

# A Brief History of and Insight in the Choice of Sensitizers/Dyes for Dye Sensitized Solar Cells




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**Abstract:**

In this review, a discussion on renewable sources of energy with clear focus on solar cell applications is presented. Especially, possible future directions for development of dye-sensitized solar cells (DSSCs) are discussed. Dye-sensitized solar cells have become an important topic of research due to its high importance in energy conversion. Current DSSCs are based on either metal dye sensitizers, metal-free organic dyes or natural dyes. They have been extensively studied due to their low cost, simple preparation methodology, low toxicity, and ease of production. Still there is a need to find more abundant DSSC materials that at same time exhibit long-term stability. Computational studies have been an important ally for developing/designing new dye sensitizers. They are reviewed here with a special emphasis on the benefit of such studies. The conceptual understanding of development and working principle of photoactive DSSC materials are the primary feature of the review followed by examples of studies on different dye sensitizers using scarce to abundant metal based dyes and metal free organic dyes with donor- $\pi$ -acceptor geometries for both n- and p-type DSSCs. The proper choice of organic dyes including donor, spacer, or acceptor is discussed and a prospective on dual donor based dyes is presented.

**Keywords:** Dye Sensitized solar cells; Scarce metal dyes; Abundant metal dyes; Donor- $\pi$ -Acceptor dyes; Double donor dye sensitizers.

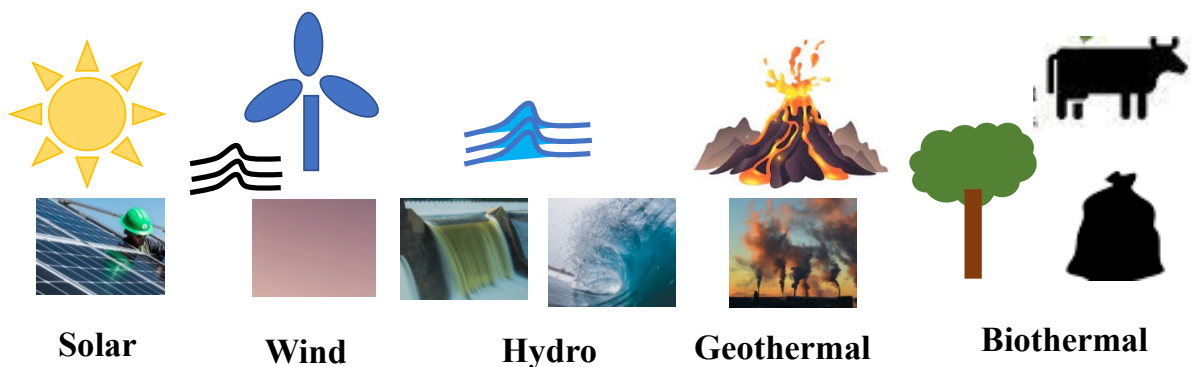
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## 1. Introduction

With the increase in the population and the advancement of the civilization, the demand of energy is escalating, raising major concerns for the adverse effects of conventional energy sources like natural gas, coal, fossil fuels etc. on the environment of the earth. Furthermore, the fast depletion of the natural resources like fossil fuels reserves is also an important motivation for many researchers worldwide to search for alternative and renewable sources of energy associated with no or low pollution of the environment.

Renewable energy sources are sustainable and can be regarded to provide an endless source of energy. In recent years, a growing amount of important household demands such as electricity, air and water heating/cooling, transportation and rural (off-grid) energy services are being provided in many countries based on renewable energy sources. The most popular renewable energies are

- a. Solar Energy
- b. Wind energy
- c. Hydro energy
- d. Tidal energy
- e. Geothermal energy
- f. Biomass energy



**Figure 1.** Different types of renewable energies.

According to a report of REN21 (Renewable Energy Policy Network for the 21st Century) in the year 2017, a total of 19.3% of the total energy consumed in the human population was provided from renewable energy sources for the year 2015-2016. The total contribution is divided into 8.9% from traditional biomass; 4.2% from geothermal and solar energy sources, 3.9% from hydroelectricity and the remaining 2.2% from wind, solar, geothermal. Investments

and jobs associated with renewable energy are increasing every year, and the efficiency of its generation is also increasing along with a decrease in the cost. Out of the five different renewable systems as given in the figure 1, the most abundant and freely and globally available source of energy is the sun providing solar energy. With respect to the other energies one can note that:

- a. The wind energy has certain drawbacks as low wind zones in many countries and transport difficulties for instruments.
- b. Although tides are typically very regular, they cannot yield hydro energy on demand and furthermore low tide periods can occur.
- c. Geothermal energy is not equally available on earth.
- d. Biomass usage for energy competes with the biomass production for food.

Thus, as previously stated, solar energy offers the most abundant, eco-friendly source with an immense capability to satisfy global energy consumption demands. Actually, the amount of the solar energy reaching the earth in an hour is more than the total energy need of mankind of one year. Still, harnessing the full amount of energy is difficult, and extensive research efforts are needed to harvest energy more efficiently. Although the sun corresponds to an abundant and efficient renewable energy source, one of the main problems in solar energy production is the volatility of its generation. Research in this field has been performed for more than five decades, providing an improved understanding of the basics underlying photovoltaic devices. The photovoltaic effect as discovered by Edmond Becquerel in 1839 is a process which generates voltage or electricity when exposed to sunlight. Such photovoltaic effects are the main backbone of a solar cell. Solar cells are typically composed of two different types of semiconductor materials (p-type and n-type), and a p-n junction is created when they are joined together. The sunlight composed of photon particles is absorbed by the photovoltaic cell. If sunlight with a proper wavelength is incident on such cells, the energy of the photon can be used in the semiconducting material to transfer the electrons to a higher energy state (valence band to conduction band), and if this transfer occurs at a p-n junction, the excited electron and the created hole move in different directions avoiding a direct electron-hole recombination. Thus, a flow of electrons is created which gives rise to electricity. A good photovoltaic cell combines three basic characteristics:

- A. The capability of absorption of light, thus generating either electron-hole pairs or excitons.
- B. Charge separation between the carriers of opposite charges.

C. Charge carriers should reach the external circuit for the completion of the energy conversion and production of electricity.

The first solar cell composed of selenium and a thin film of gold in 1884 showed a very low efficiency. Yet, in the last five decades, crystalline silicon (Si) based photovoltaic systems have dominated the solar energy market because of their many beneficial features such as high efficiency, good stability in different climatic conditions etc. Still, some drawbacks like high cost, limited transportability and low photovoltaic performance in low light intensities made researchers move from the traditional PV technologies to third generation photovoltaic technologies like perovskite solar cells (PSCs), organic solar cells (OSCs) and dye-sensitized solar cells (DSSCs). One of the most recent developments in the field of solar cells was the developments of perovskite solar cells in 2009<sup>1-3</sup>. Several applications like photolysis, photodetectors and power source, carbon electrode based cells, tandem cells, single crystal cells are known for such PSCs<sup>4-7</sup> etc due to their high power efficiency. However, limitations are present in the practical operation of the PSC, longtime stability<sup>8,9</sup>; toxicity<sup>10</sup> due to moisture, UV light, thermal effects etc.<sup>11-15</sup> Organic photovoltaic cells (OPV), also known as plastic photovoltaic cells, correspond to a renewable non-polluting energy source and are made of inexpensive and flexible materials<sup>16</sup>. The main drawback for the OPVs is their low power conversion energy (PCE) ranging from 2-8% with its most effective ones known as the bulk-heterojunction (BHJ) cells composed of an electron donor (a semiconducting polymer) and an electron acceptor (fullerene derivative). Extensive research is needed in this field to increase the efficiency of OPCs.<sup>1,17,18</sup>

### **1.1. Dye Sensitized Solar Cells**

Dye-sensitized solar cells (DSSCs) represent a technical and economical alternative to p-n junction photovoltaic devices. In the 1970's, research efforts focused on ZnO single crystals but this type of DSSCs shows a very low efficiency due to the limited light absorbance of the ZnO layers<sup>19,20</sup> which, however, can be improved by optimising their porosity. The first proper modern day DSSCs known as Grätzel cells were developed by Brian O'Regan and Michael Grätzel at UC Berkeley in 1991<sup>21</sup> which made dye sensitized solar cells very popular.

As stated above, all mentioned solar cell technologies have their short-comings: OPV's are challenged by an appropriate charge domain ordering; PSC's suffer from their stability and moisture sensitivity; DSSCs need photosensitive materials with a broad absorption spectrum to exhibit a higher efficiency. Overall, in practical outdoor environments the DSSCs have shown the best performance<sup>22</sup>. Dye sensitized solar cells exhibit a significant power generation performance throughout the day even when exposed to low-intensity light, independent of the

angle of incidence of the light<sup>23</sup>. The photophysical performance of DSSCs are based on properties on the level of single molecules. Therefore, it can relatively easily be tuned on a molecular level by changing the molecular design and adding some substituents. Furthermore, DSSCs are also stable and efficient under harsh conditions such as low temperatures and low-light environments, even in the presence of moisture<sup>24–26</sup>. Thus, DSSCs are still one of the most promising solar cell technologies, and research aiming at improving the efficiency of such solar cells is ongoing both experimentally and theoretically. The sensitizers are usually designed with functional groups such as  $-\text{COOH}$ ,  $-\text{PO}_3\text{H}_2$ , and  $-\text{B}(\text{OH})_2$  etc. ensuring high efficiencies of light absorption<sup>27–29</sup>. The theoretical power conversion efficiency of 20% predicted by H.J. Snaith<sup>30</sup> motivated extensive research on DSSCs to improve their efficiency and to expand their viability towards commercialization.

Previous reviews focused on the improvement of DSSCs, and it has been observed that the performance of the DSSC can be better than that of the silicon-based photosensitizers<sup>31,32</sup>. Many reviews have also covered the development of different metal and metal-free dye sensitizers, counter electrodes and efficiencies of DSSCs [33–38]. In this review, we will explain the importance of dye sensitized solar cells and briefly discuss their components as well as their limitations. We will also thoroughly address experimental and theoretical studies of the wide variety of dye sensitizers based on scarce as well as abundant metals and organic dye sensitizers with so-called D- $\pi$ -A, D-A- $\pi$ -A, D- $\pi$ -A-A, D-D- $\pi$ -A structures. A brief discussion of the benefits of the density functional theory on the design of the dye sensitizers is also presented in this review.

## **1.2. DSSCs Components**

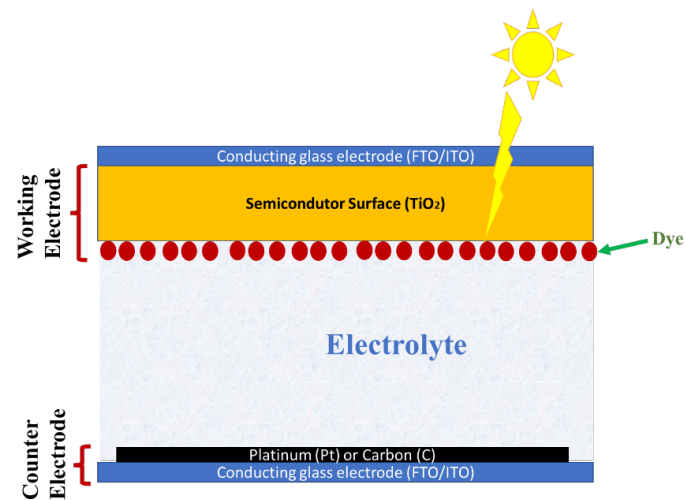
A DSSC or Dye Sensitizer Solar Cell consists of the four key components

- a. the working electrode (the photoelectrode or generally the semiconductor).
  - b. the dye sensitizer.
  - c. the redox mediator or the electrolyte and
  - d. the counter electrode.
- a. Working electrode (the photoelectrode or generally the semiconductor).**

The working electrode is generally prepared by depositing a thin layer of semiconducting material (p-type or n-type) on a transparent conducting glass plate. The conducting glass plate is placed at the top of the DSSC through which the incident light passes and reaches the dye sensitizers. The DSSCs are generally constructed with two such conductive transparent materials. Typically, fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO) are used as the transparent material whose main purpose is to



- I. keep a high transparency for the optimum sunlight to pass through to the sensitizer and
- II. enable a high conductivity so that the charge transfer within the DSSC is efficiently done and no loss due to such material is caused.



**Figure 2.** A schematic diagram of a Dye sensitized solar cell.

Different semiconducting materials such as  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$  are used for n-type DSSCs whereas  $\text{NiO}$ ,  $\text{Cu}_2\text{O}$  are employed for p-type DSSCs due to their wide band gap. Its nontoxicity, low cost and easy availability made  $\text{TiO}_2$  to most popular semiconducting material for n-type DSSCs. In detail, anatase  $\text{TiO}_2$  is better suited than rutile  $\text{TiO}_2$  due to its a wider bandgap<sup>33,34</sup>. Promising results have also been obtained for other oxides like  $\text{ZnO}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{SnO}_2$ <sup>35–38</sup>. For p-type DSSCs,  $\text{NiO}$  is among the most used semiconductors<sup>39–41</sup>. Recently  $\text{Cu}_2\text{O}$  has also been considered for p-type DSSCs by many research groups<sup>42,43</sup>. The typical process to turn the porous material into a working electrode is to immerse it into the solvent containing the dye sensitizer. These dye molecules can covalently bind to the semiconductor surface which is important for the charge transfer process.

### **b. Dye Sensitizer**

The dye sensitizer is the part of a DSSC which actually is responsible for the efficiency of the light harvesting. The main role of such a dye sensitizer is to convert the incident light into an electronic excitation and to induce the charge transfer to the semiconductor surface. Some specific photophysical and electrochemical properties are very relevant for the efficiency of a dye sensitizer within a solar cell. In particular, a good dye should have the following properties:

- I. The dye should possess a strong light absorption ability in the visible region along with the ultraviolet-visible (UV-vis) and near-infrared region (NIR) regions.
- II. The dye should be stable both in its ground state and the excited state (after absorbing the incident light).

- III. For n-type DSSCs, the energy of the highest occupied molecular orbital (HOMO) should be below the conduction band (CB) minimum of the semiconductor. Furthermore, the HOMO energy should also be significantly lower than the energy of the electrolyte redox couple. The energy of the lowest unoccupied molecular orbital (LUMO) should be close but above the CB minimum.
- IV. For p-type DSSCs, the HOMO of the dye should be well below the valence band (VB) maximum of the semiconductor to enhance the driving force for hole injection, whereas the LUMO energy should be higher than the energy of the redox shuttle similar to the case of n-type DSSCs.
- V. The outermost atoms and rest groups of the dye should be hydrophobic to ensure the long term stability while in contact with the surrounding and the electrolyte.
- VI. Anchoring groups should enable a strong interaction of the dye with the semiconductor as well as an efficient charge transfer between dye and semiconductor.

#### **c. Redox mediator or electrolyte**

A redox couple can act as an electrolyte for a DSSC provided it is soluble. Examples for such couples are  $I^-/I_3^-$ ,  $SCN^-/SCN^{2-}$  or  $Co(II)/Co(III)^{44-46}$ . Ionic liquids can also be used as an electrolyte. To act as a suitable electrolyte, the systems must have some specific properties such as:

- i. It should be stable in different conditions. Thermal, chemical or electrochemical stability issues should not be present.
- ii. There should not be any corrosive reaction of the electrolyte with the dye sensitizer or the working/counter electrodes.
- iii. The redox couple should efficiently oxidize or reduce the photosensitizer.
- iv. The absorption spectra should not overlap with those of the dye molecules.
- v. The electrolyte should exhibit a high ion mobility to enable fast charge transfer processes between the working and counter electrode.

The most often used electrolyte in DSSC is  $I^-/I_3^-$ <sup>47</sup>. It still has some limitations such as inducing corrosion effects of the electrodes or a poor long term stability<sup>48,49</sup>. Ionic liquids can also be used effectively to some extent [57], but one of their major drawbacks is related to leakage factors. Recently, solid state electrolytes have been employed to overcome these drawbacks<sup>50,51</sup>.

#### **d. The counter electrode**

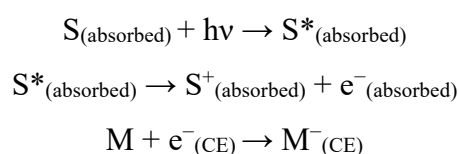
The counter electrode is a very crucial component of DSSCs. Its main significance is connected to collecting the electrons from the external circuit and catalyzing the redox reduction in the electrolyte. It is actually, acting as a cathode with typically platinum<sup>52</sup> or carbon<sup>53</sup> deposited as conducting material. It is critically influencing the photovoltaic performance, the stability of the DSSCs and also the cost of the device. Other alternative materials for counter electrodes are Carbonyl sulfide (CoS)<sup>54</sup>, AU/GNP<sup>55</sup> of alloys like FeSe<sup>56</sup>, CoNi[64] etc.

