

# Review about Main Requirements for Porphyrin Derivatives as Components of Dye Sensitized Solar Cells

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**Abstract:** The main aim of this review is to present porphyrins as an entry for developing proper light energy capture materials for photovoltaic cells. A critical opinion about the improving of required properties by changing the molecular structure of porphyrins, including various metallations and substitutions (both in *meso* and  $\beta$ -position) as well as by introducing anchoring groups, the importance of sterical hindrance and of the capacity of aggregation, was done in order to understand how these structural modifications affects the photoelectrochemical properties and the efficiencies of dye-sensitized solar cells. Using of Zn-porphyrins and of Pt-porphyrins was presented in detail.

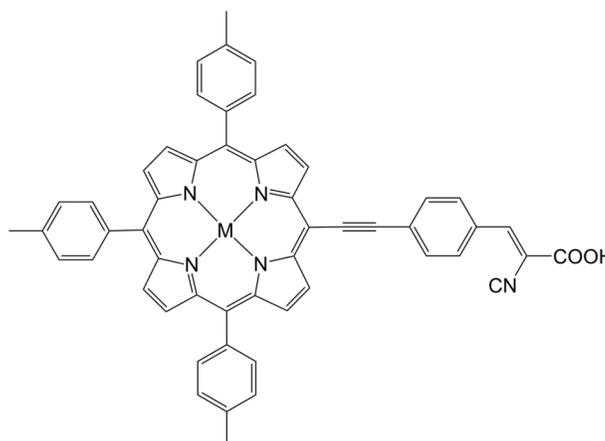
**Keywords:** Dye-sensitized solar cells (DSSCs), Porphyrins, Zn-Porphyrins, Pt-porphyrins, Aggregation.

## 1. INTRODUCTION INTO DYE-SENSITIZED SOLAR CELLS

Although conventional sources of energy (coal, oil or gas) on the Earth have depleted, solar energy that has the most impressive potential of all the sources of renewable energy, is used only in a small amount [1]. Solar energy can be harvested directly from sunlight or by indirect methods, such as: solar thermal technology, photovoltaic energy conversion or by solar hydrogen gas production technology.

Due to the limited availability of solar grade silicon and of the expensive costs, the first generation of silicon solar cells has to be replaced. One of the better alternatives is using of dye-sensitized solar cells (DSSCs), because of their advantages like low cost, light weight and easiness of processing for large-scale production. One of the main important issues in formulating of DSSCs is the selection of the photosensitizer. Porphyrin sensitizers have imposed their place because of their amazing properties: wide and strong absorption profiles, high absorption coefficients, good thermal and high photo-stability and most important the availability of more sites for structural functionalization.

Co-sensitizing these functionalized porphyrins (for instance cyanoacrylic acid porphyrins, see Figure 1) with other organic dyes to enlarge absorption bands was used to improve the photovoltaic efficiency [2].



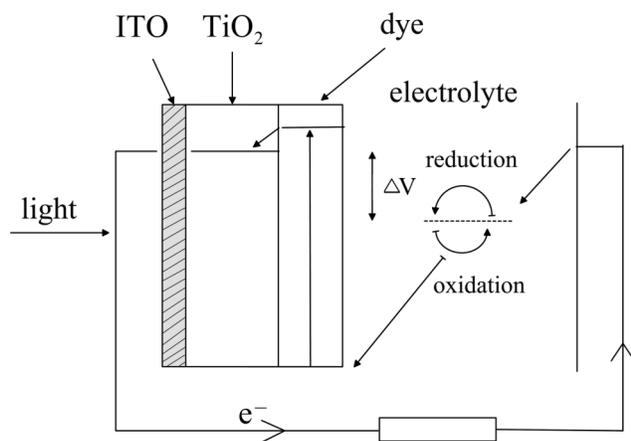
**Figure 1:** The structure of cyanoacrylic acid - substituted porphyrin, used in co-sensitizing.

In many ways, dye-sensitized solar cells (DSSCs) act in great similitude with the natural process of photosynthesis. Beginning with the pioneering work by O'Reagan and Gratzel [3], DSSCs were considered an alternative to the classical silicon-based solar cells exhibiting suitable power conversion energy. Due to the fact that DSSCs can be designed in transparent form, they have the potential to be used as smart windows.

