group. They reported an efficiency of 8.3 % when MK-2 dye was used as sensitizer [62]. Ren et al. synthesized FNE92 sensitizer, a thiophene bridged double A-π-D dye. This dye reduces the π-π intramolecular interactions to improve the electron injection, hence the photocurrent generation. They reported a photoconversion efficiency of 6.6 % [63]. Zhou et al. verified the positive effect of extending the molecular conjugation strategy. They reported that sensitizer A10 generated higher $J_{SC}$ values than the AZ6 reference sensitizer. The DSSC based on A10 shows an efficiency of 8.54 % [64]. Despite the high absorption capacity of organic dyes, the light-to-electricity conversion efficiencies of some dyes are quite modest, if it is compared to those of ruthenium(II)-polypyridyl complexes; this is due to their relatively narrow absorption bands in the visible region. A promising strategy to improve the photo-response of sensitizers is co-sensitization by using two or more different sensitizers with complementary absorption properties. This strategy has two benefits: (i) it increases the number of solar photons captured, (ii) it improves coverage of the

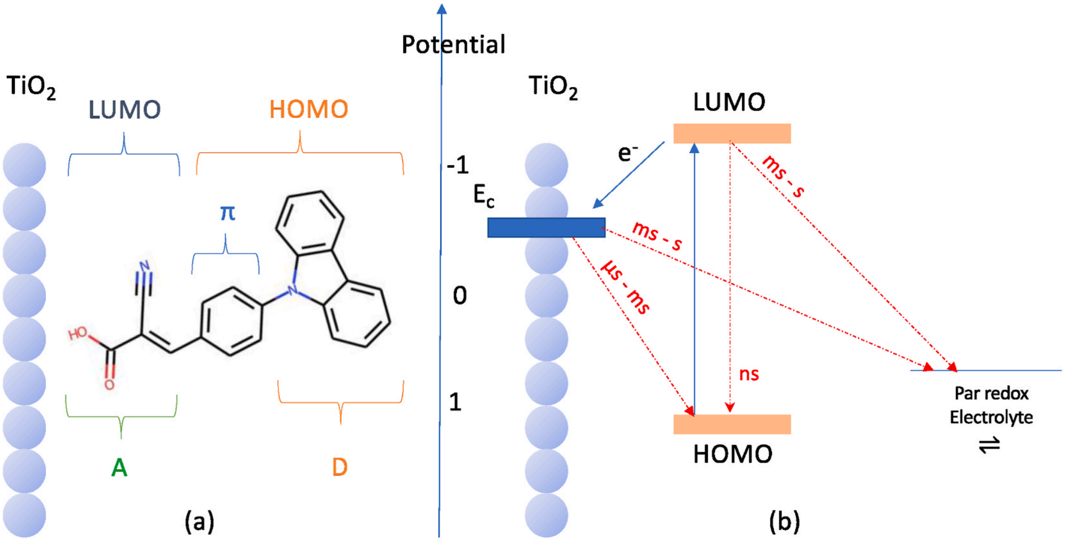


**Fig. 6.** (a) The A-π-D dye structure example with dye carbazole derivative C301 as example. (b) Timescale for the possible recombination process in DSSCs.