### 1.3. Working Principle

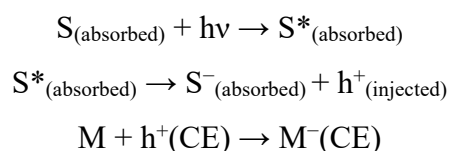
The working principle of DSSCs is based on four steps,

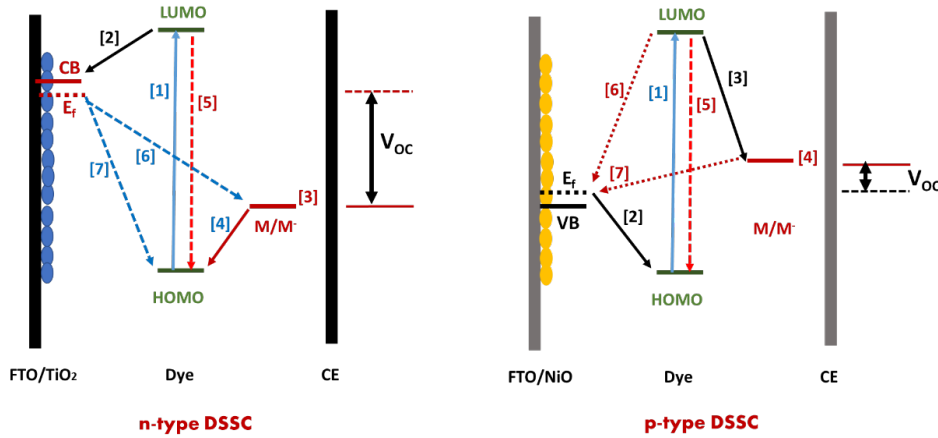
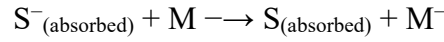
- a. Absorption of the light emitted by the sun in the dye.
- b. Injection of electrons from the dye to the semiconductor (for n-type) and from the semiconductor to the dye (for p-type).
- c. Transport of the electrons or holes in the semiconductor.
- d. Collection of the current.

As illustrated in the schematic diagram in figure 3, for a n-type DSSC, the incident light is absorbed by the photosensitizer (S), promoting S from the electronic ground state to an excited state, denoted by S\*. The excited sensitizer then injects electrons into the conduction band of the n-type semiconductor. These excited electrons have lifetimes in the order of nanoseconds. The injected electrons are propagating in the nanoparticles and reach the counter electrode through the external circuit. Back electron transfer to the dye is also possible which restricts the efficiency of the dye sensitizer. The injected electrons in the counter electrode reduce the redox couple (M/M<sup>-</sup>), and thus the regeneration of the dye takes place, which completes the circle:



In the case of p type DSSCs, an electron is transferred from the semiconductor to the dye. The excited dye transfers the electron to the redox couple to be transferred back to the semiconductor through the counter electrode or it transfers it to the catalyst for further photocatalytic activities. The hole is created in the valence band of the semiconductor. The whole electron/hole transfer mechanism is also illustrated in Figure 3:-





**Figure 3.** Schematic diagram of n-type and p-type DSSCs.

The performance or efficiency of a DSSC is assessed by using Eq.1:

$$\eta(\%) = \frac{J_{SC} * V_{OC} * FF}{P_{in}} \text{----- (1)}$$

It consists of four terms. A. open circuit voltage ( $V_{OC}$ ), B. short circuit current density ( $J_{SC}$ ), C. maximum power of the incident light ( $P_{in}$ ) and D. the filling factor (FF)<sup>57</sup>. The open circuit voltage or  $V_{OC}$  is the voltage between the two electrodes under open circuit conditions.  $J_{SC}$  is the maximum current that the solar cell can produce, it depends on the optical properties of the solar cell.  $P_{in}$  is the maximum efficiency of the DSSC to convert sunlight into electricity. The filling factor is given by the ratio of the maximum power output to the product of the open circuit voltage and short circuit current density. The external quantum efficiency or Incident Photon to Current Efficiency (IPCE) is also important for understanding the efficiency of the DSSC. It is determined by the ratio of the number of electrons flowing through the external circuit to the number of incident photons on the surface. The IPCE value is directly related to the Light Harvesting Efficiency (LHE) of the dye sensitizer.

#### 1.4. Limitations of DSSCs

Although DSSCs correspond to a promising technology allowing low cost and facile fabrication and maintenance, the development of DSSCs is still facing limitations<sup>58-60</sup>. The recent maximum efficiency that can be reached by DSSCs is around 14-15%<sup>61,62</sup>. The current maximum efficiency of DSSCs has already surpassed that of amorphous silicon-based solar cells, but it is still lower than the efficiency of common silicon based solar cells<sup>63,64</sup>. Therefore, further research and development is still needed to improve the performance of DSSCs.

One main limiting factor of DSSCs is related to the small window of operating temperatures of the electrolyte, as DSSCs are sensitive to very high and very low temperatures<sup>65</sup>. At low temperatures, the electrolyte can freeze, and at high temperatures, the liquid electrolyte expands

often making the solar cell unusable. Liquid electrolytes also cause problems such as potential instability, limitation of maximum operating temperature, danger of evaporation, and extra cost upon forming an electrical series connection caused by leakage or evaporation<sup>1-3</sup>. Such PSCs are used in several applications like photolysis, photodetectors and power source, carbon electrode based cells, tandem cells, single crystal cells<sup>4-7</sup> etc due to their high power efficiency. But limitations are present due in the practical operation of the PSCs, in particular with respect to their longtime stability.<sup>66-69</sup> In addition, an inefficient sensitizer regeneration will also influence the total efficiency of DSSCs<sup>70</sup>. And finally, the upscale fabrication of DSSC from laboratory to industry scale poses a further challenge as it determines the total efficiency upon public launch. In order to, produce competitive DSSCs, additional factors and device parts not present on the lab scale appear need to be considered, such as

1. interconnection (series or parallel) and external electrical connections
2. extensive sealing to prevent electrolyte leakage and moisture ingress
3. coating of large-scale metal oxide on TCOs
4. electrolyte filling
5. and most importantly, an anticipated device lifetime that is comparable with conventional silicon-based PV technologies<sup>63,65</sup>.

Several research groups have already started to address the challenges related to the upscaling of DSSC, such as the fabrication of DSSC modules with efficiencies up to 8.2% by utilizing so-called *W*-type interconnections, the development of solid-state DSSC modules to prolong device lifetimes, and the emergence of a flexible DSSC module that is better suitable for mass production<sup>71-74</sup>. Nonetheless, there are many open questions left with respect to the reported performance increase<sup>65</sup>.

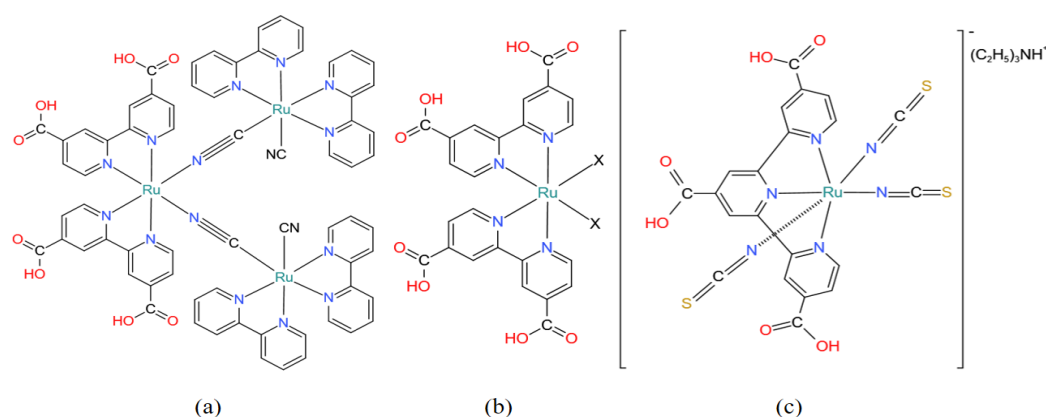
## **2. Choices of Dye Sensitizers**

As mentioned above, there are several important criteria for the appropriate choice of dye sensitizers in a DSSC device which has become one of the primary research topics of many groups worldwide after the appearance of the famous paper by Grätzel et. al.<sup>21</sup>. Two specific types of dye sensitizers have drawn special attention, metal-based dyes and more recently the metal free organic dyes. In this review, we focus both on metal-based dyes (with scarce to abundant metals) and on metal-free organic dyes with D- $\pi$ -A type of geometries.

### **2.1. Ruthenium Complexes**

The most common choice of dye sensitizers is the Ruthenium-based dye, which has been employed since the first design of DSSCs by O'Brien and Grätzel in 1991.<sup>21</sup> They utilized a trimeric ruthenium complex,  $\text{RuL}_2(\mu\text{-(CN)Ru(CN)L})_2$ , with L being a 2,2' bipyridine-4,4'-

dicarboxylic acid and L' a 2,2'-bipyridine (illustrated in Fig. 4a) together with a TiO<sub>2</sub> film as photoanode<sup>75,76</sup>



**Figure 4.** Some structures of ruthenium-based dyes: (a) Trimeric ruthenium complex that was utilized for the first realization of DSSCs, (b) N3 dyes with X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup> and SCN<sup>-</sup>, and (c) N749 dye, panchromatic dye that was synthesized by Nazeeruddin et. al.<sup>76-79</sup>

Later, Nazeeruddin et. al. developed panchromatic dyes by synthesizing a ruthenium complex sensitizer with carboxylated terpyridyl and three thiocyanate groups as ligands (shown in Figure 4c). According to the measurement under full AM 1.5 sunlight, this dye achieved a short circuit current 20.5 mA/cm<sup>2</sup> and an open-circuit voltage of 0.72 V. The overall conversion efficiency of this dye is 10.4%<sup>79</sup>.

In general, ruthenium based dyes have received particular attention as photosensitizers in DSSC applications because of their favourable photoelectrochemical properties and high stability in the oxidized state, making practical applications feasible<sup>80</sup>. Overall, the maximum efficiency that can be achieved by ruthenium-based dyes is around 11%. In Table 1, we listed the ruthenium-based dyes that were synthesized for *n*-type DSSCs with a PCE ≥ 10% where the photoanode is made of TiO<sub>2</sub>.

**Table 1.** J<sub>sc</sub>, V<sub>oc</sub>, FF and PCE of some ruthenium based-dyes for *n*-type DSSC with their. Only the dyes with a PCE of more than 10% and TiO<sub>2</sub> as photoanode material have been considered.

No.	Dye	J <sub>sc</sub> (mA·cm <sup>-2</sup> )	V <sub>oc</sub> (mV)	FF (%)	PCE (%)	References
1	N3	18.20	720.0	73.0	10.00	78
2	N749	20.53	720.0	70.4	10.40	81

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<b>3</b>	N719	17.73	846.0	72.0	11.18	82
<b>4</b>	Z910	17.20	777.0	76.4	10.20	83
<b>5</b>	C101	17.94	777.7	78.5	11.00	84
<b>6</b>	C103	18.35	760.0	74.8	10.40	85
<b>7</b>	C104	17.87	760.0	77.6	10.53	86
<b>8</b>	C105	18.90	747.0	74.4	10.06	87
<b>9</b>	C106	19.20	776.0	75.9	11.29	87
<b>10</b>	C107	19.18	739.0	75.1	10.70	85
<b>11</b>	C219	17.94	770.0	73.0	10.10	88
<b>12</b>	RC-36	19.17	721.0	74.0	10.23	89
<b>13</b>	PRT4	21.60	714.0	65.2	10.05	90
<b>14</b>	PRT14	19.70	760.0	68.6	10.30	91
<b>15</b>	PRT21	19.00	760.0	74.9	10.81	92
<b>16</b>	PRT22	20.40	740.0	73.9	11.16	92
<b>17</b>	PRT23	18.70	760.0	73.4	10.43	92
<b>18</b>	PRT24	20.10	730.0	71.6	10.51	92
<b>19</b>	TF2	20.00	790.0	66.5	10.50	93
<b>20</b>	TF3	21.39	760.0	66.0	10.70	93

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<b>21</b>	TF4	20.27	770.0	67.5	10.50	93
<b>22</b>	HIS-2	23.07	680.0	71.0	11.10	94
<b>23</b>	TFRS-4	18.70	750.0	72.9	10.20	95
<b>24</b>	TFRS-52	16.30/16.80	860.0/ 832.0	72.0/ 78.0	10.17/ 10.88	96
<b>25</b>	IJ-1	19.20	748.0	72.0	10.30	97

Note that ruthenium-based molecules can also be employed as dyes in *p*-type DSSCs in connection with *p*-type semiconductors such as NiO. To the best of our knowledge, the implementation of Ru-dyes for *p*-type DSSCs was first introduced by Odobel's group in 2011<sup>98</sup>. They utilized ruthenium tris bipyridine complexes  $[\text{Ru}(\text{bpy})_3]^{2+}$  with four different anchor variations, carboxylic acid, dithiocarboxylic acid, catechol, and methyl phosphonic acids. For this first Ru-based dye *p*-type DSSC, the methyl phosphonic acid anchor yielded the largest efficiency among the used anchors. However, the efficiency was very small (around 0.025%). Subsequently, a large number of studies has been devoted to the implementation of Ru-based dye *p*-type DSSCs (see Table 2).<sup>98-105</sup> However, the largest efficiency that can be achieved in these systems are still relatively small, below 1%, as Table 1 illustrates where the properties of Ru-based *p*-DSSCs with NiO as photoanode are listed. Therefore, there are still many open questions left related to the design of efficient *p*-type DSSCs.

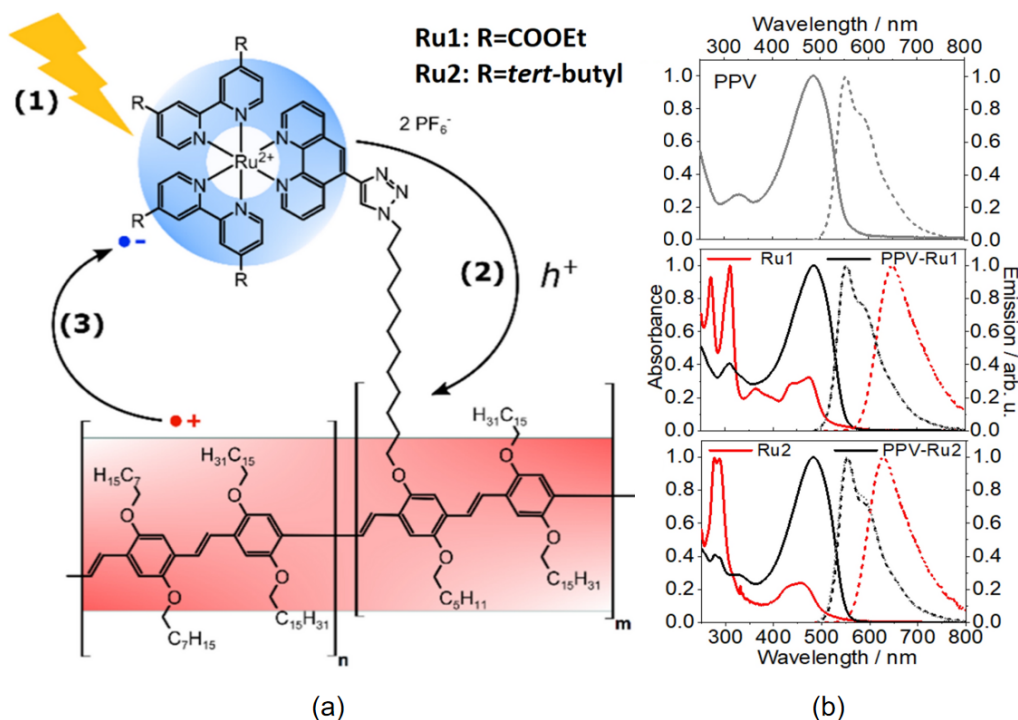
**Table 2.**  $J_{\text{SC}}$ ,  $V_{\text{OC}}$ , FF and PCE of some ruthenium-based dyes for *p*-type DSSCs

<b>No.</b>	<b>Dye</b>	<b><math>J_{\text{SC}}</math> (<math>\text{mA}\cdot\text{cm}^{-2}</math>)</b>	<b><math>V_{\text{OC}}</math> (mV)</b>	<b>FF (%)</b>	<b>PCE (%)</b>	<b>References</b>
<b>1</b>	N719	0.008	4.0	0.5	~0	99
<b>2</b>	Ru-CS <sub>2</sub> H	0.250	75.0	34.0	0.0065	98
<b>3</b>	Ru-PO <sub>3</sub> H <sub>2</sub>	0.780	95.0	34.0	0.0250	98
<b>4</b>	Ru-cat	0.650	85.0	32.0	0.0180	98



5	Ru-CO <sub>2</sub> H	0.630	85.0	34.0	0.0190	98
6	Ru(dcbpy) <sub>3</sub>	0.090	110.0	43.0	0.0040	100
7	Ru-NMI	0.280	195.0	34.0	0.0200	100
8	K1	2.910	96.0	32.0	0.0900	101
9	K2	1.960	93.0	39.0	0.0700	101
10	SL1	2.250	104.0	34.0	0.0790	102
11	SL2	1.500	77.0	33.0	0.0380	102
12	AS16	0.690	94.0	42.0	0.0280	103
13	[Ru(bpy) <sub>2</sub> (H5)]	3.380	95.0	36.0	0.1160	104
14	O8	0.440	63.0	36.0	0.0090	105
15	O11	1.160	79.0	36.0	0.0330	105
16	O12	1.840	82.0	34.0	0.0510	105
17	Ru-CO <sub>2</sub> H-CF <sub>3</sub>	0.740	104.0	33.9	0.0260	106
18	Ru-PTMS	1.600	64.0	31.0	0.0400	107
19	RuP <sub>4</sub> dppz	0.880	102.0	29.0	0.0260	108

A very recent study by Sen et. al. addressed promising choices of anchoring groups for Ruthenium bipyridine complexes of p-type DSSCs based on quantum-chemical calculations. Their work presented a step-wise approach to identify promising anchors for such dyes through surface and cluster modelling techniques<sup>109</sup>. The concept of *p*-DSSCs can be applied not only to solar cells, but can also be extended to photocatalytic hydrogen production. One recent example is the hydrogen evolution using a ruthenium dye–cobalt diimine dioxime immobilized on a NiO photocathode<sup>110</sup>. This system yielded a hydrogen production with a turnover number (TON) of 13 which is still a rather small number. Although this system has problems with inefficient electron transfer and stability, this result could be a steppingstone for the further development of fully photocatalytic hydrogen production based on the concept of *p*-DSSC.