## 2. OPERATING PRINCIPLE OF A STANDARD DSSC

A standard DSSC (Figure 2) is formed between a dye-sensitized photoanode [4] (usually  $\text{TiO}_2$ , but wide bandgap semiconductors like  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{SnO}_2$  nanoparticles were also used as an efficient photoanode), a counter electrode made from platinum and a liquid electrolyte that fills the space between anode and cathode and is usually one of the redox mediator systems:  $\text{I}_3^-/\text{I}^-$ ,  $\text{CoII}/\text{CoIII}$ ,  $\text{CuI}/\text{CuII}$ .

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**Figure 2:** The general scheme of a standard DSSC.

**The operating principle** is based on the photoexcitation of one electron of the LUMO orbital of the dye that is transferred to the excited state orbitals, followed by the injection of this excited electron into the conduction band of the semiconductor ( $\text{TiO}_2$  is the most used semiconductor [5-7], with a wide-bandgap semiconductor of 3.2 eV; modified  $\text{TiO}_2$  belongs to a class of materials called transparent semiconducting oxides (TSOs), which are simultaneously optically transparent and electrically conductive) [8]. Thus, the dye is oxidized. For having an efficient injection, the LUMO orbital of the dye has to be higher than the conduction band of  $\text{TiO}_2$ , with at least 0.2V [9]. The injected electron diffuses through  $\text{TiO}_2$  anode toward the platinum electrode. In this step, the oxidized form of the dye is reduced by the negative ions of the electrolytic mediator (for instance  $\text{I}^-$ ) and the dye comes to its initial state. The HOMO level of the dye has to be lower than the redox level of the electrolyte. For finishing the cycle, the resulting  $\text{I}_3^-$  ions are reduced to  $\text{I}^-$  ions by the counter electrode.

### 3. PORPHYRIN DERIVATIVES USED AS DYES IN DSSCS. SELECTION CRITERIA, DESIGN OF STRUCTURES & PERFORMANCES

The main aim of this paper is to present porphyrins as an entry for developing proper light energy capture materials for photovoltaic cells.

In the same way as chlorophylls in plants, a monolayer of porphyrin dye sensitizers absorbs the incident light and generates positively and negatively charged carriers. Differing from other systems, the charge generation occurs exclusively at the interface of two materials of different conduction mechanism, thus being a benefit to the charge separation efficiency [10].

Photophysical properties of porphyrin dyes can be modified by attaching different substitutes to the tetrapyrrole ring. A wide interest in metalloporphyrins as antennae was risen due to their strong electronic absorption bands from 400 to 650 nm and their long lived  $\pi^*$  singlet excited states that have a suitable LUMO energy to allow the injection of the excited electron into the  $\text{TiO}_2$  semiconductor [11]. The photoconversion of light energy into electric energy is based on the competition between the charge separation process and the deactivation processes occurring in the porphyrin dye molecules because of the (non)-radiative deactivation of the dye excited states.

A correlation between the porphyrin dye molecular structure and the dye capacity to generate photocurrent [12], was done and proved that the metalloporphyrins, due to metal presence, might cause the highest photoresponses because of electrons redistribution. The same positive effect is produced by the large aromatic groups (such as: benzene, naphthyl) because of the higher number of  $\pi$  electrons and the extended delocalization.

Contrary, the grafting of long organic chains decreases the photoresponse because of the high mobility of the long chains and the intense non-radiative deactivation of the dye excited states by thermal relaxation. A decrease of the photoresponse is also produced by aggregation of porphyrin sensitizers (by  $\pi$ - $\pi$  stacking interaction), due to both the fact that in this case the absorbed energy is mostly transformed into thermal energy and a decrease of electron injection efficiency toward  $\text{TiO}_2$  [13].

Nevertheless, positively charged tetra(4-N,N,N,N-trimethylanilinium) porphyrin and negatively charged tetrakis(4-sulphonatophenyl) porphyrin, that generate highly ordered aggregates, have been investigated in a photoelectrochemical cell consisting of a layer dye solutions sandwiched between the semiconducting and gold electrodes [14].