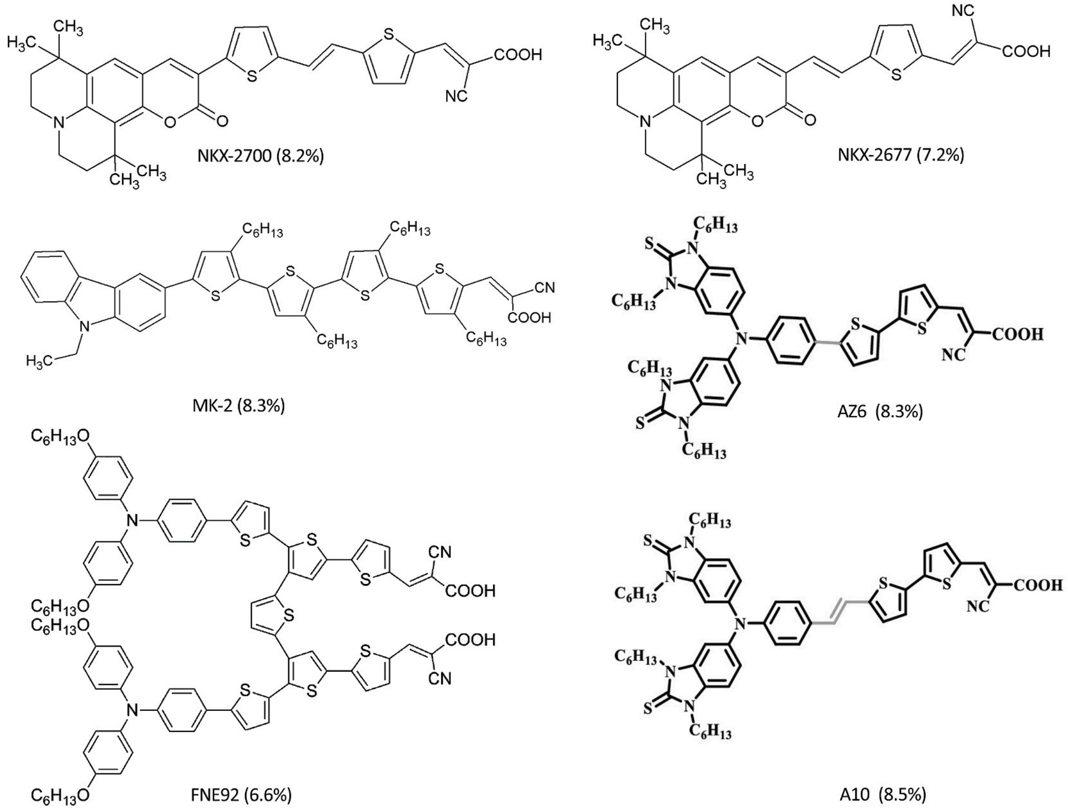


**Fig. 7.** Chemical structures of some A-π-D dyes, that show the photoconversion efficiency.

semiconductor surface and, (iii) synergetic effect between photophysical properties of sensitizers [65]. Spitler et al. studied DSSCs with a mixture of dyes (JK2 and TT1), whose absorptions covered the entire visible spectrum, They found that the $J_{sc}$ value for a solar cell with a $TiO_2$ film, it was exceeded than a cell with the dye N3 [66]. Zhang et al. examined the mechanism of co-photosensitization of Squiralyum and N3 stains by temporal resolution spectroscopy, It was demonstrated, that this dye is less efficient than N3 due to the slow injection process to the conduction band of semiconductor. A combination of cyanine dyes such as 4-(dimethylamino)phenyl cyanoacrylic acid were employed as co-photosensitizers in DSSCs [67]. Although the amount of adsorption of each dye decreased after the co-photosensitization by cooperative interactions, this approach gave a higher efficiency of 6.5 %. Finally, Nazeeruddin et al. combined the two dyes and demonstrated an overall efficiency of 7.4 % [31]. The co-photosensitization process has reported the majority of the highest photoconversion values, that have been recorded up to date. Fang et al. reported an efficiency of 7.44 % in DSSCs based on cosensitization strategy [68]. Liu et al. reported that the cosensitization based on two or multiple dyes as dye-cocktails can present synergic effect photovoltaic properties. They used SW-2 and SW39 dyes in DSSCs to reported an efficiency of 9.48 % [69]. Kakiage et al. reported that mixing ADEKA-1 and LEG4 in a DSSC with a redox pair electrolyte ($Co^{3+}/Co^{2+}$) generated a photoconversion efficiency of 14.3 % (see Fig. 8). The authors reported that the two sensitizers enable to improve the electronic injection process from the photosensitizers in the excited state. Furthermore, a redox system with a more positive potential than the traditional pair (iodine/triiodide) was employed, generating a $V_{oc}$ of 1.014 V and $J_{sc}$ of 18.27 $mAcm^{-2}$ [70]. Ren et al. reported maximum photoconversion efficiency of 15.2 %, they used a co-sensitization strategy to apply hydroxamic acid pre-adsorption as a strategy to make better the dye molecular packing. They found that adsorbing hydroxamic acid on the $TiO_2$ surface, before co-sensitization assisted the adsorption of dye molecules and inhibited the desorption of the cosensitizers [15].

They combined two sensitizers, the first one, SL9 that served as the primary long wavelength light harvester and the second one, SL10 (see Fig. 8). The role of the alkyl substituents is to increase the solubility and depress interfacial charge recombination. This system reported the highest efficiency value 15.2 % that corresponds to the cell with a value of $V_{oc} = 1.04$ V; $FF = 0.821$; $J_{sc} = 17.8$ mA/cm$^2$.

### 2.4. Natural sensitizers

In recent years, different types of natural dyes have been used as $TiO_2$ sensitizers, these materials are inexpensive and biodegradable. Obtaining this type of sensitizers is not expensive as they can be when extracting them by means of simple techniques. The efficiency of the extraction process will depend on the solvent and the specific technique that are going to be used. Moreover, natural dyes have a high coefficient of molar extension and absorption in the visible region. Over the past few years, different types of