**Figure 5.** (a) The structure of coupling PPV with Ruthenium polypyridyl based dye with two different substituent, ethyl ester (Ru1) and tertiary-butyl (Ru2). The proposed mechanism of this system consist of (1) hole injection (2) and charge recombination (3) dynamics in PPV-Ru. (b) The absorption and emission spectra of PPV only (up), PPV-Ru1 (middle), and PPV-Ru2 (bottom)(Reprinted with permission from Scientific Reports 2021 11:1, 11 (1), 1–13)<sup>111</sup>.

However, attaching Ru-based dyes to a NiO surface may have some drawbacks related to the presence of surface states on NiO, especially for dyes with electron withdrawing anchors. In this anchoring type, the electron is attracted upon excitation from the Ru-metal center to the anchor, instead of to the spacer or linker<sup>112,113</sup>. There, it might create an electron cloud which may obstruct the hole injection process, as it will facilitate the hole-electron recombination on the anchor<sup>112,113</sup>. As an alternative to using NiO, attaching Ru-based dyes to *p*-type polymer semiconductor shows also potential as an application of *p*-type DSSCs. One of the most promising candidates is poly[2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene] (MEH-PPV), as this polymer has a HOMO level (ca. 4.8–4.9 eV) that is comparable to the valence band edge of *p*-type NiO (ca. 5.0–5.1 eV)<sup>114–117</sup>.

Wahyuono and coworkers have coupled ruthenium polypyridyl complexes to the PPV backbone<sup>111</sup>. They used various substituents of different character at the bipyridine ligands, ethyl ester (Ru1) as electron withdrawing and tertiary butyl (Ru2) as electron donating substituent<sup>111</sup>. A schematic picture of PPV coupled to a Ru-based dye is shown in Fig. 5a,

whereas the measured optical spectra for both absorption and emission are presented in Fig. 5b. According to the experimental results, electron withdrawing substituents are associated with a faster hole injection process and a charge separation state with a longer lifetime than the electron donating substituent<sup>111</sup>. A theoretical study addressing the coupling of the Ru-based dye with PPV has been performed by Putra et al<sup>118</sup>. They employed density functional theory (DFT) and time-dependent DFT (TD-DFT) in a periodic and a local setup to unravel the electronic and optical properties of this system. According to the calculations<sup>118</sup>, PPV and the Ru-based dye are not strongly electronically coupled. Thus, the detrimental surface states effect observed on NiO photocathodes can be avoided by attaching dyes to *p*-type organic semiconductors. In addition, the quantum chemical calculations suggest that the charge transfer process may occur through dark state  $\pi(\text{PPV})-\pi^*(\text{Dye})$  transitions of low lying states<sup>118</sup>. Still, there are some obstacles that need to be addressed, especially related to the photostability of the polymer backbone<sup>111</sup>.

Note that Ru-based dyes are a promising material for DSSCs, but ruthenium is a rare earth metal with a low abundance on earth of about 100 parts per trillion<sup>119,120</sup>. Therefore, there is certainly a demand for alternative effective dye materials that are more abundant.

## **2.2. Osmium Complexes**

As a metal that belongs to the same group as ruthenium in the periodic table of elements, osmium should be among the candidates as an alternative to Ru-based dyes. First experiments to implement Os-based dye were done by Heimer and coworkers in 1993<sup>121</sup>. In their work, they compared the electrooptical properties of Ru- and Os-metal center together with cyanide anchors ( $\text{Ru}(\text{LL})_2(\text{CN})_2$  and  $\text{Os}(\text{LL})_2(\text{CN})_2$ ) attached to  $\text{TiO}_2$ . According to their results,  $\text{Os}(\text{LL})_2(\text{CN})_2$  does not only absorb blue light, but also expands its absorption capability to red light<sup>121</sup>, indicating that Os-based dyes have the potential to harvest light in a broader range of the light spectrum.

The favorable absorption properties in the red light spectrum of Os-based dyes are due to a strong spin-orbit coupling which is able to induce an intense (formally) spin-forbidden metal-to-ligand charge transfer (MLCT) transition<sup>122,123</sup>. However, the IPCE of  $\text{Os}(\text{LL})_2(\text{CN})_2$  is reported to be lower (IPCE=10%) than that of  $\text{Ru}(\text{LL})_2(\text{CN})_2$  (IPCE=92%)<sup>121</sup>. Several attempts have been performed to increase the efficiency of Os-based dyes. However, the maximum efficiency that has been achieved so far for Os-based dye is still lower than 10%. This is illustrated in Tab. 3 which presents a list of some Os-based dyes attached to  $\text{TiO}_2$  including their performance parameters.

**Table 3.** Some Osmium based dyes for *n*-type DSSC with their  $J_{\text{SC}}$ ,  $V_{\text{OC}}$ , FF and PCE.

No.	Dye	J <sub>sc</sub> (mA·cm <sup>-2</sup> )	V <sub>oc</sub> (mV)	FF (%)	PCE (%)	References
1	11	11.00	651.0	56.60	4.07	124
2	15	2.80	250.0	49.00	0.40	125
3	16	23.70	320.0	36.00	2.70	125
4	20	3.52	520.0			126
5	22	5.78	395.0			126
6	Os(H <sub>2</sub> L') <sub>2</sub> (CN) 2	11.60	500.0			127
7	Os(H <sub>2</sub> L') <sub>3</sub> <sup>2+</sup>	10.00	450.0			127
8	TFOS-2	15.70	610.0	63.00	6.08	128
9	Os-3	0.93	317.0	61.60	0.20	129
10	CYC-33O	19.38	474.0	62.30	5.70	129
11	CYC-33R	16.69	533.0	68.60	6.10	129
12	Os-stbpy	18.80	538.0	60.20	6.10	130
13	TF-51	20.10	560.0	66.40	7.47	131
14	TF-52	23.30	600.0	63.30	8.85	131

Although there are several studies addressing Os-based dye for *n*-type DSSCs, we are not aware of their utilization for *p*-type DSSC in combination with an NiO electrode. However, there is one study of Seidler *et al.* investigating Os-based polypyridyl dyes attached to PPV<sup>132</sup>. According to their results, changing the metal center from ruthenium to osmium leads to a reduction of the photodegradation of the polymer backbone. However, the maximum current density of this system is still lower than for Ru-based dyes<sup>132</sup>. In addition, Os-based dyes offer the possibility to extend their applicability to a photochemical molecular device (PMD) for the photocatalytic hydrogen evolution reaction (HER)<sup>133</sup>.

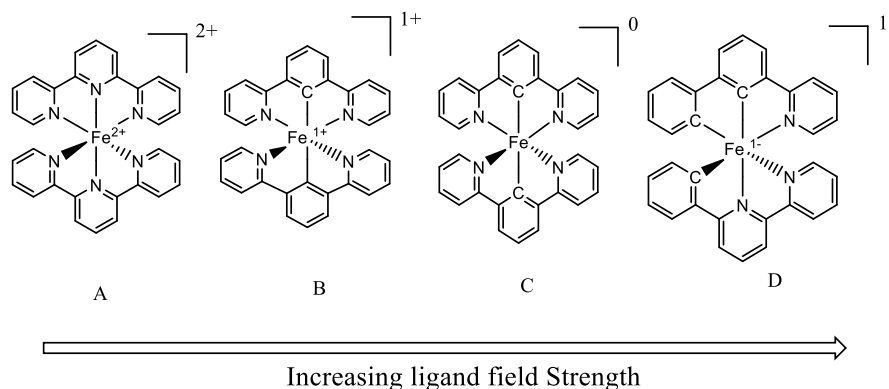
As mentioned above, Os-based dyes have not as often been used for DSSC systems as Ru-based dyes. In fact, Os-based dyes would not solve the problems associated with the low abundance of Ru as the abundance of osmium of only 50 parts per trillion in the continental crust<sup>134</sup> is even lower. Furthermore, it still has a poorer device efficiency, especially in comparison with Ru<sup>129</sup>.

### **2.3. Abundant metal complexes**

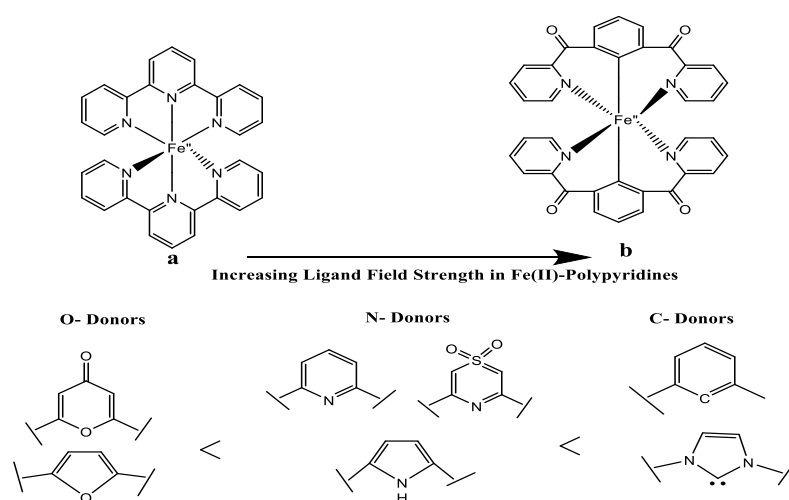
Due to the scarcity of ruthenium and osmium, the search for alternative metal complexes is still ongoing. Several scarce metals like rhenium, rhodium, iridium have been studied along with abundant metals like iron, copper, cobalt, chromium etc, whose properties in the context of dye sensitizers will be discussed in the following.

#### **2.3.1. Iron(II)**

5% of the Earth crust consists of iron making it the second most abundant metal after aluminum. Iron based dyes were first developed by Ferrere et. Al. in 1998<sup>135</sup>. However, iron-based DSSCs employing  $[\text{Fe}(\text{dcbpy})_2(\text{CN})_2]$  complexes show a very low short-circuit current density ( $J_{\text{SC}}$ ) and open-circuit voltage ( $V_{\text{OC}}$ ). This is due to the fast deactivation of the MLCT from the metal-centered state which leads to an inefficient electron injection into the semiconductor causing a lower short-circuit current density ( $J_{\text{SC}}$ )<sup>136</sup>. Attempts to increase the performance of iron-based dye sensitizers have been performed by several groups. Jakubikova, McCusker and coworkers demonstrated that the selection of more appropriate electrolytes can increase  $J_{\text{SC}}$  as well as the overall efficiency of such dyes<sup>137</sup>. Several studies concentrated on the search for better-suited ligands in iron-based dyes<sup>138–143</sup>. Sriparna et. al. recently showed that the use of Fe(II)-bis(terpyridine) and its cyclometalated analogues with pyridine ligands systematically replaced by aryl groups leads to an increase in the ligands field strength and in the efficiency of the dyes.<sup>139</sup> They analyzed the interfacial electron transfer between the Fe(II) photosensitizers and  $\text{TiO}_2$  using DFT calculations<sup>139</sup>. Their systematic change of the ligands is illustrated in Fig. 6. Bowman et. al.<sup>141</sup> showed based on computational studies that for the Fe(II) polypyridines, the central pyridine moiety (Figure 6) replaced by five-membered (N-heterocyclic carbene, pyrrole, furan) or six-membered (aryl, thiazine-1,1-dioxide, 4-pyrone) moieties modifies the ligand field strength thus changing the efficiency of such dyes (see Fig. 7).



**Figure 6.** Geometries of different Iron polypyridines. (Reprinted with permission from *Inorganic Chemistry*, 54 (2), 560–569)<sup>139</sup>



**Figure 7.** Geometries of the Iron polypyridines with different donors and ligand field strength (Reprinted with permission from *Inorganic Chemistry*, 54 (17), 8786–8793)<sup>141</sup>.

According to a recent study by Gros et al., in the presence of the  $\text{Mg}^{2+}$  ions and guanidium thiocyanate in the  $\text{I}^-/\text{I}_3^-$  electrolyte, a higher efficiency of 1% for Fe based dyes can be achieved<sup>144</sup> up to the record of 1.44% efficiency<sup>144</sup> for Fe(II)-based DSSCs with heteroleptic iron(II) NHC dyes using a similar addition of  $\text{Mg}^{2+}$  ions in combination with Bu4NI and poly(3,4-ethylenedioxythiophene (PEDOT) coated counter electrodes<sup>145</sup>.

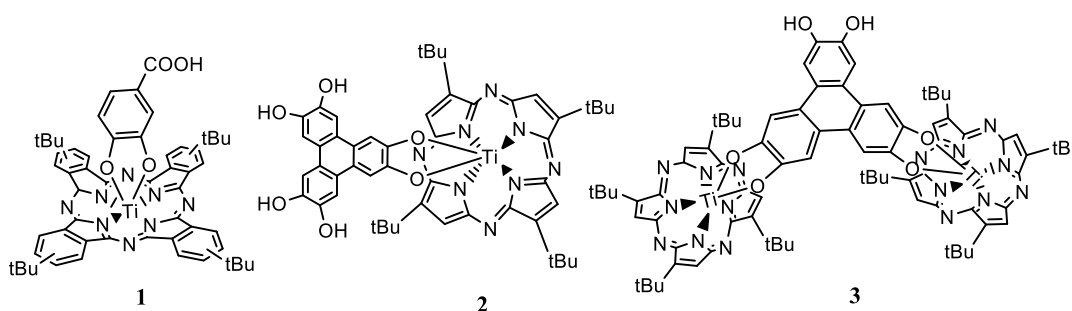
A recent study by Becker et al. investigated the effect of changing the concentration of iodine in the  $\text{I}^-/\text{I}_3^-$  electrolyte and choosing different ionic liquids (ILs) in DSSCs with a Fe(II)-NHC dye<sup>146</sup>. They showed that the structure of the different ILs influences various parameters such as the diffusion resistance in the electrolyte, the resistance at the counter electrode and the charge diffusion in the semiconductor. The HMII ionic liquid showed the poorest performance, whereas the ILs with short alkyl-chains (DMII and EMII) caused an increase in  $J_{\text{sc}}$ . The highest efficiencies for their DSSCs with different ILs and various iodine concentrations were found to be in the range 0.62–0.67%.<sup>146</sup>

### 2.3.2. Magnesium

Magnesium, another abundant material (2.1% in the earth crust) has also been used in DSSCs, but not as an alternative metal in the photoactive metalorganic complexes but rather as a dopant for TiO<sub>2</sub>/ZnO electrode surfaces. Ringleb et al. showed that Mg-doped ZnO (MZO) photoanodes based on nanoparticles with varying Mg concentrations significantly increase V<sub>OC</sub>, leading to an increase in the total efficiency of the dye<sup>147</sup>. In a recent study by N. Siregar et al., a maximum efficiency of 3.53% at an annealing temperature of 500°C was achieved using a Mg-doped ZnO thin film as the photoanode and the rose myrtle natural dye (Rhodomyrtus tomentosa)<sup>148</sup>. This work also demonstrated that the annealing temperature of the photoanode can sensitively affect the efficiency of a DSSC device. Similar surface modifications of TiO<sub>2</sub> photoanodes using magnesium nitrate were performed by M. Asemi et al. resulting in a reduced recombination of photogenerated electrons<sup>149</sup>.

### 2.3.3. Titanium

Titanium, being another abundant material, and has widely been used as the most applicable semiconductor material for n-type DSSCs. However, some studies have also focused on titanium-based dye sensitizers. M.V. Martínez-Díaz et al. studied phthalocyanine-based dyes with titanium metal centres, as illustrated in Fig. 8, which exhibit absorption in the near IR region. An efficient electron injection along with slow recombination has been reported. Still, due to poor charge separation, an overall efficiency of only about 0.2% has been observed<sup>150,151</sup>. DFT studies of Zarate et al. indicated that a better performance can be reached by using porphyrazine titanium (IV) complexes<sup>152</sup>.



**Figure 8.** Dye sensitizers based on Titanium centres.<sup>150–152</sup>

### 2.3.4. Zinc

Porphyrazine-based dyes have in fact been considered recently for Zn-metal dye sensitizers. A computational study of Flores identified a series of highly efficient zinc phthalocyanine dyes with various electron-donating substituents and anchors<sup>153</sup>. Further studies have been performed with similar Zn-metal based dyes using both theoretical and experimental approaches indicating the potential of Zn-based dye sensitizer for DSSCs<sup>151,154–156</sup>. Recent

studies also addressed the involvement of the Zn-phthalocyanine derivatives for dye sensitized solar cells (DSSCs) such dyes have enough driving force to inject electrons into the conduction band of TiO<sub>2</sub><sup>157</sup>. Similar studies have also been performed on asymmetric zinc phthalocyanine dyes bearing electron donating tert-butylsulfanyl or hexylsulfanyl groups and a carboxylic acid anchoring group. Quantum chemical calculations were also performed which yielded similar results. Zinc porphyrin ring based dye sensitizers have been studied which exhibit high power conversion efficiencies of 7.13%<sup>158,159</sup>. C. Li et al. showed the highest overall efficiency of 10.7% for Zn-porphyrin based dye sensitizers (a record for non-ruthenium iodine-based DSSCs in the absence of a co-sensitizer and a co absorbate)<sup>160</sup>. Porphyrins along with the phthalocyanin have also been employed as dye sensitizers. Their preparation has been inspired by the structure of chlorophyll as will be discussed in this review below.