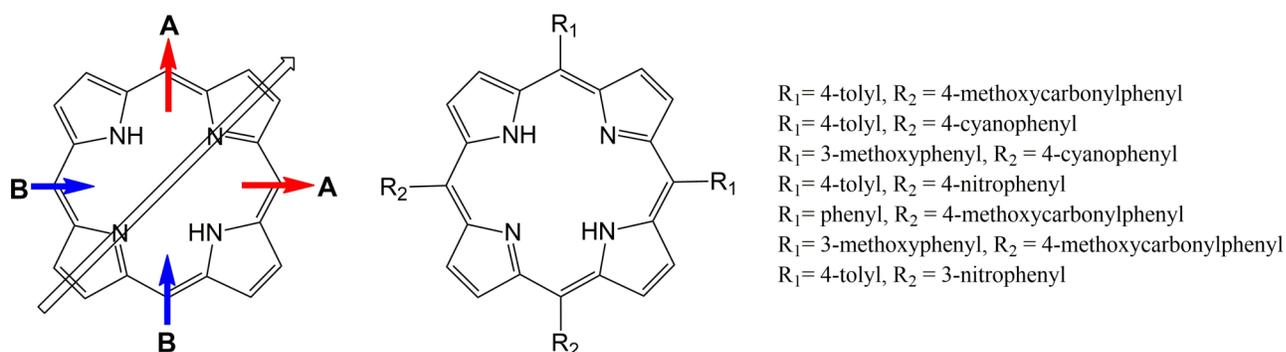
In liquid-junction photovoltaic cells [15], a light-harvesting dye is attached to a thin film of nanocrystalline  $\text{TiO}_2$ . In order to construct optoelectronic devices in nanometric scale, it was measured the time resolved equal-pulse transmission correlation of tetrakis (4-methoxyphenyl) porphyrine J-aggregate in the near field. The observed decay and the lifetimes of are similar (10-50 ps) and are of the same order with that of J-aggregate of tetrakis(4-sulphonatophenyl)-porphyrins [16].

Novel organic solar cells have been prepared using quaternary self-organization of porphyrin (donor) and fullerene (acceptor) units by clusterization with gold nanoparticles on nanostructured SnO<sub>2</sub> electrodes [17].

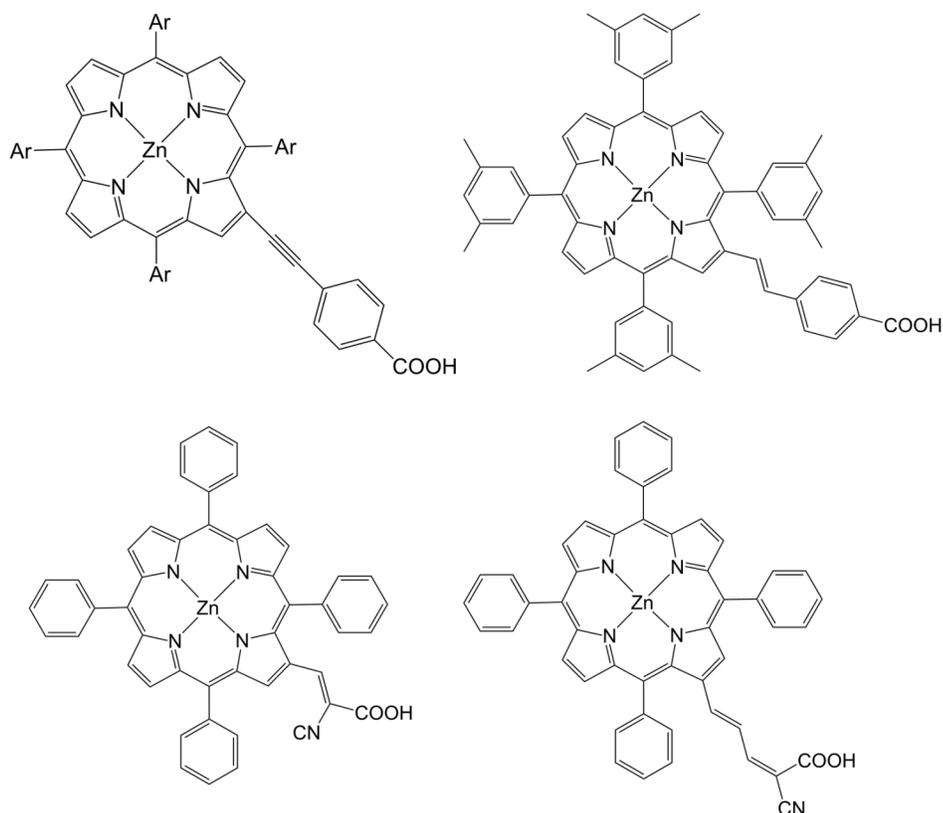
Although it was thought that porphyrin dyes having 5,10-A<sub>2</sub>B<sub>2</sub> push-pull systems [18] arranged on the *meso* substitution pattern (Figure 3), to have the best performances in DSSCs, they exhibited comparable photon-to-current efficiencies with tetraaryl  $\beta$  substituted porphyrins (Figure 4).