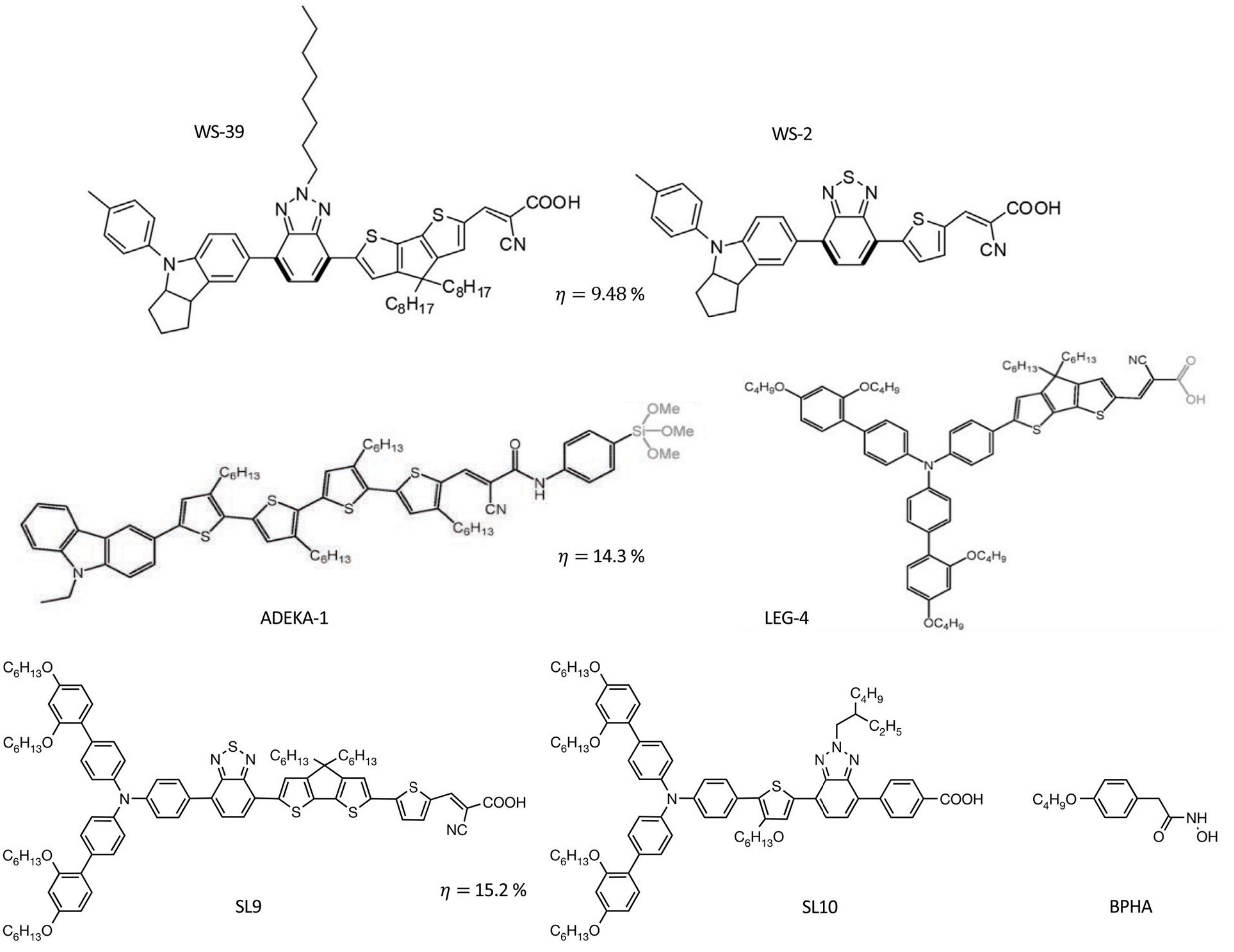
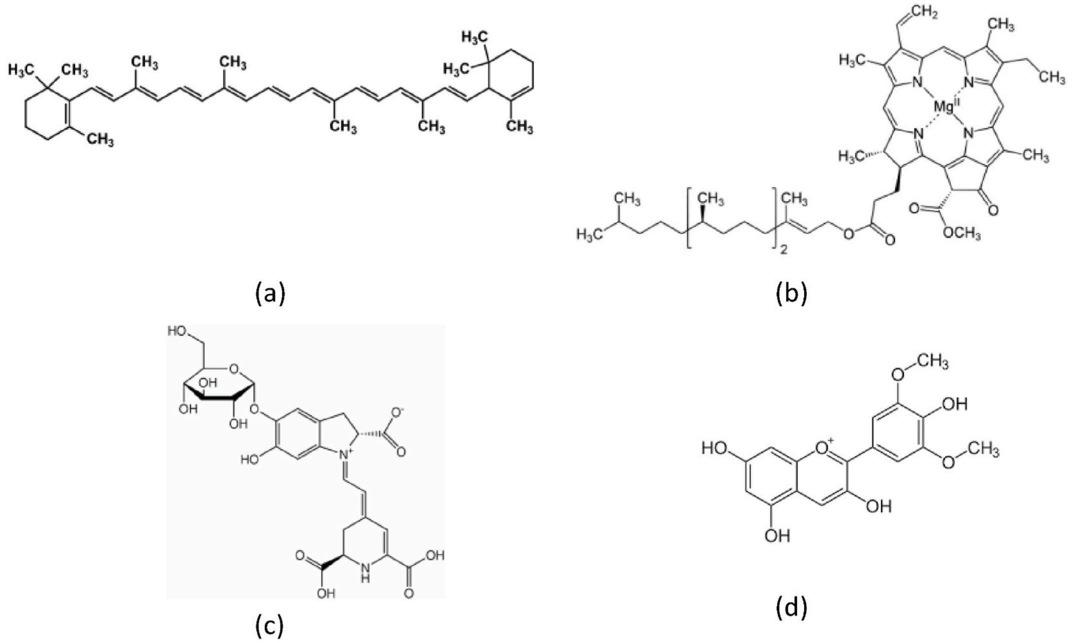


**Fig. 8.** Chemical structure of organic compounds employed in DSSCs based on co-sensitizers with highest photoconversion efficiencies.

sensitizers have been explored, such as chlorophyll derivatives, carotenoids, anthocyanins and betalains [71]. Fig. 9 shows some of the most representative natural sensitizers: (i) carotenoids present in all photosynthetic and bacterial plants (Fig. 9(a)), (ii) chlorophylls present in all photosynthetic plants (Fig. 9(b)), (iii) betalains (betacyanins and betaxanthins) present in fungus and cactus (Fig. 9(c)), and (iv) anthocyanins, fruit and flowers with a reddish-violet color (Fig. 9(d)). Natural dyes offer an economical and environmentally friendly alternative to sensitize the surface of $TiO_2$ in DSSCs applications [72].