### **2.3.5. Rare Earth Metals**

In our literature survey we did not find any studies in which dye sensitizers based on rare earth metals were addressed. However, rare earth metals have been used to dope TiO<sub>2</sub> surfaces in order to increase their efficiency<sup>161-163</sup>. C. Cavallo et al. synthesized solid solutions of the rare earth (RE) cations Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Er<sup>3+</sup> and Yb<sup>3+</sup> in anatase TiO<sub>2</sub> which was used as the electrode in DSSC applications with N719 as dye and a nonvolatile, benzonitrile based electrolyte<sup>164</sup>. It turned out that doping with Er<sup>3+</sup> led to the highest conversion efficiency whereas Pr<sup>3+</sup>, Nd<sup>3+</sup> reduced the performance of the DSSC.

### **2.3.6. Vanadium**

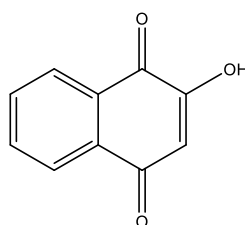
To the best of our knowledge, so far vanadium metal complexes have not been used for dye sensitizer in solar cell devices. Still, vanadium oxide<sup>165</sup> and vanadium sulfide<sup>166</sup> have been considered as low cost alternatives to replace the costly platinum electrodes in DSSC applications. These studies showed that the efficiency of the DSSCs is low for vanadium oxide electrodes (0.38%) but it increased to 6.24% upon using vanadium sulfide. In a recent theoretical study by our group, we addressed for the first time the usage of a vanadium complex as a dye sensitizer<sup>167</sup> for a p-type DSSC. According to our calculations, vanadium and chromium based dye sensitizers correspond to the most promising among the considered dyes based on abundant metals, they even outperformed ruthenium based complexes for p-type DSSCs.

### **2.3.7. Chromium**

Chromium doped TiO<sub>2</sub> as fabricated by Narottam Prasad et al.<sup>168</sup> exhibit an increased surface area and an overall increase in the efficiency. Further studies also confirmed the positive impact of doping TiO<sub>2</sub> photoanodes with chromium on the physical properties, electronic band



structure and photovoltaic characteristics of DSSCs devices<sup>168-171</sup>. For example, Momeni found an energy conversion efficiency increase from 1.05 % to 3.89 % upon doping by chromium<sup>171</sup>. Dye sensitizers based on chromium have been rarely considered so far for n-type<sup>172</sup> and p-type DSSCs<sup>167</sup>. As one example, the Lawsone ligand, as illustrated in Fig. 9, and their metal complexes were used as dye sensitizers for DSSCs by K. S. Sreelatha et al.<sup>172</sup>. Several transition metals such as manganese, zinc, nickel, cobalt, copper, iron and chromium were complexed with the Lawsone dye. Together with TiO<sub>2</sub> nanoparticles as the electrode, chromium complexes caused an increased efficiency and stability for the DSSC compared to the other metal complexes. These findings are in agreement with the results of the recent computational study mentioned above which found an improvement of the properties of p-type DSSCs upon employing vanadium and chromium based dye sensitizers<sup>167</sup>.



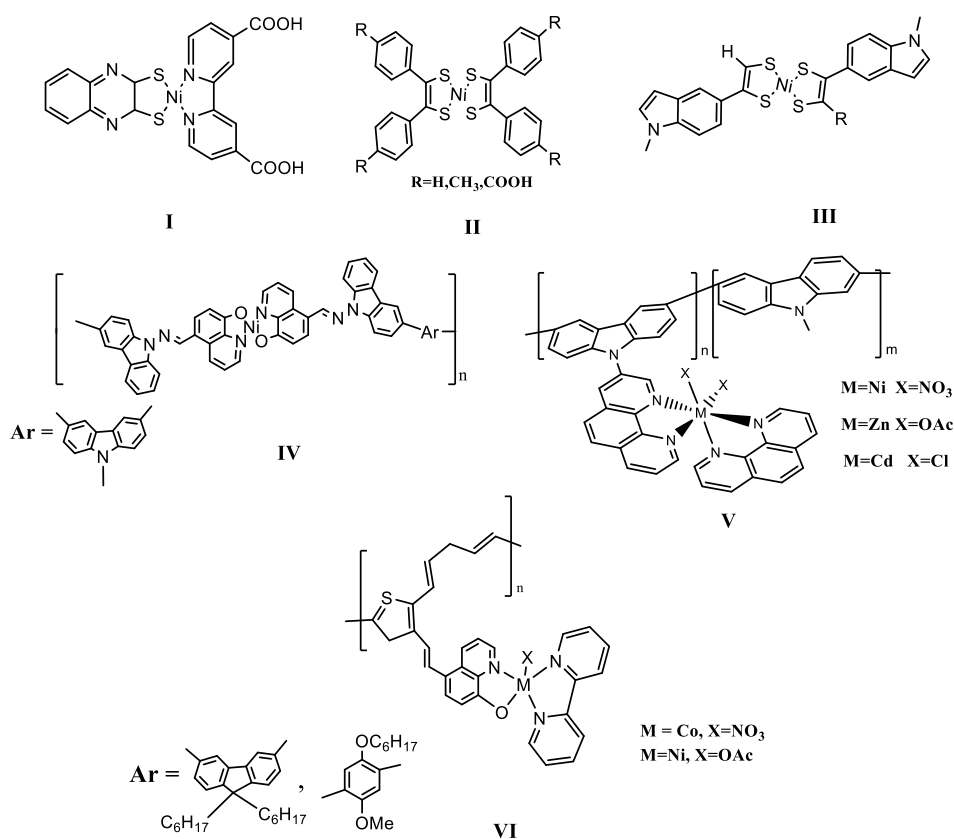
**Figure 9.** Lawsone Ligand.

### 2.3.8. Nickel

Similar to titanium, nickel has been widely employed in DSSCs in dye sensitizers, semiconductor surfaces, working electrodes as well as counter electrodes. It has been predominately used in the form of nickel oxide (NiO) as the p-type semiconductor in p-type DSSC. Several studies have been focusing on NiO as a p-type semiconductor for DSSCs in the last decade<sup>40,167,173,174</sup> which, however, still exhibit a lower efficiency than n-type DSSCs. Morandeira et al. studied coumarine sensitized p-type-nanostructured NiO films, but found a very low efficiency<sup>175</sup>. p-type DSSCs have still been studied much more rarely than n-type DSSCs. These studies have either focused on designing new sensitizers for p-type DSSCs<sup>176-179</sup> or on improving the quality of the NiO photocathode<sup>180-183</sup>. The best results for the p-DSSC efficiency have been obtained so far by Perera et.al. accomplishing an efficiency of 2.5%<sup>184</sup>. Hence, further research in this field is still needed to design new sensitizers as well as semiconductors with better efficiencies. This will also be critical in the design of tandem cells containing both n- and p-type DSSCs.

Nickel has also been used as counter electrode by S. Nair et. al.<sup>185</sup> They have synthesized nickel doped tungsten diselenide as counter electrodes for the DSSCs which significantly increased the efficiency of the studied dye sensitizer. Further studies have also been performed using

nickel sulfide, nickel polypyrrole<sup>186,187</sup> or nickel doped cobalt sulfide<sup>188</sup>, in all cases resulting in an increased efficiency compared to platinum counter electrodes. In addition, nickel based sensitizers have been studied for both n-type and p-type DSSCs. The recent theoretical study by Sen and Groß indicated that nickel-based dye sensitizers with catechol as an anchor can lead to a high hole injection efficiency from the dye to the semiconductor in p-type DSSCs.<sup>167</sup> Several studies on dithiolene complex based Ni-metal dyes as illustrated in Fig. 10 revealed a good absorbance in the visible and NIR region, but still a low efficiency of around 0.006% - 0.11%.<sup>189–192</sup> Similar studies were performed by J. Deng et al. to reveal the photosensitizing abilities of nickel and zinc based polycarbazole backbones.<sup>193</sup> Still low efficiencies were observed for the nickel based dyes which has been associated with the weak interaction of the dye with the semiconductor, low charge separation and low hole transport to the electrolyte by L. Guo et al.<sup>194</sup>

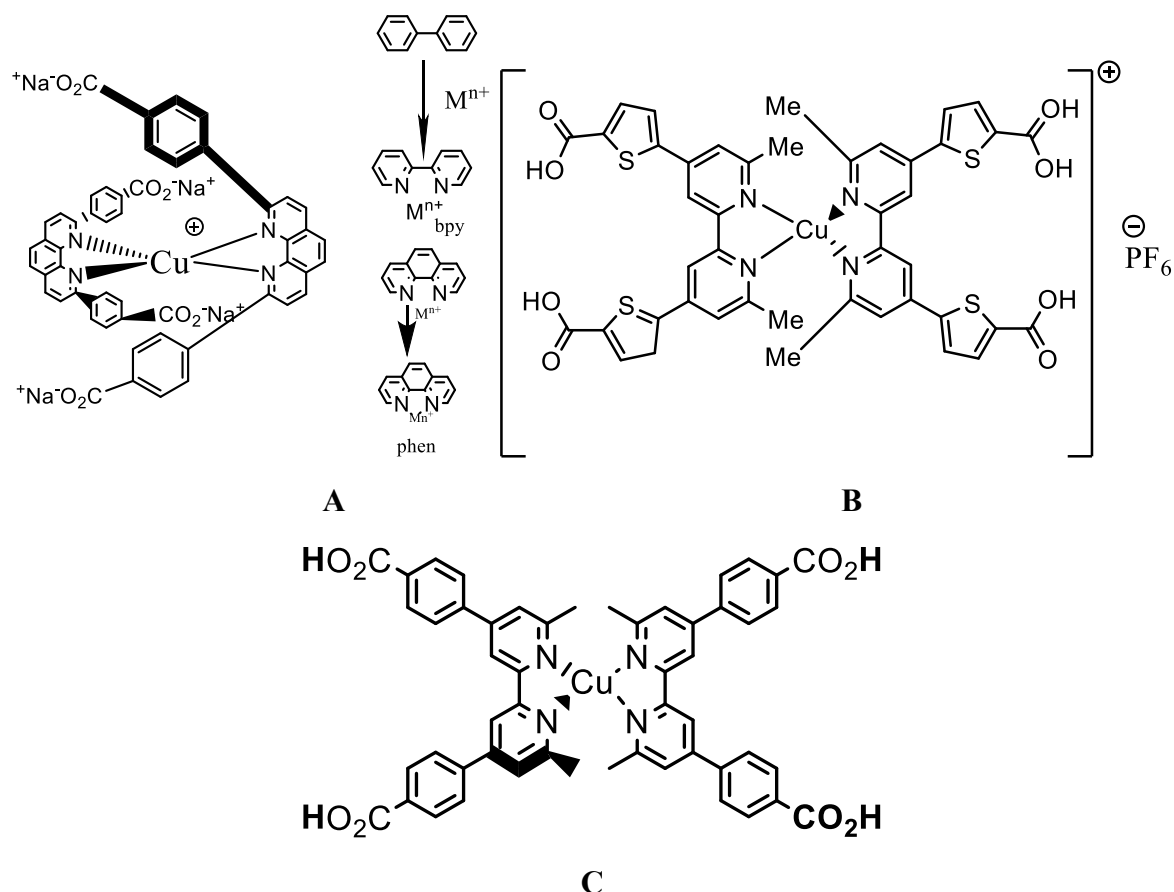


**Figure 10.** Nickel based dye sensitizers.<sup>189–194</sup>

### 2.3.9. Copper

Sauvage et al. first introduced a copper based dye sensitizer (Figure 11) for solar cells<sup>195</sup> in 1994 which showed a good absorption maximum at 440 nm. This was later confirmed by N. Armaroli et al. who found similar photophysical properties of copper (I) and the ruthenium (II) complexes<sup>196,197</sup>. Several further theoretical and experimental studies have been addressed

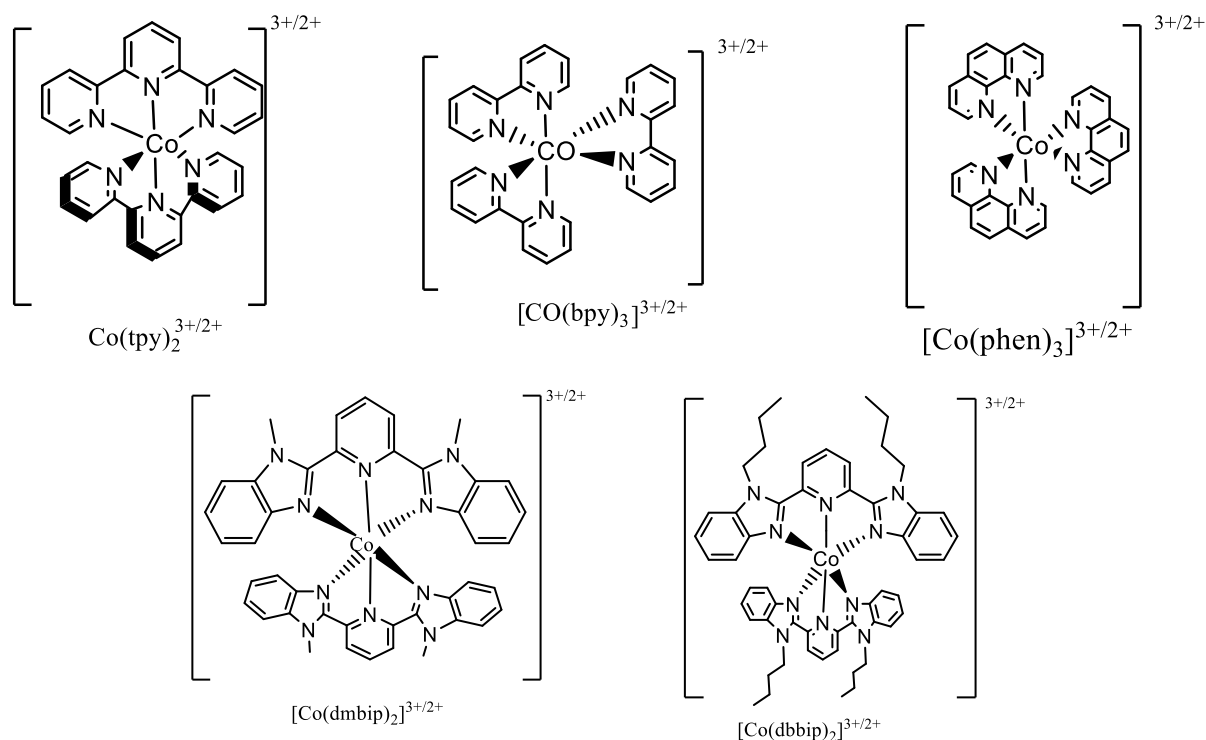
copper based dye sensitizers motivated by its high earth abundance<sup>198–208</sup>. A copper dye sensitizer based on a bipyridine complex and COOH anchors (see Fig. 11) synthesized by Constable et al. reached an efficiency of 1.9%<sup>209,210</sup> suggesting strategies for the synthesis of copper based dyes with improved properties. In contrast, homoleptic copper(I) based dye sensitizers exhibit low efficiencies, as revealed by K. A. Wills et. al.,<sup>211,212</sup> whereas Odobel et al. developed several heteroleptic copper complexes as dye sensitizers with high efficiencies up to 4.6%.<sup>213–215</sup> Studies of the effect of anchors, halogen substituents etc. on copper based dye sensitizers found phosphate based anchors to be most favorable.<sup>204,216,217</sup> K. A. Wills et al. introduced thiophene motifs in copper dye sensitizers (see Fig. 11) leading to an efficiency of 1.41%.<sup>204</sup> A recent study by A. Colombo et al. showed a way to increase the efficiency of the copper based heteroleptic dyes through modifications of the electrolyte.<sup>218</sup> They performed the DSSC fabrication using the  $\Gamma^-/I_3^-$  couple and the recently reported copper electron shuttle E1/E2 at various concentrations. They observed an increase in the short circuit current density on dilution of the redox shuttle which led to an improved performance of the copper based dyes reaching an efficiency of 3.05% which again demonstrated the potential of earth-abundant components for DSSCs.<sup>218</sup> Heteroleptic copper(I) sensitizers bearing 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid anchored to a  $TiO_2$  surface also exhibit a good performance as DSSCs, as shown by C. Dragonetti et al. in a combined experimental and theoretical study.<sup>219</sup> An recent review on copper complexes was performed by A. Colombo et al.<sup>220</sup> elaborating on the wide usage of copper based redox mediators which could successfully replace the  $\Gamma^-/I_3^-$  couple. Furthermore, they also showed that the combination of copper dyes with such mediators could yield good and efficient low-cost full-copper solar cells. Still, there are problems that need to be addressed such as the volatility of iodine gas or corrosion issues.