Electrochemical investigations demonstrated that the porphyrin ring oxidation is done more easily for the  $\beta$ -substituted porphyrins than for their *meso*-substituted analogues [19].

The electronic properties of porphyrins might be tuned by acting both on metal coordination and on the nature of substituents in pyrrolic- or *meso*- positions thus influencing their HOMO-LUMO energy gaps. A steric hindrance acting on both the porphyrin faces and in the same time the shielding of Zn(II) metal center



**Figure 3:** General scheme of porphyrin systems having high intramolecular dipole moments. Examples of A<sub>2</sub>B<sub>2</sub>-type porphyrins with electron donating and accepting substituents [18].



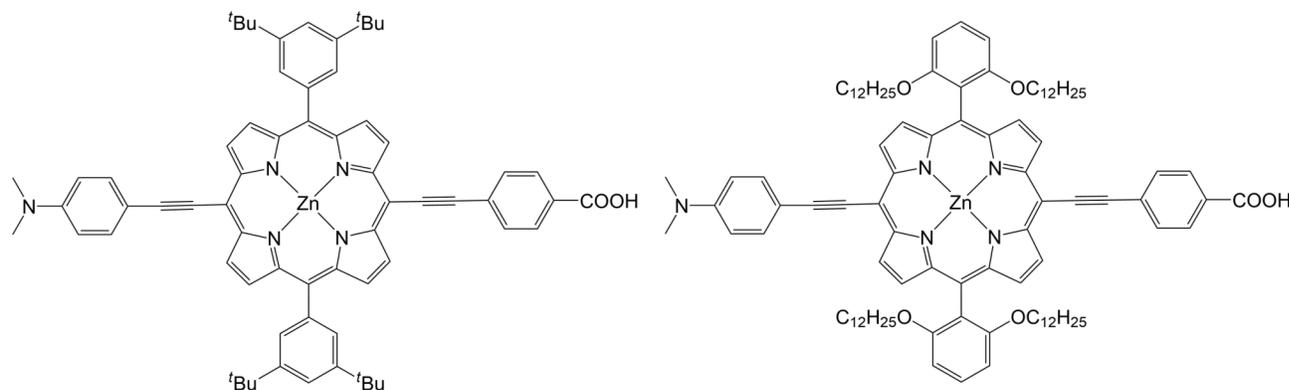
**Figure 4:** Examples of tetraaryl  $\beta$  substituted porphyrins.

from the possible coordination [20], was developed by substitution of porphyrins with long alkoxy chains, for instance at the *ortho* position of the two opposite phenyl rings in the 5,15 push-pull *meso*-disubstituted Zn(II)-diaryl-porphyrins (Figure 5).