Some fruit, plants, flowers and, leaves contain various pigments, which can be easily extracted and then used as sensitizers, almost all green plants have significant amounts of chlorophyll, a compound of vital importance for the absorption of photons during the process of photosynthesis. Chlorophylls can absorb electromagnetic radiation in the wavelength range (400–500 nm) and between the range (600–700 nm) and it is precisely this absorption capacity that allows them to be presented as potential natural sensitizers in DSSCs. Al-Alwani et al., studied the properties of DSSCs sensitized with chlorophyll extracted from spinach, the authors reported $V_{oc}$ values of 0.550 V and $I_{sc}$ of 0.46 $mAcm^{-2}$, in addition to an *FF* close to 51 % with an efficiency of 0.130 %. Al-Alwani et al., reported on chlorophyll extracted from wormwood in DSSCs values of $V_{oc}$ 0.585 V, $I_{sc}$ of 1.96 $mAcm^{-2}$ and an *FF* close to 47 % with a photoconversion efficiency of 0.538 % [73]. Narayan et al. demonstrated the sensitizing potential of native species with the study of 20 dyes extracted from natural materials such as flowers, leaves and, fruit. The photoelectric conversion efficiency of the solar cell sensitized with the ethanolic extract of the unpurified mangosteen pericarp reached 1.17 %. Ahliha et al. conducted a comparative study between anthocyanins and chlorophyll as sensitizers for DSSCs [74]. Another important group of potential sensitizers are flavonoids, these compounds are a group of heterocyclic pigments widely distributed among plants, they constitute the vast of the yellow, red and blue colors of these species and their fruit; in this case, the most representative are: anthocyanins, flavones, flavonols, flavans, flavanones and isoflavonids. Anthocyanins belong to a prominent group within the group of flavonoids, they have a variety of characteristics that make them attractive as sensitizers: (i) They have high values of light absorption coefficients in a wide range of the electromagnetic spectrum ranging from 450 to 600 nm. (ii) It has hydroxyl groups in its structure, which allows a better anchoring to the surface of $TiO_2$. (iii) They have sufficient conjugated bonds π. Normally, glycosylated anthocyanins are found in different fruit and are associated with their intense colorations (e.g., strawberries, blackberries). Inbarajan et al. reported an efficiency of photo-conversion of 1.17 % when using anthocyanins extracted from the peels of Allium cepa as sensitizer for DSSCs [75]. In other



(a) (b) (c) (d)

**Fig. 9.** Representative natural pigments used as sensitizers in DSSCs. (a) Carotene, (b) chlorophyll, (c) betalian, (d) anthocyanin.

study, Maulina et al. reported an efficiency of photo-conversion of 0.59 % when using anthocyanins extracted from the Mangosteen peel as sensitizer for DSSC [76]. The carotenoids are another type of dye to be used in DSSCs. They can absorb photons of sunlight in the visible region in the wave range of 400–510 nm. They also have a carboxyl group that allows them to bind to the $TiO_2$ interface. All carotenoids are polysoprenoid, they have a system with conjugated single and double bonds, these molecules are highly reactive and degrade more quickly, due to the small amount of oxygen [77]. When the $TiO_2$ surface is modified, nanoparticles with carotenoids that contain different terminal functional groups, such as carboxyl groups, the $TiO_2$ surface results in different types of surface interactions that strongly affect electron transfer from carotenoids to $TiO_2$ nanoparticles [78]. Carotenoid extraction can present challenges because there is no optimal solvent to prevent the degradation process. Sipriyanto et al. conducted research with tomato, orange and carrot extracts to conclude that their efficiencies are 0.03 %, 0.02 % and 0.009 % respectively [79]. Finally, betalains are another type of metabolites with the potential to be used as natural sensitizers. This type of natural dye is made up of two main compounds, bexanthins that give it a yellow-orange color and betacyanins that give it a red-purple color. Their coloration is attributed to conjugated double bonds, it exhibits the maximum light absorption at 480 nm for yellow betaxanthins and at 540 nm characteristic of red betacyanins. Shalini reported the efficiency of photoconversion 0.46 % when extract form beta vulgaris was used as sensitizer [80]. Purushothamreddy et al. reported an efficiency of photo-conversion of 0.56 % when betacyanins are used and extracted from Prickly pear fruit as sensitizer on DSSCs [81]. Regarding DCCSs based on natural dyes, the co-photosensitization processes have been reported as a suitable alternative to improve photoconversion efficiency. Puspitasari et al. used a mixture of natural dyes consisting about anthocyanin, chlorophyll and curcumin, generating an efficacy of 0.0566 % [82]. Cai et al. compared the use of the anthocyanin-chlorophyll co-sensitizers, the efficacy results in 1.14 % to DSSCs based on cosensitization and 0.25 % to DSSCs based on only one sensitizer respectively, it concludes that the presence of both sensitizers was synergistic to the DSSCs performance [83]. Golshan et al. reported sensitization is an effective strategy to enhance DSSCs performance, they reported a maximum PV efficiency of 1.39 % using acid cocktail of natural dyes [84]. Cahya et al. used a mixture of anthocyanin and ruthenium complex N719 as a sensitizer giving an efficacy of 3.6 % in a solid-state DSSCs [85]. Different studies have also reported how extraction conditions affect the natural sensitizers' final properties. Conventional solvents are ethanol and water. In addition, acetone also gives positive results by improving the efficiency of the device. Acid treatment has been investigated to give a higher absorption capacity of betalains. However, this must be controlled to avoid a lower pH condition [86]. There are different reviews in the literature that address the evolution of DSSCs with a wide range of natural sensitizers that can be consulted to have more information in relation to this type of compound. Shalini et al. reported a review of the functioning of DSSCs based on natural dyes. They detailed and tabulated the various plant pigments present in the natural products that are employed as sensitizers in DSSCs [27,72,80,87–89].