**Figure 11.** Geometries of copper based dye sensitizers.<sup>195,204</sup>

### 2.3.10. Cobalt

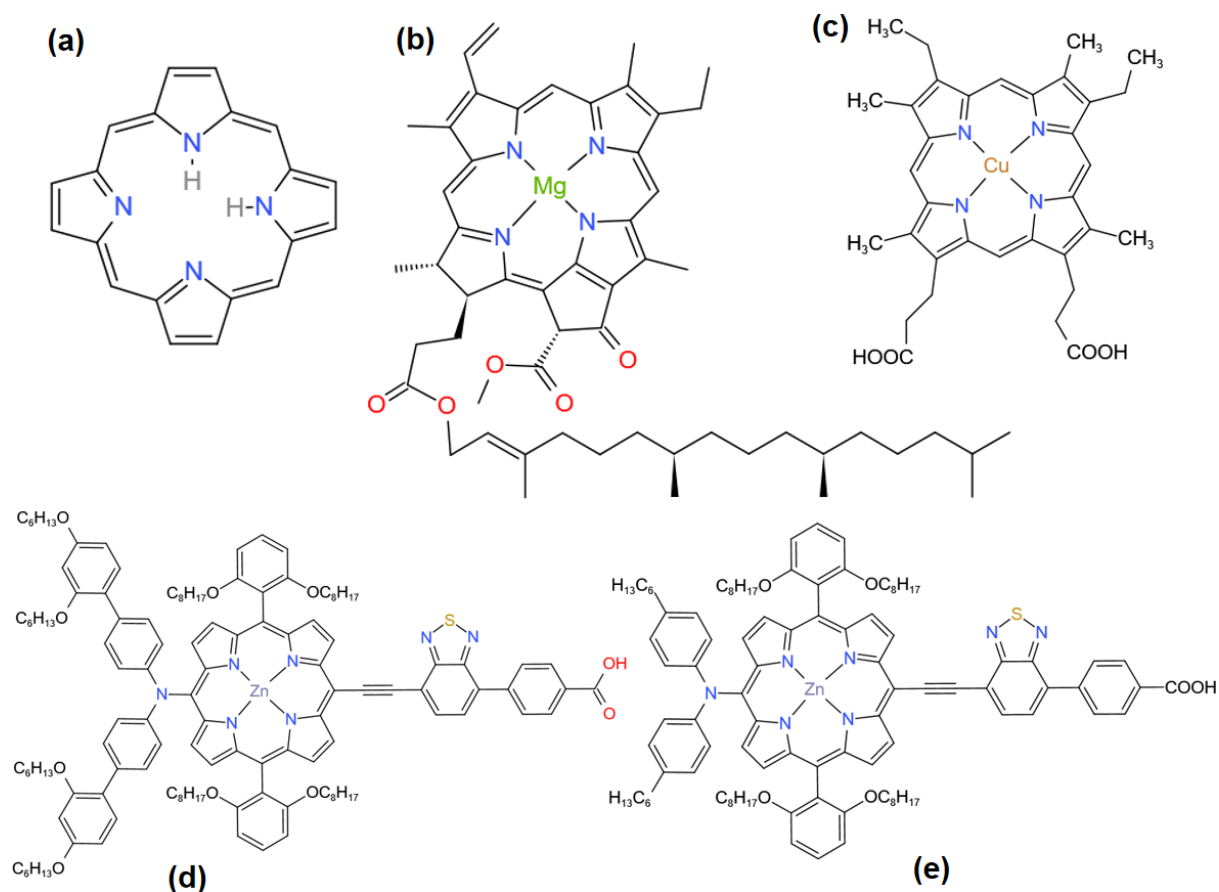
Cobalt has not been used in dye sensitizers but it is a very well-known redox mediator (Co(II)/Co(III)) for the DSSCs. The  $\text{I}^-/\text{I}_3^-$  redox couple exhibits various disadvantages such as its high reactivity causing, i.e., corrosion, and cobalt based redox mediators are considered to be a promising alternative. The progress with respect to cobalt (III)/(II) polypyridyl complexes as organic dyes was reviewed by Hamann et al.<sup>220</sup> Many redox couples such as  $[\text{Co}(\text{tpy})_2]^{2+/3+}$ ,  $[\text{Co}(\text{bpy})_3]^{2+/3+}$ ,  $[\text{Co}(\text{phen})_3]^{2+/3+}$ ,  $[\text{Co}(\text{dmbip})_2]^{2+/3+}$  and  $[\text{Co}(\text{dbbip})_2]^{2+/3+}$ , as illustrated in Fig. 12, have been considered,<sup>221</sup> and there is a rich literature demonstrating the improved solar cell performance of different dye sensitizers together with cobalt based redox mediators.<sup>222–228</sup>



**Figure 12.** Cobalt redox couples for DSSCs.<sup>220</sup>

### 2.3.11. Porphyrin Dyes

As mentioned above, dyes based on porphyrins and phthalocyanines are rather promising showing good efficiencies. Porphyrins are a group of heterocyclic macrocycle organic compounds, composed of four modified pyrrole rings fused together.<sup>229</sup> Several porphyrin based structures have been proposed as an alternative for Ru-based dye, as they correspond to promising compound for solar cell application, due to their low-cost and low toxicity combined with the ease to synthesize them.<sup>230–232</sup> The structure of porphyrins has a rigid geometry, and it is also relatively stable.<sup>232</sup> Furthermore, porphyrins have favourable electron transfer properties,<sup>233</sup> yielding high molar absorption coefficients and promising light harvesting potentials.<sup>234</sup> Porphyrin has in general two optical absorptions bands, one between 400 and 500 nm and another between 550 and 750 nm<sup>235–237</sup>. The position of the LUMO level is located above the conduction band of  $\text{TiO}_2$ , while its HOMO level is below the redox couple of typical electrolyte solution which is suitable for good charge transfer properties.<sup>229</sup> Furthermore, the macrocyclic structure of porphyrin can be functionalized by several metal centers such as zinc (Zn), manganese (Mn), calcium (Ca), etc, in order to produce suitable dyes for DSSC applications.<sup>235,238,239</sup>



**Figure 13.** (a) Porphyrin structure, (b) Chlorophyll a (chl a) structure, and several structure of porphyrin-based dye: (c) Cu-mesoporphyrin, (d) SM315, and (e) GY50.

The first successful implementation of a porphyrin as dye in a DSSC was reported in 1993 by Kay and Grätzel.<sup>240</sup> They synthesized a Cu-mesoporphyrin dye and found a maximum PCE of the device at around 2.6%, which is still lower than the ruthenium dye at similar conditions due to the ohmic losses at high current densities.<sup>240</sup> Several studies have been performed since then to improve the performance of porphyrin-based DSSC via several strategies, such as selecting specific adsorption structures of porphyrin on  $\text{TiO}_2$ , using various anchoring groups, employing push-pull porphyrins,  $\pi$ -extended porphyrins, Co-sensitization, etc.<sup>241</sup>

In 2000, Cherian and Wamser, achieved an improvement of the PCE of porphyrin-based dye to 3% which was followed by a further enhancement to 5% by Wang and colleagues in 2005.<sup>242,243</sup> The development of porphyrin-based DSSC in early 2000s still yielded efficiency that are lower than those of Ru-based DSSC.<sup>238</sup> In 2009, the push-pull-structured porphyrin, where the strategy was to develop a donor and an acceptor to generate the push-pull mechanism, **YD2** could achieve an efficiency close to ruthenium dye N719 at similar conditions.<sup>244</sup> A further improvement of **YD2**, was accomplished by Yella and colleagues in 2011, named **YD2-o-C8**, which is associated with an efficiency of 12.3%.<sup>245</sup> The highest

efficiency of porphyrin-based DSSC as achieved by the **SM315** and **GY50** dyes in 2014 reaching the efficiency of around 13%, and infact these belong to the highest certified values ever reported in DSSC for a single dye.<sup>246–248</sup>.

**Table 4.** Performance of several porphyrin-based *n*-type DSSC. All of porphyrin-based dyes are attached to TiO<sub>2</sub>.

Dye	Metal Center	PCE (%)	Ref.
Cu-mesoporphyrin	Cu	2.6	240
Chlorophyll	Mg	0.055	249
H <sub>2</sub> TFP	-	0.110	249
ZnTFP	Zn	0.080	249
TCPP	-	3.0	250
Zn-1	Zn	7.0	251
YD2	Zn	11.0	244
ZnPBAT	Zn	10.1	252
LD4	Zn	10.1	253
LD14	Zn	10.2	254
LD22	Zn	8.10	255
LW4	Zn	9.5	256
LWP1	Zn	9.7	257
YD2-o-C8	Zn	12.3	245
WW-6	Zn	10.5	258
SM315	Zn	13.0	248
GY50	Zn	12.7	247
WW-5	Zn	10.3	258
WW-4	Zn	0.3	258
YDD2	Zn	< 0.5	259
YDD3	Zn	< 0.5	259
YDD0	Zn	4.1	259

Besides the application of the porphyrin rings as *n*-type DSSC, there are also reports on the implementation of porphyrin-based dye in *p*-type DSSC which required certain structural modifications of the dye and the electrodes. For example NiO and Copper oxide based material were employed as photocathode. But still the efficiency of such *p*-type DSSCs are lower

compared to Ru-based dyes. A list of porphyrin dyes that were synthesized for *p*-type DSSC is provided in Table 5.

**Table 5.** Performance of several porphyrin-based *p*-type DSSC.

Dye	Metal Center	Photocathode	PCE (%)	Ref.
TPPC	-	NiO	0.0033	260
D1	Zn	Cu <sub>5</sub> Ta <sub>11</sub> O <sub>30</sub>	$2.75 \times 10^{-4}$	261
D2	Zn	Cu <sub>5</sub> Ta <sub>11</sub> O <sub>30</sub>	$8.31 \times 10^{-5}$	261
ZnP0	Zn	NiO	0.26	262
ZnP1	Zn	NiO	0.92	262
ZnP-Co <sub>2</sub> H-NO <sub>2</sub>	Zn	NiO	0.020	263
ZnP-eCo <sub>2</sub> H-NO <sub>2</sub>	Zn	NiO	0.019	263
ZnP-Co <sub>2</sub> H-eNO <sub>2</sub>	Zn	NiO	0.013	263
ZnP-eCo <sub>2</sub> H-eNO <sub>2</sub>	Zn	NiO	0.022	263
ZnP-Co <sub>2</sub> H-eNDI	Zn	NiO	0.056	263
ZnP-Co <sub>2</sub> H-BV <sup>2+</sup>	Zn	NiO	0.018	263
C <sub>60</sub> trZnP <sub>COOH</sub>	Zn	NiO	0.076	264
C <sub>60</sub> trZnP <sub>trCOOH</sub>	Zn	NiO	0.074	264
C <sub>60</sub> ZnP <sub>COOH</sub>	Zn	NiO	0.063	264
PhtrZnP <sub>COOH</sub>	Zn	NiO	0.015	264

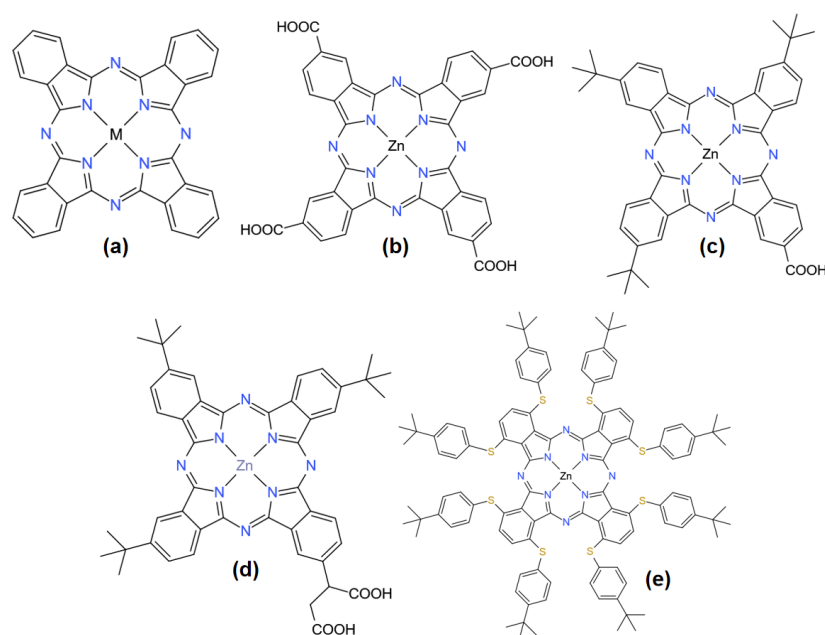
### 2.3.12. Phthalocyanine Based Dye

Phthalocyanine based dyes are the other group of heterocyclic macrocycle organic compounds which have been implemented as dyes in DSSCs. They are composed of four iso-indole units linked by a ring of nitrogen atoms with 18 delocalized *p*-electrons.<sup>265</sup> Phthalocyanines are thermally and chemically stable with their optical absorption in the red/near-infrared (NIR) region.<sup>265</sup> Due to these physical and optical properties they were proposed as promising candidate materials for many applications in fields such as organic electronics<sup>266–269</sup>, photovoltaics<sup>270–272</sup>, catalysis<sup>273</sup> and photodynamic therapy (PDT)<sup>274</sup>.

To the best knowledge, the first utilization of phthalocyanine with respect to solar cell technology was realized in the field of organic photovoltaics (OPV), with magnesium phthalocyanine (MgPc) sandwiched between two glass electrodes in a single-layer mode, yielding a photovoltage of 0.2 V in 1958.<sup>275</sup> Later, Bard and coworkers also observed a photocurrent response after photosensitization of various single-crystal n-type semiconductors



(TiO<sub>2</sub>, WO<sub>3</sub>, SrTiO<sub>2</sub>, ZnO, CdS, CdSe, SnO<sub>2</sub>, SnS<sub>2</sub>, etc...) by unsubstituted H<sub>2</sub>Pc<sup>276</sup> or MPcs<sup>277</sup> thin films in the 1980's, though the efficiencies were still low. In 1986, Tang et. al., first achieved an overall efficiency of 1% under simulated AM2 illumination with a thin-film of a two-layer cell composed of CuPc as the electron-donating layer and a perylene tetracarboxylic derivative as the electron-accepting counterpart <sup>278,279</sup>. Furthermore, Shen et. al. first implemented the Pcs on DSSC technology in 1995 achieving an IPCE ~ 4% at  $\lambda = 690$  nm.<sup>280</sup>



**Figure 14.** (a) Structure of phthalocyanine with M, a metal center or H<sub>2</sub>, and several example of phthalocyanine-based dye: (b) H<sub>2</sub>TcPc, (c) ZnTcPc, (d) FeTcPc, (e) TT1, (f) PCH001, and (g) Zn-Thio-Pc.

**Table 6.** Performance of several Pcs-based *n*-type DSSC. All of Pcs-based dyes are attached to TiO<sub>2</sub> surface.

Dye	Atom Center	PCE (%)	Ref.
TT1	Zn	3.50	281
PCH001	Zn	3.05	282
PcS6	Zn	4.60	283
PcS20	Zn	6.40	284
PcS15	Zn	5.30	285
PcS16	Zn	4.70	285
PcS22	Zn	3.20	286
PcS23	Zn	6.10	286
PcS24	Zn	4.60	286

TT40	Zn	6.01	287
TT58	Zn	5.50	288
Zn-Pc-dg	Zn	2.45	289
Co-Pc-dg	Zn	2.26	289
Zn-Pc-dp	Zn	2.07	289
Co-Pc-dp	Zn	2.01	289
7	Ru	0.24	290
9	Ru	0.25	290
1a	Ru	0.29	290
1b	Ru	0.34	290
LGB1	Si	0.90	291
LGB3	Si	4.50	291
(Pc)Zr(OAc) <sub>2</sub>	Zr	1.05	292
(Pc)Hf(OAc) <sub>2</sub>	Hf	0.59	292
Zn-thio-Pc	Zn	0.40	293

Following the study by Shen et. al., several modification of the chemical structure of the dye were performed with respect to the variation of metal centers, anchors and spacers, symmetrical and unsymmetrical substituents, push-pull phthalocyanines, co-sensitization, in order to increase the efficiency of such Pcs as dye sensitizers. Successfully synthesized Pcs-based dyes are listed on Table 6. Note, however, that the highest efficiency that can be obtained by Pcs-based DSSC is still lower than 10% inspite of the fact that they exhibit a very favourable absorption in the NIR region. Several factors are important for the limits the performance of Pcs-based dye:

1. Pcs based dyes have a tendency to aggregate, which can lead to a drastic degradation of the electron-injection efficiency. The common strategy for preventing the aggregation is to add co-absorbent, e.g. *chenodeoxycholic acid* (CHENO), but the required amount of CHENO per dye molecule in order to attain the optimal efficiency is usually rather large (typically there is a CHENO/Pcs ratio of 100:1). This represents a major disadvantage of this strategy since it reduces the total number of adsorbed molecules on the surface and thus consequently the absolute amount of injected electrons from the excited-dye to the electrode, which limits the current density of the DSSC.<sup>265</sup>
2. The LUMO level is quite low, which is a constraint for the electron-injection process into the conduction band of TiO<sub>2</sub>.<sup>265</sup> A common way for solving this limitation is by lowering the conduction band of TiO<sub>2</sub> via several strategies, e.g. by modifying the electrolyte

composition, but this usually will also decrease the  $V_{oc}$ . The third solution can be a modification of the structural design of Pcs-based dyes.<sup>284</sup>

Similar to porphyrin-based dyes, Pcs-based dye can also be considered to be implemented in *p*-type DSSCs. Here, the development is not only focused on the properties of the structural dye and the electrolyte, but also on the choice of the photocathode. For example, Langmar and his coworkers proposed in 2015,<sup>294</sup> to deposit Pcs-based dye, i.e. **ZnPc1** and **ZnPc2**, on CuO nanoparticles, instead of NiO. However, the PCE that can be achieved in this proposed system is relatively small, below 0.2%. Note that the list of phthalocyanine dyes that have been used in *p*-type DSSC are given in Table 7.