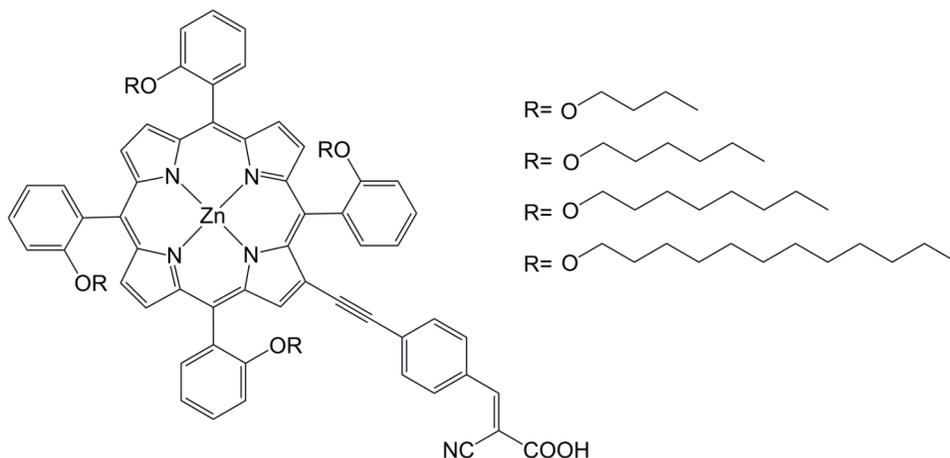
Substitution with different alkoxy chains (Figure 6) do not perturb the optoelectronic properties of the dyes nevertheless, the photovoltaic characteristics of the DSSCs based on these show almost linear relationship between the length of the alkoxy chain and the power conversion efficiency. This comes as a result of a better enveloping of the porphyrin core, leading to a better anti-aggregation and increased photoanode-shielding effect. The presence of longer alkyl chains increases also the charge injection properties [21]. As a consequence, the efficiencies of the DSSCs, varied from 5.42 to 6.32 if the chain is increasing from four atom of carbon to twelve atoms of carbons.

Zn(II) 5,15-bis(4-carboxylphenyl)porphyrin, substituted with one triarylamine unit (Figure 7a) and with two triarylamine units (Figure 7b) were synthesized, their optical absorption were measured (very large redshift effects and broadening of the absorption energies were noticed) and were incorporated as sensitizers in TiO<sub>2</sub> solar cells. Using these porphyrins, the incident photon-to-current conversion efficiency reached a yield of approx. 24%, for the only one triarylamine group substituting the porphyrin derivative [22].

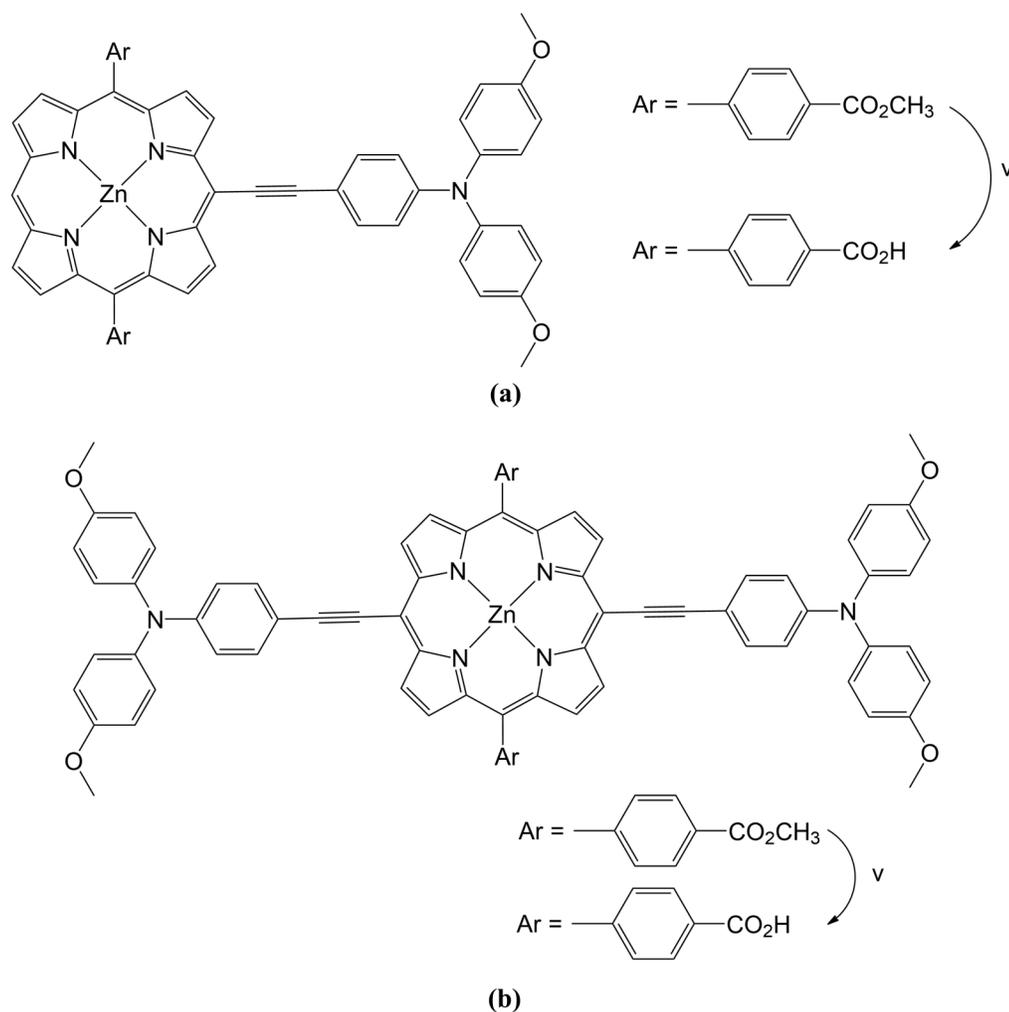
In comparison with the only one triarylamine group substituting the porphyrin derivative, the disubstituted derivative has a much lower energy conversion efficiency (only 7%), that is both attributed to the high potential of aggregation of these last porphyrin molecules and the geometry of the anchoring group.