## 3. Experimental

### 3.1. DSSC meta-study

In this study, Scopus was used as the database to screen the information. This editorial reported more than 25,100 titles from more than 5000 international publishers. We employed the Preferred Reporting Items to carry out some Systematic Reviews and Meta-

Analyses (PRISMA 2020) methodology to analyze the reports related to three types of dyes [90]: (i) Organometallics, (ii) non-metal organic dyes and, (iii) natural dyes and their performance in DSSC. PubMed was also consulted as a secondary database to complement the search in Scopus [91]. The publications related to the three types of DSSC dyes were obtained through the search key shown in Fig. 10. In the first step, it was identified 1338 studies. After screening shown in Fig. 10, it was included 329 articles for this study. In supporting information, we listed the link of each article and included the IV curve parameters in this report.

## 4. Results

### 4.1. Reports IV-curve for DSSC

In this work, three different types of dyes were studied, and 329 publications were consulted in the 1991–2023 period. The DSSCS IV-curve characterization parameters were used to compare their performance ($I_{sc}$, $V_{oc}$, $FF$, η) according to the type of dye, it was used the following nomenclature: (i) Natural, all those sensitizers obtained from natural sources without any type of synthetic structural modification. (ii) Organometallic, all those synthetic organic sensitizers that contain metal ions within their chemical structure and (iii) Organic, all those synthetic organic sensitizers without metals within their chemical structure. The range of data collected can be found in the supporting information (See Table S1). Fig. 11 shows the distribution of conversion efficiency of different DSSCs according to the type of dye used as a sensitizer based on collected data. Inside each plot, the points of each report (dark points) were included.

Fig. 11 shows differences among the conversion efficiency values, depending on the type of dye. In general, the best DSSCS results are the ones reported based on organic and organometallic and organic sensitizers. In DSSCs based on organometallic compounds, the average efficiency is approximately 9.1 %, it demonstrates the best average results; the maximum efficiency value recorded for DSSCs sensitized to organometallic compounds is 13.0 % [92]. About the DSSCs based on synthetic organic sensitizers without the presence of metals in their structure, the average efficiency is approximately 7.1 % and the maximum efficiency values is 15.2 % (DSSCs that use the co-photosensitization system and dye pre-adsorption treatment) [15]. DSSCs based on natural sensitizers showed an average efficiency value of 0.5 % and the maximum efficiency value recorded is 2.3 % [93]. The highest efficiency values of DSSCs systems based on organometallic sensitizers are associated with factors such as: (i) wide absorption spectrum in the visible range of the electromagnetic spectrum, including the near-infrared, (ii) high molar absorptivity values, (iii) presence of the MLCT phenomenon to charge transfer processes, (iv) high coupling to the $TiO_2$ surface, (v) high chemical and physical stability. In DSSCs based on transition metal-free organic compounds, the strategy that has reported the best results corresponds to: (i) the process of co-photosensitization and, (ii) to use a redox electrolyte with a more positive redox potential than the reported for the redox pair ($I^-/I_3^-$) and, (iii) to employ co-adsorbents during sensitization process. Kakiage et al. used two organic dyes, ADEKA-1 and LEG-4, as co-sensitizers. The efficiency