**Table 7.** Performance of several phthalocyanine-based *p*-type DSSC.

Dye	Electrolyte	Metal Center	Photocathode	PCE (%)	Ref.
ZnPc1	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	Zn	CuO	0.067	294
ZnPc2	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	Zn	CuO	0.103	294
ZnPc1	Co <sup>2+</sup> /Co <sup>3+</sup>	Zn	CuO	0.141	294
ZnPc2	Co <sup>2+</sup> /Co <sup>3+</sup>	Zn	CuO	0.191	294
ZnPc3	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	Zn	CuO	0.075	295
ZnPc4	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	Zn	CuO	0.069	295
ZnPc2	Co <sup>2+</sup> /Co <sup>3+</sup>	Zn	NiO	0.270	296
ZnPc2	Co <sup>2+</sup> /Co <sup>3+</sup>	Zn	NiO/CuO	0.500	296

#### **2.4. Organic Dyes D- $\pi$ -A, D-A- $\pi$ -A structures**

As discussed in the previous sections, for a long time DSSC research focused on Ru-based dyes because of their high efficiency, but research and development addressing other metal based dyes, both scarce and abundant, demonstrated that there are promising alternatives. Metal free organic dyes are common in many fields such as pharmaceutical chemistry, anticancer and anti-viral drug research, textile industries etc. Yella et al. demonstrated in 2011 the high efficiency of porphyrin based dyes,<sup>245</sup> which still contained the metal center, but the change in the organic moiety opened the path towards extensive studies of organic dyes for DSSC applications. Due to their low cost, high molar extinction coefficients, ease of synthesis and high stability under elevated temperature metal-free organic dyes have currently become increasingly popular compared to metal based, in particular Ru-based complexes.<sup>297,298</sup>

The structure of a metal free organic dye is comprised of three key parts which are termed donors, spacers or linkers and acceptors, respectively. The structure of the metal-free organic

dyes is illustrated in Fig. 15. The donor moieties consist of electron donating groups and are denoted by 'D'. Linkers or spacers usually consist of  $\pi$ -conjugated systems which link the donor and the acceptor groups. The fast transfer of the electrons from the donor site to the acceptor site depends on these ' $\pi$ -spacers'. The acceptor groups denoted by 'A' are electron acceptors and play a major role in the interaction with the semiconductor surface. As discussed above, the donor groups of such D- $\pi$ -A sensitizers are selected from electron rich moieties such as phenylamine, coumarine, indoline, triphenylamine, carbazoles etc. The  $\pi$ -spacers can be selected from simple to complex conjugated compounds like thiophene, pyrrole, ethenyl, phenylene, benzotriazole, quinoxaline etc.<sup>40</sup> The acceptor groups can be chosen from different compounds which can interact easily with the semiconductor surface such as carboxylic acid, sulphonic acid, salicylic acid, cyanoacrylic acid, pyridine etc.<sup>109</sup> Recent research has focused on improving the performance of DSSCs through a suitable alteration of donors,<sup>299-301</sup> spacers<sup>40</sup> and acceptors.<sup>109</sup> The chemical structure of metal-free organic dyes is very crucial for the efficiency and stability of the DSSC devices.<sup>302</sup> Therefore, many studies have been devoted to the optimization of the chemical structure of metal-free organic dyes. Up to now, several scaffolds for organic dyes have been developed such as D-( $\pi$ -A)<sub>2</sub>, D- $\pi$ -A, D-D- $\pi$ -A, D-A- $\pi$ -A and (D- $\pi$ -A)<sub>3</sub>L<sub>2</sub>. However, donor- $\pi$ -bridge-acceptor (D- $\pi$ -A) structures correspond to the most popular design for metal free organic dyes for DSSCs due to their easy synthesis, low cost, high molar absorption coefficient, high efficiency, enhanced environmental compatibility and abundance of their constituents. These compounds have the structure of a push-pull device which facilitates the intramolecular charge transfer (ICT) from subunit A to D through the  $\pi$ -bridge. Furthermore, a decrease of the HOMO-LUMO gap and improved absorption properties can be achieved by modifying the D,  $\pi$  and A moieties. In general, sensitizer dyes are attached to the semiconductor surface via the electron acceptor group. Applying the afore mentioned concepts, hundreds of metal-free organic dyes have been successfully tested as sensitizers for DSSC over the past two decades. Among the metal-free organic dyes, dye molecules having donor groups such as triphenylamine (TPA), substituted triphenylamine,<sup>303-313</sup> carbazole<sup>314-316</sup> and indoline dye<sup>317-320</sup> achieved a remarkable efficiency.<sup>321</sup>

Carbazole is one of the most widely used auxiliary donors due to its strong electron-rich nature, excellent hole-transporting ability and excellent stability.<sup>322,323</sup> As one of the first applications, Koumura et al employed the carbazole based organic dye as a sensitizer in DSSC.<sup>324,325</sup> Many more carbazole-based dyes have been tested, and most of them have shown excellent power conversion efficiencies.<sup>326,327</sup> Hara et al. designed and synthesized indolo[3,2-*b*]carbazole dyes (**MKZ-21** and **MKZ-22**) for DSSCs and demonstrated their strong electron donating ability

facilitating a better photovoltaic performance with **MKZ-21** having a better PCE than **MKZ-22**.<sup>326</sup>

In 2009, the same group designed and synthesized hexyloxyphenyl substituted carbazole dyes for DSSCs coined **MK-14** and **MK-16**. They found that a hexyloxyphenyl substituent augments the electron lifetime as well as improves the open circuit voltage.<sup>327</sup> Aiming at also improving the PCE by carbazole based dyes, Hara et al. further synthesized three new thieno[3,2-*b*]indole based organic dyes **MKZ-39**, **MKZ-40**, and **MKZ-41**.<sup>328</sup> A computational study demonstrated that thieno[3,2-*b*]indole has a greater donor ability than carbazole. Nonetheless, thieno[3,2-*b*]indole as the donor part makes the molecule more planar compared to carbazole-based dyes. Among the three dyes **MKZ-40** displayed the highest efficiency of 7.8% indicating that thieno[3,2-*b*]indole can be used as a promising donor group for DSSCs. The Triphenylamine (TPA) unit is an excellent electron donor, and furthermore it inhibits the dye aggregation due to its nonplanar nature. Nevertheless, TPA also shows favourable hole-transport properties.<sup>303</sup> Therefore, TPA based dyes have been extensively used in DSSCs. In 2004, Kitamura et al. employed TPA compounds as an electron donor in DSSC.<sup>304</sup> Furthermore, Zhu and co-workers explored the effect of  $\pi$ -conjugation of various TPA donor group containing dyes (**TQ01**, **TQ02**, and **TQ03**) on the PCE<sup>305</sup> finding a PCE of 2,3-dioctylquinoxaline  $\pi$ -spacer containing dye of 8.20%. However, dye molecules with the more coplanar and conjugated dithieno[2,3-*a*:3',2-*c*]phenazine moiety displayed a lower efficiency due to an extreme aggregation. Grätzel and co-workers developed a novel D- $\pi$ -A dye (**C203**) which contains a difluorenylaminophenyl donor group<sup>329</sup> exhibiting an excellent PCE (8.0%) and high stability. To further develop more efficient TPAs, Murakami and co-workers introduced a stronger steric hindrance in the dye structure (**MK-89**, **MK-123** and **MK-136**).<sup>330</sup> The enhanced steric hindrance inhibits charge recombination and thereby increases  $V_{oc}$ . Among the studied dyes, **MK-136** displayed the best PCE of 8.9%.

The effect of  $\pi$ -spacer on the optical properties, energy levels, and electron transfer from donor to acceptor units was examined by Kim and co-workers.<sup>331</sup> They introduced various heteroaromatic units such as phenyl, pyridine, thiophene, thienothiophene and benzothiadiazole- thiophene into the triphenylamine (TPA)-based dyes **SGT-(141-145)**. According to this study, the thiophene containing dye **SGT-144** exhibits a PCE of 7.40% with  $J_{sc} = 14.38 \text{ mA cm}^{-2}$ ,  $V_{oc} = 694 \text{ mV}$  and  $FF = 0.74$ , values that are much higher than in many other dyes. In another study, An and co-workers addressed a series of sensitizers having furan, bifuran, furan-thiophene as  $\pi$ -linkers and cyclic thiourea functionalized triphenylamine as the

donor group.<sup>332</sup> Interestingly, they found the absorption spectrum of furan-thiophene based dye to be broader than the one of the bithiophene dye.

A series of cyclic thiourea/urea functionalized triphenylamine based dyes (**AZ1-AZ6**) were also employed as potential sensitizers by An and co-workers.<sup>333</sup> These dyes displayed wide absorption bands as well as a high molar extinction due to the presence of cyclic thiourea/urea functional groups which are responsible for their high performance. Furthermore, long alkyl chains attached to cyclic thiourea/urea functional groups inhibit dye aggregation and improve the  $V_{oc}$ . To enhance the electron-donating ability of TPA, Hagfeldt and co-workers synthesized **L156** and **L224**, where the electron-rich groups are attached to the phenyl ring.<sup>313</sup> They have employed two different  $\pi$  bridges like thiophene (**L156**) and 4,8-bis(4-hexylphenyl)benzo[1,2-b:4,5-b']dithiophene (**L224**), to examine their effect on the PV performance. It was observed that dye **L156** exhibited an excellent PCE of 9.3%. More recently, Promarak and co-workers studied a series of metal free organic dyes (**T2-4**) with donor substitutions at the terthiophene  $\pi$ -spacer.<sup>310</sup> They observed that the presence of the electron donating TPA substitutes on the  $\pi$ -spacer enhance the open-circuit voltage ( $V_{oc}$ ) and the short-circuit current ( $J_{sc}$ ). Wan et al. developed TPA dyes (**CRD-I**, **CRD-IV** and **CRD-VII**) containing alkyl chains in the electron acceptor group and examined their performances as sensitizer in DSSCs.<sup>311</sup> The long alkyl chain at the N position of the rhodanine effectively reduces the aggregation and charge recombination and subsequently increases the  $V_{oc}$  values. The electron lifetime of the examined dyes improved upon lengthening the alkyl chain. The DSSC based on the **CRD-IV** sensitizer displayed an excellent long-term stability and a high PCE of 9.02%.

Horiuchi and Uchida were the first to apply an indoline dye in a DSSC.<sup>317</sup> The DSSC based on this system exhibits a PCE of 6.1 % under AM 1.5 radiation (100 mW cm<sup>-2</sup>) which is comparable to the **N3** dye (6.3%) under the same conditions. An interesting indoline dye (**D149**), reported by Grätzel and co-workers, exhibits an extinction coefficient of 68700 mol<sup>-1</sup>cm<sup>-1</sup> at 526 nm and a high PCE of 8% using a volatile organic electrolyte.<sup>334</sup> To develop a more efficient indoline dye, the same group synthesized **D205** by extending the previously reported dye **D149**. In this dye, a n-octyl chain replaced the ethyl group of **D149** at the rhodanine ring. The dye exhibited an efficiency of 9.52% which was higher than for the previously reported sensitizer **D149**.<sup>318</sup> Three planar indoline dyes with various alkyl chains **CS-32-34** were designed and synthesized by Liu *et al.*, and their performance was compared with the previously reported dye **CS-31**.<sup>335</sup> The alkyl chains facilitate the anti-aggregation process and reduced charge recombination processes. The measured  $V_{oc}$  of the four considered

DSSCs follows the order **CS-33** (755 mV) > **CS-34** (751 mV) > **CS-32** (743 mV) > **CS-31** (733 mV). Ganguly et al. reported that the introduction of silicon substituted group as a donor and a silole group as a spacer unit can facilitated the efficiency of DSSC.<sup>336</sup> They observed that the silicon substituted dyes reduce the band gap and increase the ICT in the system for better optical properties than that of silicon free dyes. In another study they predicted that fused-pyrrole ring can be a better alternative spacer group compared to tetrathienoacene in highly efficient organic dye.<sup>337</sup>

However, in spite of tremendous efforts by both experimental and computational groups, still very few metal-free organic dyes have achieved a photoconversion efficiency higher than 10%, which would be comparable to the **N719** dye. Hanaya and co-workers obtained a power conversion efficiency of 12.5% by using the carbazole dye **ADEKA-1** as a single sensitizer.<sup>338</sup> In this dye molecule, the trimethoxysilyl group serves employed as the anchor group which forms three titanosiloxane (Si–O–Ti) bonds upon adsorption on TiO<sub>2</sub>. Cobalt complexes ([Co(bpy)<sub>3</sub>]<sup>3+/2+</sup> and [Co(Cl-phen)<sub>3</sub>]<sup>3+/2+</sup>) were used as the redox electrolytes in this study. An efficiency higher than 10% with metal free organic dyes was also achieved by the Peng Wang group.<sup>322</sup> They obtained an impressive power conversion efficiency of 10.4% by using a structurally simple donor-acceptor (D-A) perylene dye **C272**.<sup>322</sup> The dye molecule is composed of N-annulated perylene as electron-donor group and of ethynyl benzothiadiazole-benzoic acid (EBTBA) as the electron-acceptor group. The molecular orbital diagram and cyclic voltammograms (CVs) suggest that the dye **C272** has a narrow LUMO/HOMO energy gap of 1.80 eV which is suitable for red-shifting the maximum absorption wavelength. It should also be noted that the high efficiency achieved with **C272** without the use of any co-adsorbate is very much comparable to the one of the well-known **YD2-o-C8** dye. Furthermore, Wang et al. also reported a new donor-acceptor dye **C275** which reached a high-power conversion efficiency of 12.5%.<sup>339</sup> Herein, a new electron-donor N-annulated indenoperylene was used with ethynyl benzothiadiazolyl benzoic acid as the electron-acceptor in this champion dye. This molecule has a smaller LUMO/HOMO energy gap of 1.76 eV. Time-dependent density functional theory (TD-DFT) calculations suggest that the S<sub>0</sub>→S<sub>1</sub> vertical electronic transitions to the LUMO are mainly initiated (92%) from the HOMO, which can favour the intramolecular charge-transfer.<sup>339</sup> To further design and develop more efficient N-annulated perylene dye molecules, **C277** and **C278** were synthesized by Wang et al.<sup>340</sup> In detail, they have synthesized two coplanar, electron-rich N-annulated thienobenzoperylene (NTBP) and its isomer N-annulated thienocyclopentaperylene (NTCP) molecules. In these dyes, an aliphatic chain was introduced as a side chain to inhibit the intermolecular π–π stacking. Both the NTBP and the

NTCP have a very low LUMO/HOMO energy gap. **C277** and **C278** both exhibit high PCEs of 11.5 and 12.0% which is higher than the 10.6% of the well-known zinc porphyrin dye **YD2-o-C8**.<sup>340</sup> In another study, Wang *et al.* reported a novel blue dye, **R6**, containing a strong electron-donating polycyclic aromatic hydrocarbon (PAH) core 2H-benzophenanthrothienobenzophenanthrothiophene coupled with a diarylamine as electron donor group in a D- $\pi$ -A organic sensitizer.<sup>341</sup> Computational studies suggest that the S1 $\leftarrow$ S0 vertical electronic transitions to the LUMO originate from the HOMO. The DSSC with **R6** based dye-sensitized solar cell showed an excellent power conversion efficiency of 12.6% in the presence of a Co(II/III) tris-(bipyridyl)-based redox electrolyte, which to the best of our knowledge is the highest reported performance in literature for metal-free organic dyes. Kim *et al.* designed and synthesized a series of metal free organic dyes coded as **SGT-121**, **SGT-129**, and **SGT-130** containing thieno[3,2- b][1]benzothiophene (TBT) as  $\pi$ -bridge.<sup>342</sup> Using **SGT-130** as the sensitizer, the pertinent cell exhibited an excellent power conversion efficiency of 10.47%. Recently, Kim *et al.* further extended their work to thieno[3,2-*b*]indole-based organic dyes for DSSCs.<sup>343</sup> In this work, they synthesized four fluorene-based donor dyes coded as **SGT-146**, **SGT-147**, **SGT-148**, and **SGT-149**. It was observed that the introduction of alkoxy and alkoxyphenyl substituted fluorene moieties in **SGT-147**, **SGT-148**, and **SGT-149** significantly enhances the maximum absorption spectra compared to **SGT-146** which facilitated the intramolecular electron push-pull effect. Among the studied systems, **SGT-149** achieved the highest efficiencies of up to 11.7% and 10.0% using a Co(bpy)<sub>3</sub><sup>2+/3+</sup> and an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte, respectively. Tetrathienoacene (TTA), a rigid planar structure, was employed as a promising bridging unit in metal-free organic dyes by Chen and co-workers.<sup>344</sup> They synthesized four organic sensitizers (TPA-TTAR-A, TPA-T-TTAR-A, TPA-TTART-A and TPAT-TTAR-T-A) with a triphenylamine (TPA) donor and CA acceptor. The highest efficiency was achieved using the **TPA-TTAR-T-A** dye (PCE of 10.1% with  $V_{oc} = 0.833$  V,  $J_{sc} = 16.5$  mA/cm<sup>2</sup>, and FF = 70.0 %) where a thiophene spacer was introduced between the TTA bridge unit and the cyanoacrylic acid. Thus, it can be expected that tetrathienoacene can act as an alternative favorable  $\pi$ -spacer group. The tetrathienoacene (TTA) based dye was further modified by Chen and co-workers.<sup>345</sup> They incorporated a branched 3-methyl-5,5-dimethylhexane group in the TTA unit to inhibit the dye aggregation and reduce charge recombination. Because of a higher  $J_{sc}$ , **TTAR-b8**-sensitized DSSC devices displayed the highest efficiencies of 11.2%. A recent computational work by Sen *et al.* addressed the screening of donor groups for DSSCs by aza based  $\pi$ -spacers.<sup>301</sup> They studied a series of donor groups based on aza spacers and carboxylic acid donors to identify a set of donors suitable for



such types of dyes. Their work also included a specification of the best acceptors based on such dyes.