**Figure 5:** Steric hindrance due to substitution of 5,15-push-pull *meso*-disubstituted Zn(II)-diaryl-porphyrins with long alkoxy chains, at the *ortho* or *meta* positions.



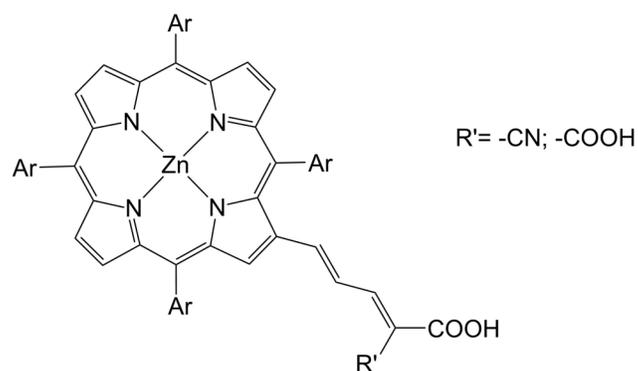
**Figure 6:** Porphyrin substitution with different alkoxy chains length.



**Figure 7:** Zn(II)-5,15-bis(4-carboxylphenyl)porphyrin, substituted with one (a) and two triarylamine units (b).

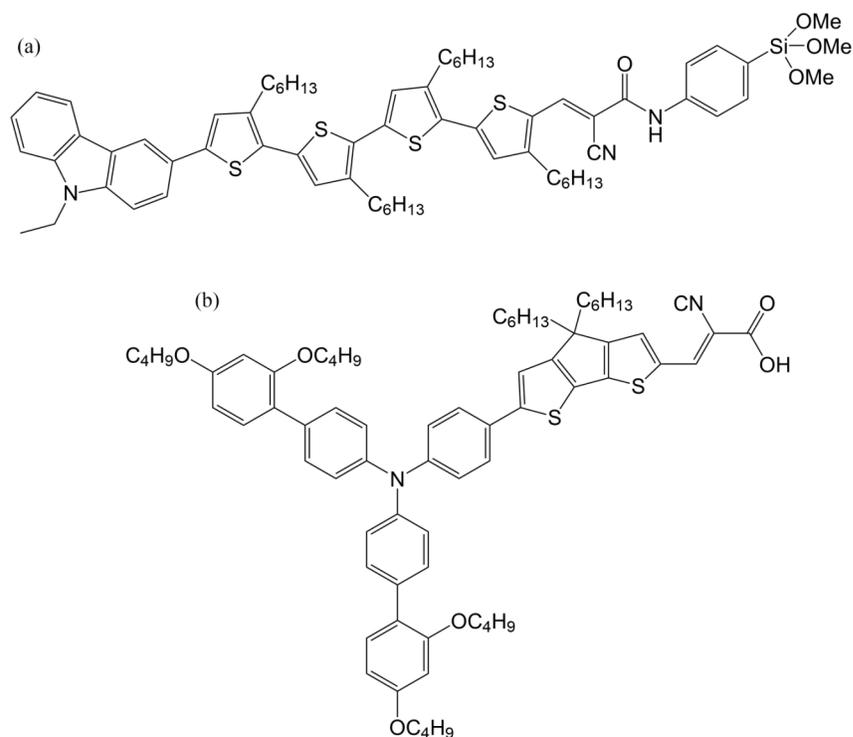
Tetra-aryl- $\beta$ -ethynyl and butadienyl substituted porphyrins (Figure 8) might be considered as promising DSSC photosensitizers because this kind of dyes are able to offer excellent passivation of the photoanode, reducing in this way the possibility of charge recombination at the TiO<sub>2</sub> surface by limiting the approach of oxidized species from electrolyte. Another relevant aspect regarding the performance of DSSCs is the importance of introducing and the role of the linkers (Figure 9) [23] on the energy levels and therefore on the electron transfer transitions, in  $\beta$ -substituted Zn(II)-porphyrins.