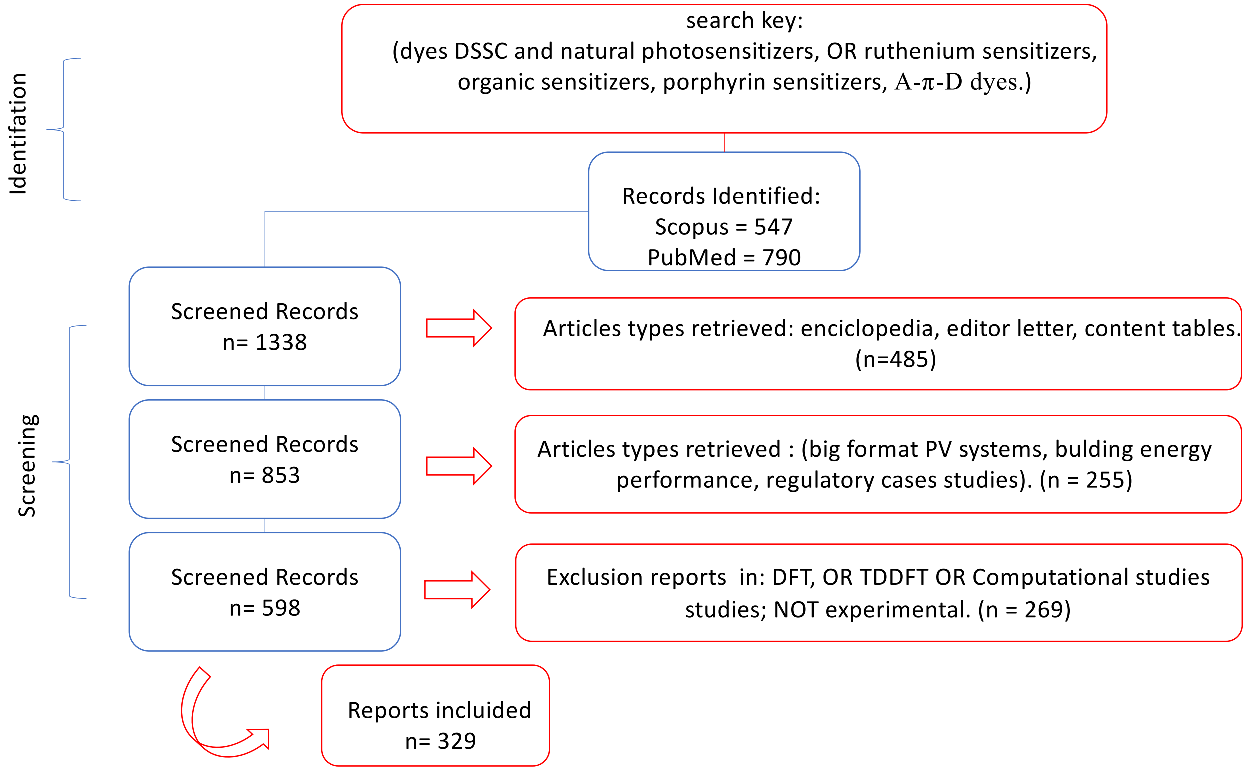


**Fig. 10.** Flowchart of methodology implemented in the bibliometric assay.

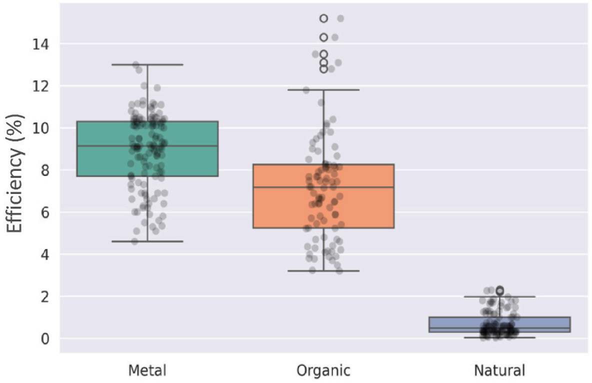


**Fig. 11.** It was used the box plot to measure conversion efficiency of different DSSCs, considering the type of dye that was used as a sensitizer (data in supporting information).

of this system was 14.3 %, it corresponds to the cell with a value of $V_{oc} = 1.014$ V; $FF = 0.771$; $J_{sc} = 18.25$ mA/cm$^2$ [70]. Ren et al. combined two sensitizers, first one SL9 that served as the primary long wavelength light harvester and SL10. Furthermore, they pretreated $TiO_2$ films with BPHA (Fig. 8) to increase the absorbance of co-sensitizer onto thin films. This system reported the highest efficiency value 15.2 % until now [15]. In regards to DSSCs based on natural sensitizers, a similar trend is observed; the better results are obtained by DSSCs based on co-sensitization of dyes. In this matter, co-photosensitization is an effective strategy to increase the absorption capacity of electromagnetic radiation in the visible range and improve the efficiency of the DSSCs. The higher efficiency values are associated with (i) Greater capacity to absorb radiation in the visible range. (ii) Greater dispersion on the surface of $TiO_2$ by dyes. (iii) Lower steric effect. (iv) Greater stability of dyes. (v) Greater number of anchor groups to the $TiO_2$ surface [84]. With respect to DSSCs based on natural compounds, the efficiency values never exceeded 3 %. In spite of that, Kumar et al. reported an atypically high efficiency of 9.23 % that corresponds to a DSSC in which it was used the extract obtained from Malabar spinach seeds as a sensitizer [94]. This result significantly surpassed any previous report, however, Kumar et al. reported that the $I_2$/KI redox system was used as an electrolyte in ethylene glycol and acetonitrile as a solvent. During the development of this review, no other report was found with this system or a replication that would corroborate the results obtained by these authors; in accordance with the foregoing, it was not considered in the documentation the behavior of DSSCs based on natural dyes. The reduced extract that was obtained from natural sources is used as a sensitizer without fully identification of the extract's components. Thus, it is difficult to replicate the reported results, since there is not full certainty about the identity and proportion of the metabolites that were used as sensitizers. Along with the stability of these types of compounds under the operating conditions of photovoltaic cells is always a matter of concern. To improve the stability of natural compounds, DSSCs can be built in inert atmospheres. However, one of the main reasons associated with low reported values in DSSCs photoconversion percentages based on natural dyes is the low stability of natural sensitizers to the environmental operating conditions of photovoltaic cells. The differences among characterization parameters of DSSCs become more evident when comparing the characterization values of the I-V curve according to the type of dye used. Fig. 12 shows the photoconversion efficiency values as a function of different characterization parameters that were obtained from the I-V curve related to the different types of DSSCs and the dye that was used as a sensitizer. Fig. S1 shows a complete comparison about IV-curve parameters in all the manuscripts reviewed.