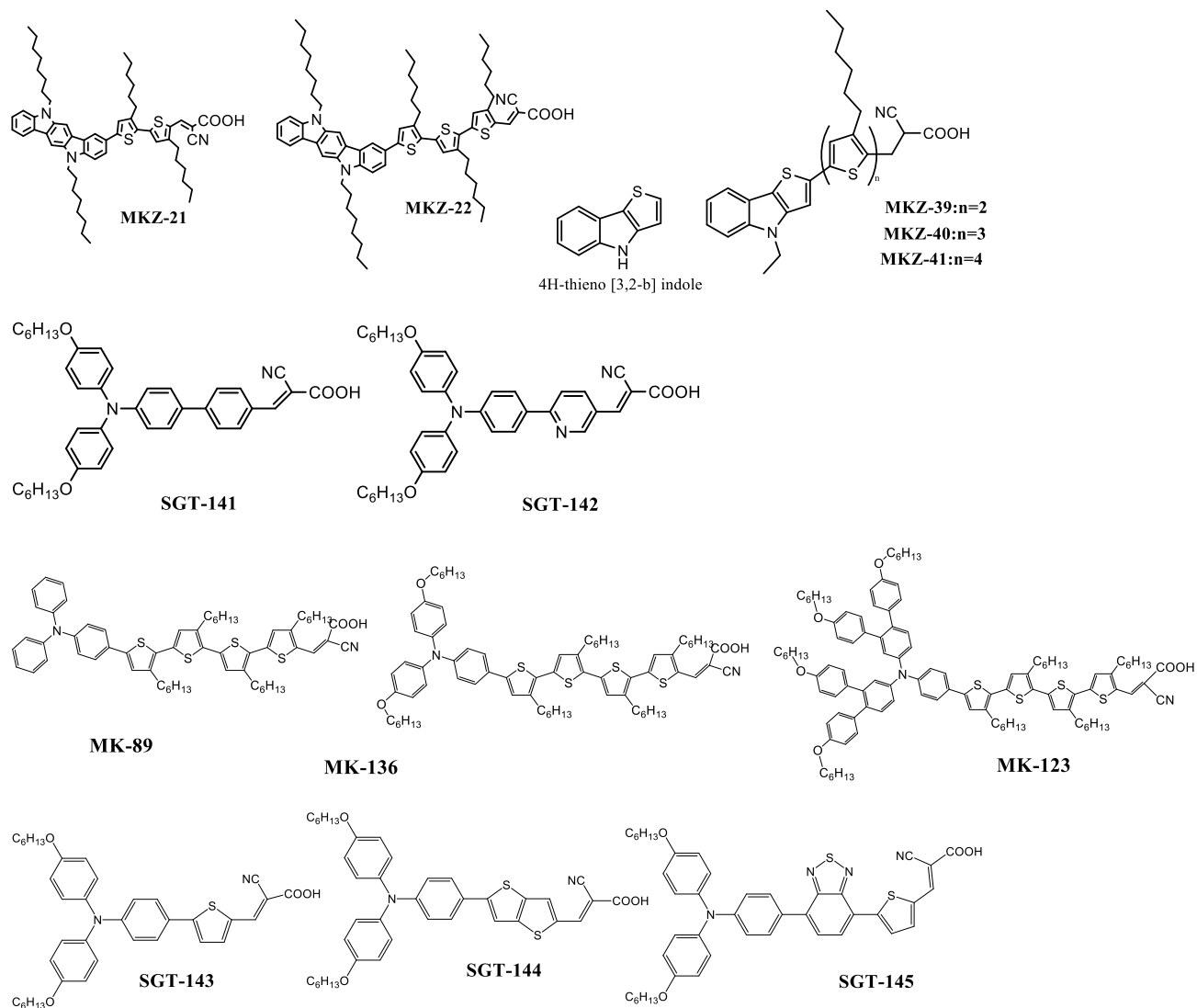
**Table 8:** List of studies addressing the DSSCs with metal-free organic dyes including the most important performance parameters.

Organic dyes	$\lambda_{\max}$ (nm)	$J_{sc}$ ( $\text{mA} \cdot \text{cm}^{-2}$ )	$V_{oc}$ (mV)	FF (%)	$\eta$ (%)	Ref.
<b>MKZ-21</b>	429	15.4	710	0.67	7.3	326
<b>MKZ-22</b>	437	15.5	700	0.62	6.7	326
<b>MK-14</b>	483	16.0	710	0.71	8.1	327
<b>MK-16</b>	480	14.5	730	0.69	7.3	327
<b>MKZ-39</b>	502	13.8	700	0.77	7.4	346
<b>MKZ-40</b>	496	14.6	700	0.76	7.8	346
<b>MKZ-41</b>	490	15.0	660	0.74	7.3	346
<b>C203</b>	372	14.33	734	0.76	8.0	306
<b>MK-89</b>	495	13.4	822	0.70	7.7	307
<b>MK-123</b>	497	10.9	907	0.64	6.3	307
<b>MK-136</b>	495	14.3	880	0.71	8.9	307
<b>SGT-141</b>	405	9.20	744	0.76	5.2	312
<b>SGT-142</b>	426	10.46	752	0.79	6.2	312
<b>SGT-143</b>	443	12.79	742	0.75	7.1	312
<b>SGT-144</b>	451	14.38	694	0.74	7.4	312
<b>SGT-145</b>	392	14.70	653	0.74	7.1	312
<b>AZ6</b>	491	17.03	710	0.64	7.69	309
<b>Z954</b>	484	14.48	744	0.69	7.44	309
<b>Z970</b>	502	16.71	717	0.64	7.66	309

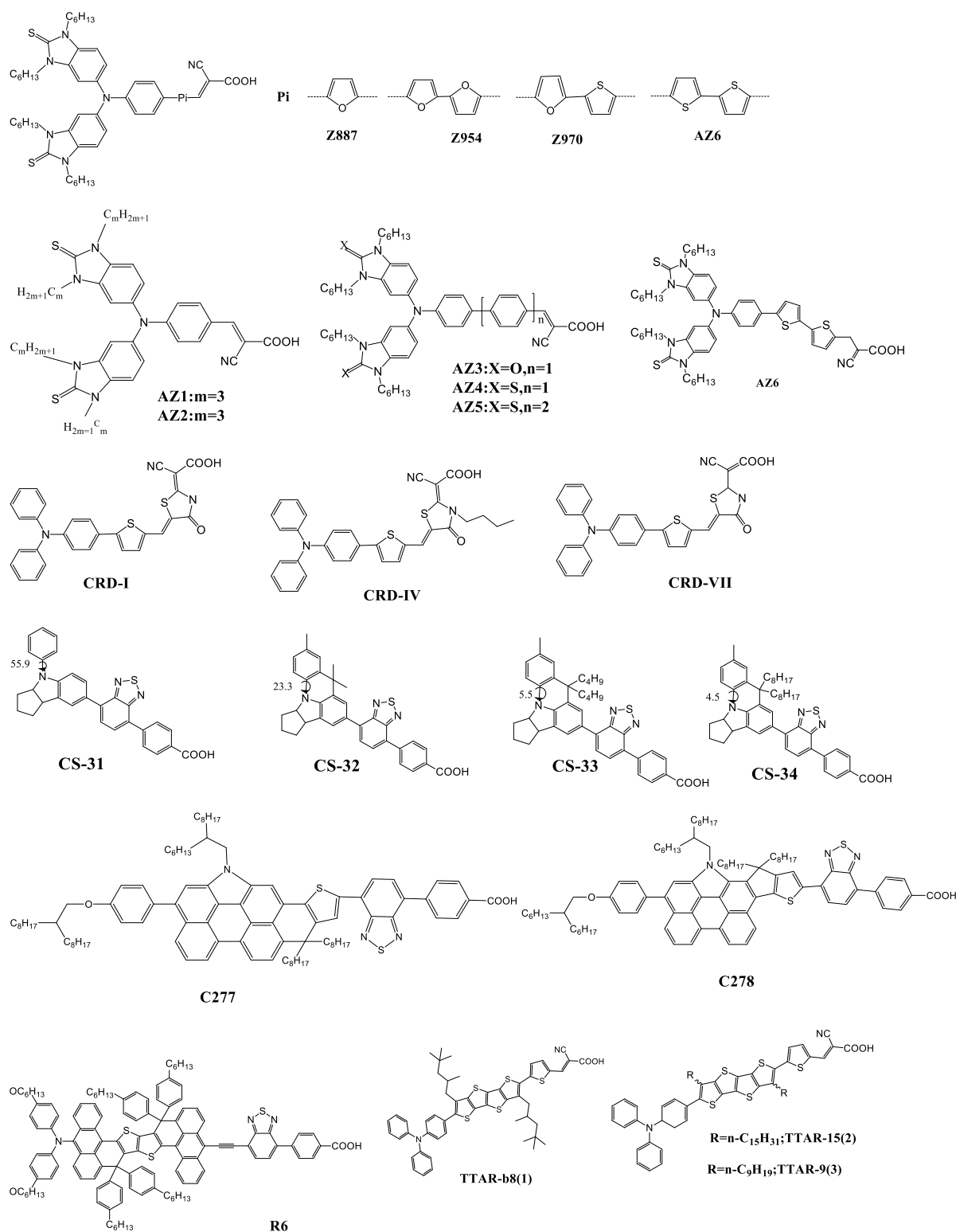
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<b>Z887</b>	478	13.84	726	0.68	6.81	309
<b>AZ1</b>	423	9.7	739	0.63	4.51	308
<b>AZ2</b>	423	9.9	770	0.66	4.94	308
<b>AZ3</b>	428	9.3	739	0.69	4.73	308
<b>AZ4</b>	426	9.9	780	0.69	5.33	308
<b>AZ5</b>	347	9.0	780	0.64	4.44	308
<b>AZ6</b>	443	14.8	749	0.66	7.29	308
<b>L156</b>	491	12.20	1.096	0.69	9.26	313
<b>L224</b>	487	11.32	1.095	0.68	8.27	313
<b>CRD-I</b>	496	13.62	690	0.72	6.77	347
<b>CRD-IV</b>	499	16.43	752	0.73	9.02	347
<b>CRD-VII</b>	488	14.08	721	0.72	7.31	347
<b>D149</b>	526	19.96	653	0.70	8.00	319
<b>D205</b>		18.68	710	0.71	9.52	318
<b>CS-31</b>	488	12.84	733	0.72	6.73	320
<b>CS-32</b>	503	13.23	743	0.71	6.93	320
<b>CS-33</b>	519	15.79	755	0.71	8.38	320
<b>CS-34</b>	520	15.21	751	0.71	8.08	320
<b>ADEKA-1</b>	498	15.6	1.036	0.774	12.5	316
<b>C272</b>	512	15.42	908	0.743	10.4	348
<b>C275</b>		17.03	956	77.0	12.5	325
<b>C278</b>	565	19.64	843	72.8	12.0	349
<b>R6</b>	631	19.69	850	75.4	12.6	350
<b>SGT-130</b>	389	17.49	898	72.2	11.4	342

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**Figure 15.** Geometries of different D- $\pi$ -A and D-A- $\pi$ -A structures.<sup>307,312,326,327</sup>



**Figure 16.** Geometries of different D- $\pi$ -A and D-A- $\pi$ -A structures.<sup>308,311,320,345,349,350</sup>

### 2.5. D- $\pi$ -AA, D-A- $\pi$ -A structures

As stated earlier, the chemical structures of metal-free organic dyes are very critical for the efficiency and stability of the DSSC devices.<sup>352</sup> Therefore, many researchers have devoted themselves to optimize chemical structures of metal-free organic dyes. Up to now, several

organic dye scaffolds have been developed such as D-( $\pi$ -A)<sub>2</sub>, D- $\pi$ -A, D-D- $\pi$ -A, D-A- $\pi$ -A and (D- $\pi$ -A)<sub>3</sub>L<sub>2</sub>. However, the donor- $\pi$ -bridge-acceptor (D- $\pi$ -A) structure is still the most popular design for metal free organic dyes in DSSCs. Based on a D- $\pi$ -A configuration, an additional acceptor was incorporated into the traditional D- $\pi$ -A framework resulting in an alternative effective molecular engineering strategy for “D-A- $\pi$ -A” configurations.<sup>302</sup> In 2011, Zhu and co-authors reported the first D-A- $\pi$ -A molecules by introducing an electron-deficient benzothiadiazole group as auxiliary acceptor.<sup>302</sup> The presence of the auxiliary acceptor introduced several advantages, such as wide absorption and emission bands in UV-visible region, efficient intramolecular charge transfer, easily tunable molecular orbital energy levels, high redox stability and optoelectronic properties, and a narrow bandgap energy for harvesting more NIR light.<sup>353</sup> Consequently, the use of “D-A- $\pi$ -A” organic sensitizers has been regarded as a promising approach to increase cell efficiency and improve photovoltaic performances in solar cells with respect to the traditional D- $\pi$ -A framework. As one of the most successful dyes, WS-6, as described by Zhu and co-authors and illustrated in Fig. 17, achieved a value of  $\eta = 7.76\%$  on a 16  $\mu\text{m}$ -thick TiO<sub>2</sub> film device.<sup>354</sup>

Encouraged by the successful performance of the first D-A- $\pi$ -A organic sensitizers, different auxiliary acceptors were tested to further augment their efficiency. An improved efficiency was demonstrated by a new D-A- $\pi$ -A organic dye **WS-9** (see Fig. 17). This dye was derived by Wu et al. from the previous dye WS-2 (Fig. 17) through incorporating an n-hexylthiophene unit into the  $\pi$ -conjugation.<sup>355</sup> In this dye, the bulky hexylthiophene unit present on the  $\pi$ -bridge prevents the dye aggregation which facilitates a high power conversion efficiency (PCE) of 9.04%. Very recently, a new series of dyes having benzothiadiazole as an internal acceptor (A) was introduced by Rakitin et al.<sup>356</sup> They have taken a previous dye **WS-2** as a reference dye and varied the donor fragment resulting in the **MAX144**, **MAX155** and **MAX157** structures (see Fig. 17). Here, N-substituted indolines fused with cyclopentane or cyclohexanes were employed as donor fragments. The **MAX157** dye with a 9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole donor fragment exhibits a PCE of 5.2%. The dyes have a shorter-wavelength absorption maximum and larger molar extinction coefficient than the other dyes studied previously. Another series of benzothiadiazole containing dyes (**PZ-1-4**, Fig. 18) were designed in which hexyloxy and diphenylamine attached phenothiazine groups are used as electron donor groups. The **PZ-4** dye yields the best efficiency due to a more suitable torsion structure and donor unit.<sup>357</sup> The effect of  $\pi$ -bridge groups on the properties of D-A- $\pi$ -A organic dyes has been studied by Hua et al by varying the  $\pi$ -bridge.<sup>358</sup> They have used indeno[1,2-b]thiophene as the donor and 2,3-diphenylquinoxaline (QT) as the auxiliary acceptor. The  $\pi$ -