The introduction of 2,1,3-benzothiadiazole as a  $p$ -conjugated linker between the anchoring group and the porphyrin chromophore was used to widen the absorption spectra and to fill the gap between the Soret and Q bands in the absorption spectrum.

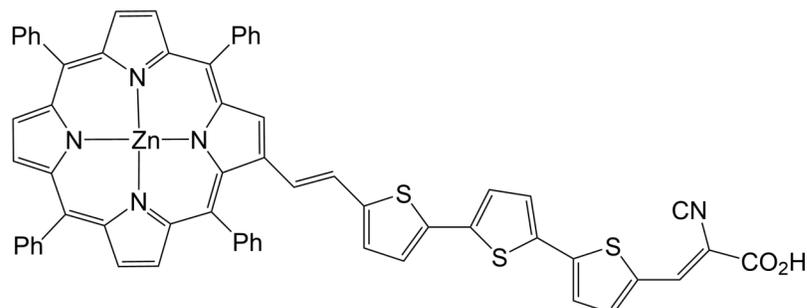


**Figure 8:** Tetra-*meso*-aryl- $\beta$ -butadienyl substituted Zn(II)-porphyrins.

A decade ago, work was reported [24], proving that the presence of a thiophenic functional group of high length in the  $\beta$ -substituent of a porphyrin (Figure 10), results in the generation of additional molecular orbitals from the parent metalloporphyrin and increases the



**Figure 9:** Examples of silyl linker (a) and carboxyl anchor (b).



**Figure 10:** Zn-metalloporphyrin  $\beta$ -substituted with high length thiophenic functional group.

LUMO's splitting. Besides, a longer thiophenic chain leads to increasing of donor-acceptor character of the porphyrinic system and in accordance, to a decrease of the HOMO-LUMO energy gap.

**About Efficiencies of DSSCs.** In 2004 Grätzel, Nazeeruddin and co-workers [25] developed a family of  $\beta$  substituted metalloporphyrins with Cu (II) or Zn(II), grafted with COOH or PO<sub>3</sub>H<sub>2</sub> groups concluding that the Zn(II) porphyrin with a carboxylic anchoring group, was performing with 4.8% efficiency.

The studies performed up to 2010, showed that the energy conversion efficiency for DSSC based on porphyrinic dyes was lower than those based on ruthenium complexes. This situation was changed by the use of the new developed push-pull porphyrinic

systems. These push-pull porphyrins are capable of a strong HOMO-LUMO transition around 600 nm and if some bulky substituents are introduced into their structure, for avoiding the  $\pi$ - $\pi$  aggregation on the photoanode, they can significantly improve the efficiencies of the DSSCs based on Zn(II)-porphyrin dyes reaching 12.3% [26] and if the push-pull porphyrinic dye is co-sensitized with an organic dye to about 13%, by using as redox mediator, a cobalt based redox couple [27, 28].

### 3.1. Pt-metalloporphyrins as Sensitizers in DSSCs

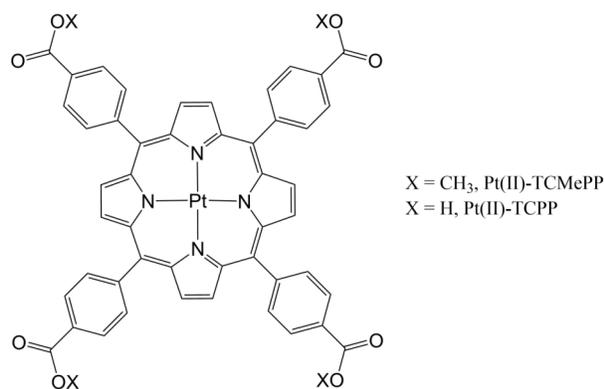
An interesting co-adsorption approach, expected to improve the efficiency of the triplet energy transfer uses as donor, a Pt(II)-porphyrin dye with an attached carboxylic alkyl chain spacer and diphenyl-anthracene

dye as acceptor both adsorbed on mesoporous TiO<sub>2</sub>. The alkyl chain molecular spacer was introduced between the dye and the TiO<sub>2</sub> anchor to prevent the quenching of by electron injection and energy transfer into TiO<sub>2</sub> [29].