Fig. 12 agrees with the results shown in Fig. 11. Two trends are observed: (i) The results obtained in relation with cells based on natural dyes present the lowest values of $V_{oc}$ and $J_{sc}$. This result agrees with the lowest values of photoconversion efficiency for this

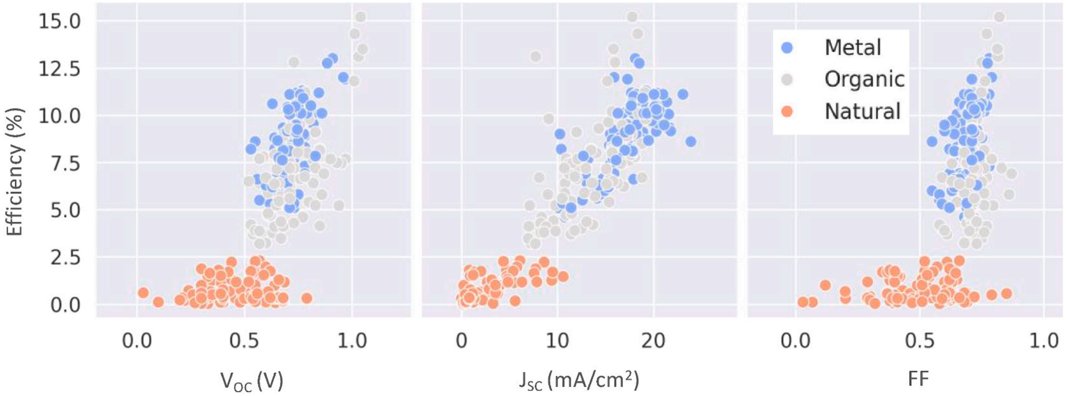


**Fig. 12.** Comparison among characterization parameters of the IV-curve DSSCs, according to the type of dye that was used as a sensitizer.

type of device (orange dot Fig. 12). These lower values can be attributed to the high charge transfer resistance at the $TiO_2$/dye/electrolyte interface when a natural dye is used as sensitizer assist in recombination processes [81]. However, some authors reported *FF* covers a broad range between 0.2 and 0.85 even with photoconversion efficiency values of less than 1 % [95,96]. Some authors associated this trend with the intimate adherence between natural dye and $TiO_2$ (e.g., the presence of carbonyl and hydroxyl groups is common in natural dyes) this better interaction between natural dye and $TiO_2$ surface could improve the fill factor [97,98]. (ii) The best values of $J_{sc}$ were reported for cells based on organometallic dyes (blue dots Fig. 12). For DSSCs based on ruthenium compounds, the higher $J_{sc}$ values can be directly associated with the presence of the charge transfer process via MLCT and greater facilities for the electron injection process from the sensitizer to the $TiO_2$ surface. (iii) The highest values of $V_{oc}$ and *FF* were reported on cells based on metal-free organic dyes (grey dots Fig. 12). Higher values of $V_{oc}$ and *FF* are associated with electrolytes with both the higher redox potential than the traditional pair (iodide/triiodide) and the implementation of co-sensitization systems on $TiO_2$ surface.

### *4.2. New trends and future perspectives on DSSCs*

The so-called Shockley-Queisser limit on solar cell efficiency which considers the fundamental energy loss mechanisms for a single-junction semiconductor (an ideal silicon cell) is defined as 30 % [99]. Notwithstanding, DSSCs are not ideal, and they differ from traditional solid heterojunction. Snaith estimated the maximum power conversion efficiency feasible on DSSCs in 20 % [100]. If we compare this theoretical limit with the best report ($\eta = 15.2$ %) [15] of DSSCs efficiency (Grätzel et al., 7.1 %) [14], no more than 30 years, the efficiency has increased twice. In the lasts works, researchers address their investigations to develop green-structures (free of toxic components), stable and more efficient DSSCs. Bella et al. reported an efficient and stable solar cell based only on water and using dyes, electrolytes and cathodes without metals. The best results reported an efficiency of 7.02 % [101]. Hwang et al. reported an interesting configuration: C-14 powered Dye Sensitized Betavoltaic Cell (DSBC). In this device, carbon-14 is simultaneously used as the β-particle source and the counter electrode. The emitted β-radiations are absorbed by the dye and the PV-cycle continues the same as in a traditional DSSC. Despite the lower efficiency values reported (0.4–0.55 %), they opened the new horizon to explored the field of β-voltaic devices [102].

Tandem architecture is an interesting strategy to stack system with complementary absorption characteristics to increase the solar cells efficiency beyond the Shockley-Queisser limit of a single-junction device [103]. Moon et al. reported a solar cell efficiency of 13 % to a tandem solar cells (CIGS/DSSC), they reported a synergist effect in comparison with the efficiency of individual solar cells (7.25 %) to the DSSC and (6.2 %) the CIGS [104]. The solid-state dye-sensitized solar cells (SSDSSC) try to solve durability problems that result from organic liquid electrolytes that contain redox couples [105]. Burschka et al. reported SSDSSC based on $TiO_2$ sensitized with lead iodide perovskite ($CH_3NH_3PbX_3$) with a power conversion efficiency of approximately 15 % [106]. Seok et al. reported efficiency of 12.3 % to perovskite SSDSSC based on $CH_3NH_3PbI_{3\text{-}x}Br_3$ [107]. Recently, Sumona et al. reported an efficiency of 9.60 % by incorporating different electron transport layers in a SSDSSC based on ZnO sensitized by using X60 as the hole transport layer [108]. The perovskite materials have superior functions not only as light absorbers, but also as electron and hole transporters [109]. Perovskite solar cells have achieved higher efficiencies than DSSCs, Zhou et al. reported a Perovskite solar cells with the highest efficiency of ~19.3 % in a planar geometry without using antireflective coating [110]. The current record in efficiency for these solar cells is 25.2 % [111]. Due to the higher conversion efficiency values, perovskite solar cells are suitable candidate to fabricate tandem solar cells. Recently, the perovskite/CIGS system reached 29.9 % [112]. Despite their great efficiency values, the Pb-based perovskite solar cells have two main drawbacks: (i) poor stability and (ii) high toxicity [113]. New research in this field is aimed at gaining stability and replace the toxic materials [114].