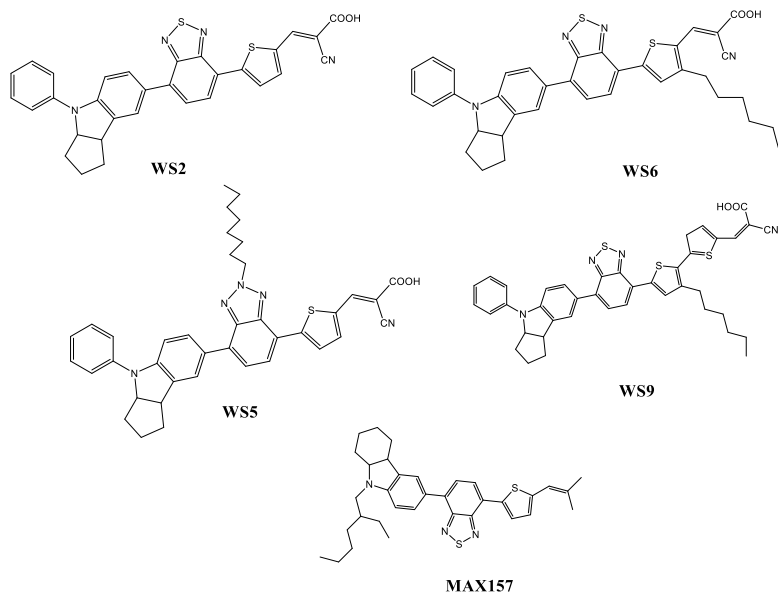
bridge of the **SD1**, **SD2** and **SD3** dyes (Fig. 18) corresponds to cyclopentadithiophene-benzene/thiophene/furan, respectively. Electrochemical experiment and density functional theory (DFT) calculations suggest that the improved performance may be due to the introduction of the benzene  $\pi$ -bridge in **SD1**. This additional benzene ring triggered a large torsional angle between CPDT and benzene, which inhibited dye aggregation and charge recombination. With a cobalt electrolyte, the **SD1** dye reached an impressive PCE of 8.96 %. Shen et al. studied dyes with a bulky indoline donor, 2,3-diphenylpyrido[3,4-b]pyrazine as an auxiliary acceptor, CPDT and EDOT as  $\pi$ -bridges, and cyanocarboxylic acid as the acceptor.<sup>359</sup> They found a PCE of 5.07% for the more planar dye with a CPDT spacer. The effect of isoindigo as an auxiliary electron withdrawing unit were examined by Hua et al. A maximum overall conversion efficiency of 5.98 % was observed for these dyes.<sup>360</sup> Wang et al. synthesized two novel benzotriazole-containing organic dyes having the D–A– $\pi$ –A scaffold with octyl and methyl groups.<sup>361</sup> They identified several benefits upon using these additional acceptor groups such as (i) enhanced electron transfer from the donor to the acceptor group; (ii) easy structural modification at the 2-position of the benzotriazole unit; and (iii) enhanced open-circuit photovoltage. Aiming to disclose a new series D–A– $\pi$ –A organic dye, Dessi et al. synthesized a series of dyes having 2,1,3-benzothiadiazole (BTD) as an internal electron-accepting moiety. 3-cyanopyridine can also be an important auxiliary acceptor in D–A– $\pi$ –A organic dye.<sup>362</sup> The newly synthesized dyes have broader absorption spectra and reduced band gaps which cause an improved power conversion efficiency.<sup>363</sup> Nonetheless, apart from the aforesaid auxiliary acceptor, various other auxiliary acceptors have also been used in an diketopyrrolopyrrole (DPP) (PDPP), benzo[c][1,2,5]thiadiazole organic solar cell.<sup>364</sup>

Furthermore, the effect of structural modifications in D–A– $\pi$ –A sensitizers was examined by Sekar et al. They have exploited newly synthesized sensitizers containing Diphenylphosphoryl Azide (DPPA) and Dipropylenetriamine (DPTA) as the donor along with a strong electron-withdrawing cyano group (–CN) as the auxiliary acceptor group and cyanoacetic acid and rhodamine-3-acetic acid as anchoring groups.<sup>365</sup> A highest efficiency of 4.7% was obtained for one of the synthesized dyes. Sekar et al. concluded that the enhanced efficiency of such dye sensitizers could be attributed to the presence of the strong electron-withdrawing cyanoacetic acid anchoring group and the presence of the thiophene linker at the N-aryl core. Moreover, the effect of 3-dimensional organic dyes on the efficiency of DSSCs were explored by Huang et al.<sup>366</sup> They have synthesized several 3-dimensional dyes with a novel 3D triarylamine derivative (IDTTPA) as the electron donor unit, 2,1,3-benzothiadiazole derivative (BT and DFBT) unit as the auxiliary acceptor, and formic acid as the acceptor/anchor (see Fig. 18). It

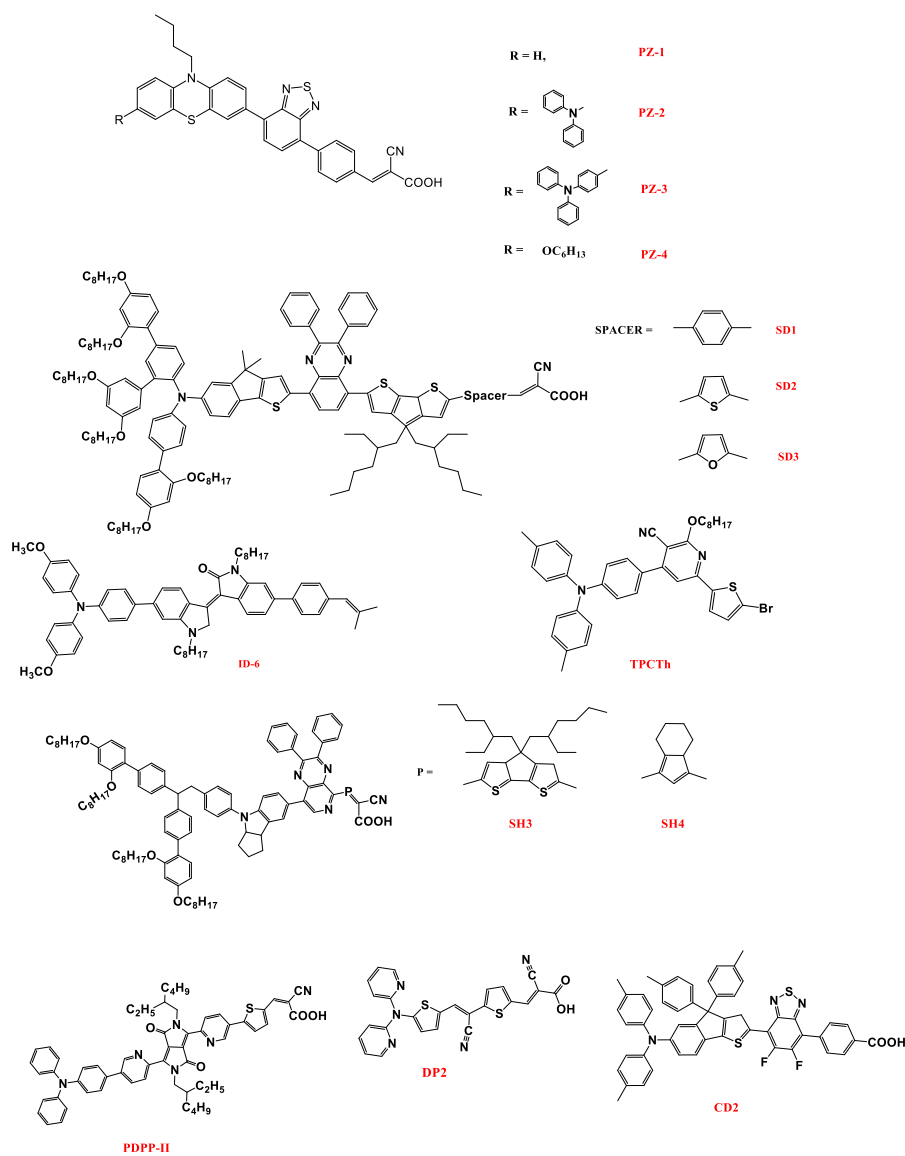
was concluded that the 3D structure inhibit dye aggregation and charge recombination thus augmenting the power conversion efficiency (PCE).

**Table 9.** Photovoltaic performances of DSSCs employing different types of D-A- $\pi$ -A organic dyes.

Dye	Efficiency	Reference
WS2	8.7	302
WS6	7.76	354
WS9	9.04	355
MAX157	5.20	356
PZ-4	6.35	357
SD1	8.96	358
SH3	5.07	367
ID6	5.98	360
WS5	8.02	361
TPCTh	4.42	363
PDPP-II	5.26	364
DP2	4.7	365
CD2	7.91	366



**Figure 17.** Geometries of different D-A- $\pi$ -A structures.<sup>302,354–356</sup>





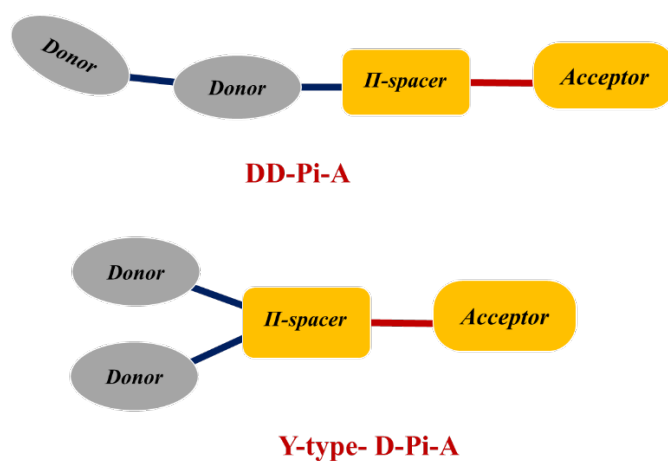
**Figure 18.** Geometries of different D- $\pi$ -AA and D-A- $\pi$ -A structures.<sup>357,358,360,363–367</sup>

## **2.6. Double Donor Effects**

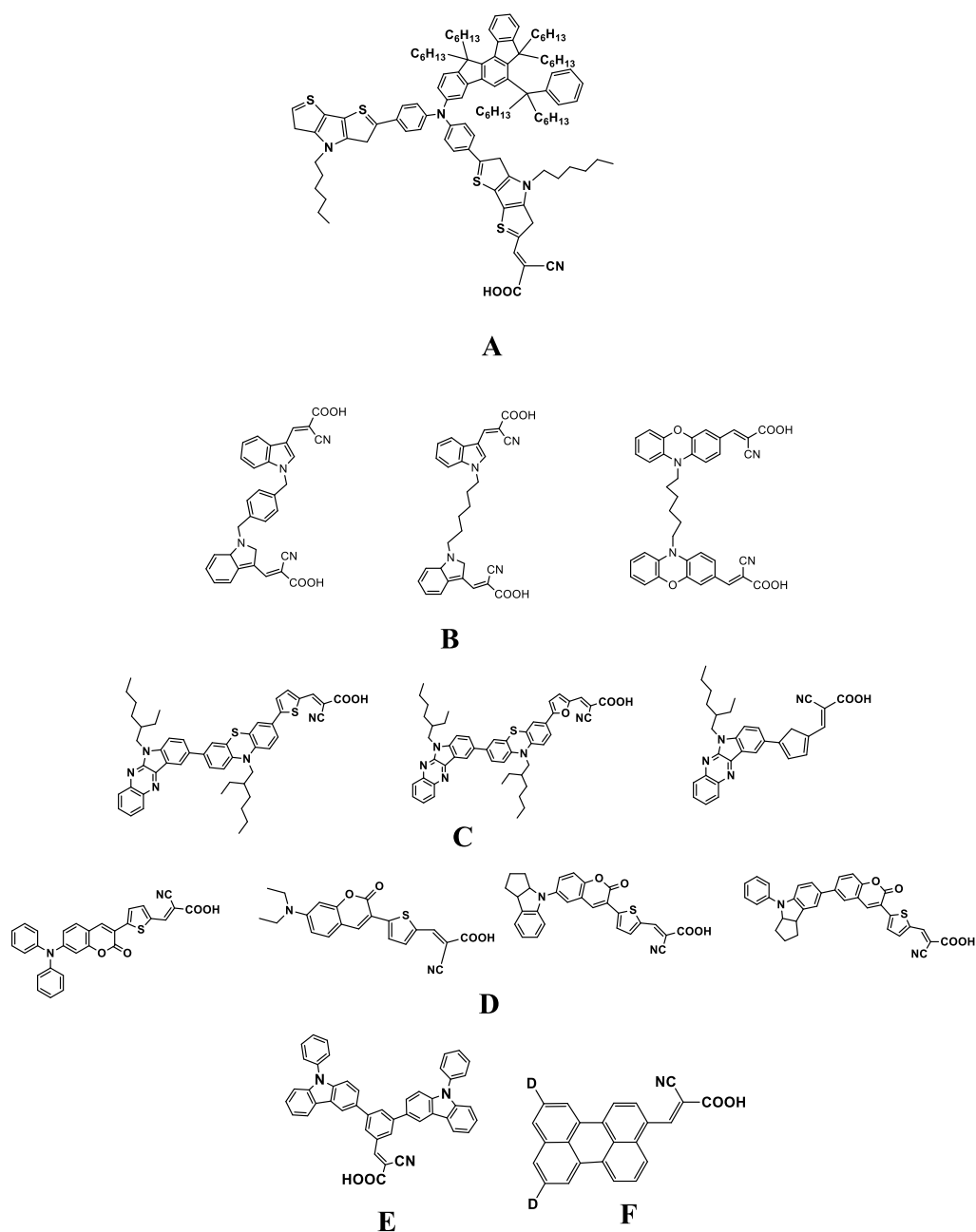
Dual Donor based dye sensitized solar cells correspond to a rather novel strategy in order to improve the solar cell efficiency of organic dye sensitizers. Two different strategies can be used for the structure of dual donor based dye sensitizers. One is based on the formation of a DD- $\pi$ -A structure, and the other involves the formation of Y-type D- $\pi$ -A dye sensitizers (Scheme 1). Several studies revealed that double donor based dyes show higher light harvesting efficiencies than the single counterparts and thus an increased DSSC conversion efficiency.<sup>368–373</sup> The double donor based dye sensitizers are associated with a (i) high light absorption capacity, (ii) low gap between HOMO and LUMO energy level and (iii) broad absorption spectra which all contribute to the high efficiency of these DSSCs. Ning et al. were the first to introduce a D-D- $\pi$ -A configuration with a series of novel triarylamine-based dyes which confirmed the high potential of such Y type dual donor dyes.<sup>374</sup> Further D-D- $\pi$ -A organic dyes have been developed and characterized in recent years.<sup>375–379</sup> Dai et al. demonstrated a power conversion efficiency of 9.02% for dual donor based dye sensitizers (Fig. 19A).<sup>376</sup> Y. Hong et al. synthesized novel metal-free organic sensitizers with indole and phenoxazine based double donor dye sensitizers Fig. 19B). They studied their photophysical, electrochemical, and DSSC characteristics finding that such dyes can have high efficiency comparable to the one of the N719 dye (Fig. 19B).<sup>370</sup> Y. H. Lee et al. created a series of double donor-acceptor organic dyes with varying alkyl chain lengths between the two chromophores to check their performance in DSSCs<sup>380</sup>. They observed that longer alkyl chain showed a broader and higher IPCE as well as a high photo-current density ( $J_{sc}$ ) with an enhanced photovoltage ( $V_{oc}$ ) and with increased efficiency. X. Qian et al. designed and synthesized D-D- $\pi$ -A type dyes consisting of both indoloquinoline and phenothiazine donors and cyanoacrylic acid as the anchoring groups. Such double donor solar cells exhibit excellent photoelectric properties compared with their single donor counterpart and high power conversion efficiencies of up to 8.28% (Fig. 19C).<sup>381</sup> Indole and coumarin double donor based dyes were also addressed by S. Jiang et al. recently (Fig. 19D).<sup>379</sup> They synthesized different dyes with indole coumarin linkage involving C-C and C-N bonds. Both dyes showed good power conversion efficiency. The C-C bound double donor is well-suited to reach higher short circuit current densities for the C-C linked dyes which results in a better photovoltaic performance.

Y-type dual donors are the second type of dye sensitizers in this category. Recently L. Jin et al. developed N phenyl carbazole based Y-type dual donor dyes which showed a good solar conversion efficiency (Fig. 19E). These new dyes display strong UV-vis absorption with high

molar extinction coefficients which makes them to very good co-sensitizers for ruthenium-based DSSCs with power conversion efficiencies (PCEs) in the range of 7.24–7.96%.<sup>382</sup> Similar Y-type or butterfly type dye sensitizer have been studied computationally by Z. Yang et al.<sup>377</sup> They designed a series of butterfly type organic dyes introducing several electron donors like triphenylamine, phenothiazine, coumarin groups etc. and calculated the absorption spectra, concluding that double coumarin donors can be promising dual donor dye sensitizers Fig.19F).<sup>377</sup> Still the usage of such type of dual donors corresponds to an emerging field and promising for high efficiencies in the near future.



**Scheme 1.** Schematic diagram of two different Double donor based metal free dye sensitizers



**Figure 19.** Geometries of different D-D- $\pi$ -A structures.<sup>370,376,377,379,381</sup>

### 3. SUMMARY AND OUTLOOK

The main aim of this review is to provide a comprehensive study addressing the use of solar cells as a renewable source of energy with the emphasis on dye sensitized solar cells (DSSCs) in order to provide a better understanding of the factors underlying their performance. We have presented a brief history of the emergence of the DSSCs followed by a discussion of the working principle of these devices along with its limitations. The efficiency of metal-based dye sensitizers, as derived by many experimental and theoretical studies, has been thoroughly discussed, first focusing on the traditionally used scarce metals ruthenium and osmium, but then also addressing how either other scarce, but also more abundant metals could capture their

place. Furthermore, we have reviewed the progress with respect to low cost metal free dye sensitizers, based on an immense literature on D- $\pi$ -A based organic dye sensitizers, particularly focusing on structural changes involving dual acceptors, dual spacers or dual donors as well as the addition of different electron withdrawing or donating groups. Theoretical methods and studies aiming at a better understanding and concurrently on a better design of dye sensitizers have also been covered. Finally, we stressed that, the emergence of dual donors many open the door for developing better and more efficient organic dye sensitizers. It is our hope that this review will contribute to the development of new dye sensitizers with improved properties.

### **Acknowledgments**

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