Platinum octaethylporphyrin have been studied also in photoanode based on ZnO formulations and the weight ratios of ZnO:PtOEP were modified in the trying to optimize the performance of the DSSC. The optimum performance characterized by a more rapid electron transport with increased lifetime and superior charge efficiency was realized by using a weight ratio ZnO:PtOEP (1:0.009) [30].

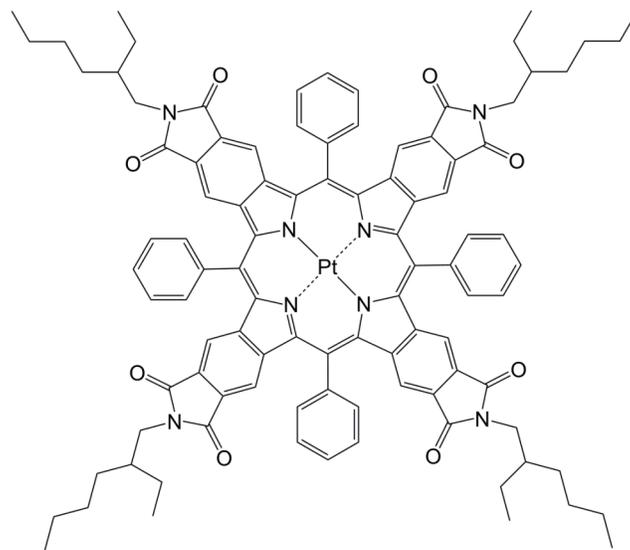
Under neutral phosphate buffer conditions, a water-soluble Pt(II)-porphyrin (Figure 11) shows higher stability than the commonly used [Ru(bpy)<sub>3</sub>]<sup>2+</sup> photosensitizer and might be a good alternative photosensitizer to be used in future DSSCs [31].

The Pt(II)-porphyrin exhibits a comparable integrated molar absorptivity to that of chlorophyll a and the photon absorption rate is also similar to that of chlorophyll a.



**Figure 11:** The structure of the water-soluble Pt-porphyrin with similar behaviour as chlorophyll a.

The actual design of molecular materials to be used in solar concentrators has as main purposes to remove the drawbacks regarding solubility, photostability, and luminescent properties [32]. To achieve this purpose, tetrabenzoporphyrin was functionalized. The cyclic imide moiety and the branched 2-ethylhexyl group were introduced (Figure 12) for both avoiding oxidative degradation (via lowering the HOMO energy) and for improving the solubility. So, the main result is that the fused electron-withdrawing imide substituents at the periphery of the tetrabenzoporphyrin macrocycle suppress the photooxidation by lowering the HOMO level of the molecule.



**Figure 12:** Structure of tetrabenzoporphyrin functionalized with cyclic imide moiety and the branched 2-ethylhexyl group.

An efficient luminescence at 755 nm ( $\Phi_P=0.45$ ) accompanied by strong absorption in all spectral regions, and almost no self-absorption make this Pt-porphyrin dye highly applicable as luminescent solar concentrator.

#### 4. CONCLUSIONS AND PERSPECTIVES

The progress in the field of DSCs highly depends of design and the proper selection of the component materials (photosensitizer, photoanode, redox mediator).

The use of organic dyes with high extinction coefficients such as push-pull Zn porphyrins or of co-sensitized organic dyes and the replace of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> with cobalt complexes as redox mediators [33, 34], increased the efficiencies over 13% [35, 36]. New concepts in hole transport materials associated to environment and cost friendly systems paved the way to more stable full solid-state devices to provide efficiencies over 20% that is a must for deployment to commercialization [37].

#### ACKNOWLEDGMENTS

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