An important advance in the DSSCs manufacturing was the incorporation of plastic substrates to replace typical Soda Lime Substrate (glass) and introduce the flexible concept about the dye-sensitized solar cells. The plastic substrate based on DSSCs can be installed quickly on buildings with flat or curved surfaces, due to their light weight and flexibility, in comparison with classic rigid solar panels. Flexible DSSCs are important not only for user convenience, but also for realizing roll-to-roll mass production [115]. Regarding great scale, one of the main applications of DSSCs rely on their easiness to be integrated into towards building-architectures and indoor developments under low illumination. In addition, semi-transparency, low manufacturing cost and facile fabrication procedures explain the growing of commercial attention of last years of DSSCs [117,118]. Still, several major advancements are required for industrialization (e.g., typical sealing materials based on UV or light curing adhesives, bicomponent resins and thermoplastic films). Applications of DSSCs promise results in lab scale; however, they must find the adequate route to become feasible at pilot and industrial scale [116].

Finally, DSSCs have the potential to become an important agent among energetic matrix that is required to supply the energetic needs of the world in the near future. Currently, according to authors, the research field of DSSCs are opened to develop continuous improvements in two different scales: (i) Molecular engineering, all of the solar cell components (e.g., engineering design of dyes, improve anchoring to semiconductors, electrolytes best redox potential and, counter-electrodes) increase the charge carrier transport efficiency in order to reduce the recombination losses and improve the efficiency of the device (ii) Great format (e.g., flexible DSSCs technique layers deposition, sealing materials and module assembling methods). guarantees long-term stability of the DSSC modules.

## 5. Conclusions

To develop a society in a sustainable way throughout the decarbonization of the energy matrix, represents one of the greatest challenges that humanity faces as a collective; therefore, the energy transition requires the incorporation of renewable energies. Among the available options, photovoltaic solar energy represents the most important in the medium term. In this document, a detailed review of the latest reports on DSSCs technology was presented, it exposes, conceptual aspects related to the physicochemical phenomenon that governs the energy transformation process and the most salient aspects in relation to its conceptual and technological evolution of organic compounds used as sensitizers. Information was collected from 329 publications in the 1991–2023 period, about the characterization parameters of DSSCs based on three different types of dyes: ruthenium and porphyrin-based complexes, metal-free organic compounds, and natural organic compounds. The most important contributions made in the framework of this work are summarized below.

- Transition metal-free organic compounds have reported high photo-conversion values and have become promising candidates to replace ruthenium-based DSSCs in the last decade.
- The highest $V_{oc}$ and $FF$ values that are reported in regards to DSSCs and based on organic dyes without transition metals, they are associated with the use of electrolytes with higher redox potential than the $I^-/I_3^-$ pair and the combination with co-sensitization systems.
- The co-sensitization processes improved the performance of the DSSCs in both cases, when synthetic and natural compounds are used, the co-sensitization process improves the capacity of radiation absorption in the visible range, this allows greater dispersion on the surface of the $TiO_2$ by the dyes and reduces the steric effect to improve the electronic injection processes towards the semiconductor.
- In DSSCs based on organometallic compounds, the average photoconversion efficiency is about 10 % and the maximum efficiency value recorded is 13.0 %. About cells based on metal-free synthetic organic sensitizers, the average efficiency is approximately 7.1 % and the maximum efficiency value recorded is 15.2 %. Finally, In DSSCs based on natural sensitizers, the average efficiency is about 0.5 % and the maximum efficiency value recorded is 2.6 %.
- The high-efficiency values reported on DSSCs systems based on organometallic sensitizers are associated with their wide absorption spectrum in the visible range of the electromagnetic spectrum, high molar absorptivity values, the presence of the MLCT phenomenon for charging transfer processes, in addition to the high surface coupling of $TiO_2$ and the high chemical and physical stability of this type of compounds.
- The main strategies to improve photoconversion efficiencies of DSSC's included: co-(i) photosensitization with two complementary dyes, (ii) the use of a redox electrolyte with a more positive redox potential than the reported on the redox pair ($I^-/I_3^-$), (iii) addition of a co-adsorbent agent during sensitization process.
- The efficiency reported on DSSCs based on natural dyes is in a range that is between 4 and 10 times lower than those reported on DSSCs based on other types of organic compounds. However, natural sensitizers are economical, non-toxic, and biodegradable. They are an environmentally sustainable alternative as they can contribute in the medium term to the development of sustainable solutions for energy production.

## CRediT authorship contribution statement

**William Vallejo:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Mileidy Lerma:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization. **Carlos Díaz-Uribe:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization.

## Ethical approval

Not required.

## Data availability

All data accessed and analyzed in this study are available in the article and its supplementary materials.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e41092.

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