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REVIEW

Phthalocyanines: colorful macroheterocyclic sensitizers for dye-sensitized solar cells

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Abstract Dye-sensitized solar cells (DSSCs) have gained great attention as lower-cost alternatives to conventional photovoltaic devices. One way to improve the excellent efficiencies (ca. 11%) exhibited by DSSCs based on ruthenium polypyridyl dyes would consist in using sensitizers with enhanced light-harvesting properties in the red region of the spectrum. Phthalocyanines (Pcs) are very robust molecules which present extraordinary high extinction coefficients in the 600- to 700-nm spectral region. Intensive research has been focused on reducing the undesired aggregation phenomena of Pcs on the metal oxide surface, while keeping a good electronic coupling between the LUMO of the Pcs and the TiO_2 conduction band, and a good solubility of the dye in organic solvents. Recently, unsymmetrically substituted "push–pull" Pcs have emerged as efficient red-absorbing dyes, reaching power conversion efficiencies of up to 4.7%, when used as single sensitizers.

Keywords Solar cells · Phthalocyanines · Panchromatic absorption · Near-infrared sensitizers · Cosensitization

Introduction

In the search for efficient, stable, and low-cost alternatives to well-established but expensive silicon-based solar cells, dye-sensitized solar cells (DSSCs), mainly developed by Grätzel's group, offer the potential of making affordable the dream of organic solar cells, because high overall power conversion efficiencies (ca. 11% η) under standard (Global Air Mass 1.5, AM1.5) illumination have been reached [1–5]. In these devices, photons are collected by molecules acting as *sensitizers*, which cover a film of wide band gap nanocrystalline semiconducting metal oxide, typically *mesoporous* TiO_2 (anatase). The third important component is the *redox electrolyte*, usually an I^-/I_3^- solution which interpenetrates the TiO_2 layer. Excitation of the sensitizer leads to injection of electrons from the dye excited state to the conduction band of TiO_2 (Fig. 1). Subsequently, the ground state of the dye is regenerated through reduction by the electrolyte (Fig. 1). The maximum voltage corresponds to the energy difference between the quasi-Fermi level of illuminated TiO_2 and the redox potential of the electrolyte. However, some loss processes limit the maximum photocurrent and photovoltage that can be extracted from these devices: (1) decay of the excited state of the dye to the ground, (2) reduction of the oxidized dye by an electron from TiO_2 conduction band (called recombination), and (3) reduction of I_3^- ion at the TiO_2 surface by an electron from the conduction band (called dark current) (Fig. 1).

The performance of DSSCs firstly depends on the relative HOMO–LUMO energy levels of the sensitizer. Thus, efficient electron injection requires the LUMO level of the dye to be higher in energy than the TiO_2 conduction band edge, whereas the HOMO of the dye level may lie below the energy level of the electrolyte to allow efficient regeneration of the oxidized dye. Secondly, the relative kinetics of the injection and regeneration steps with respect to the recombination and dark current processes will also influence the device performance.

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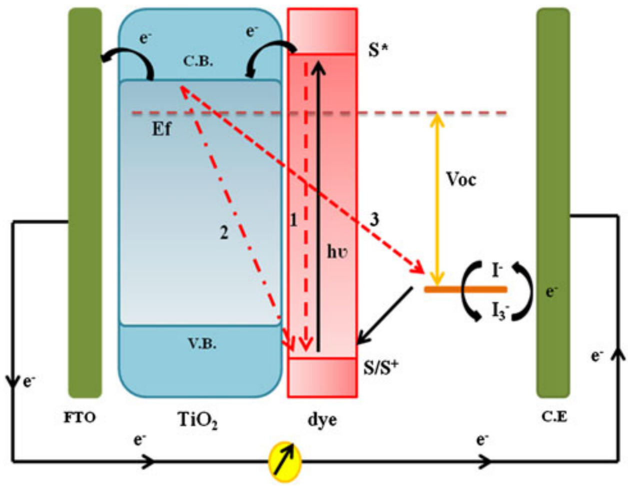


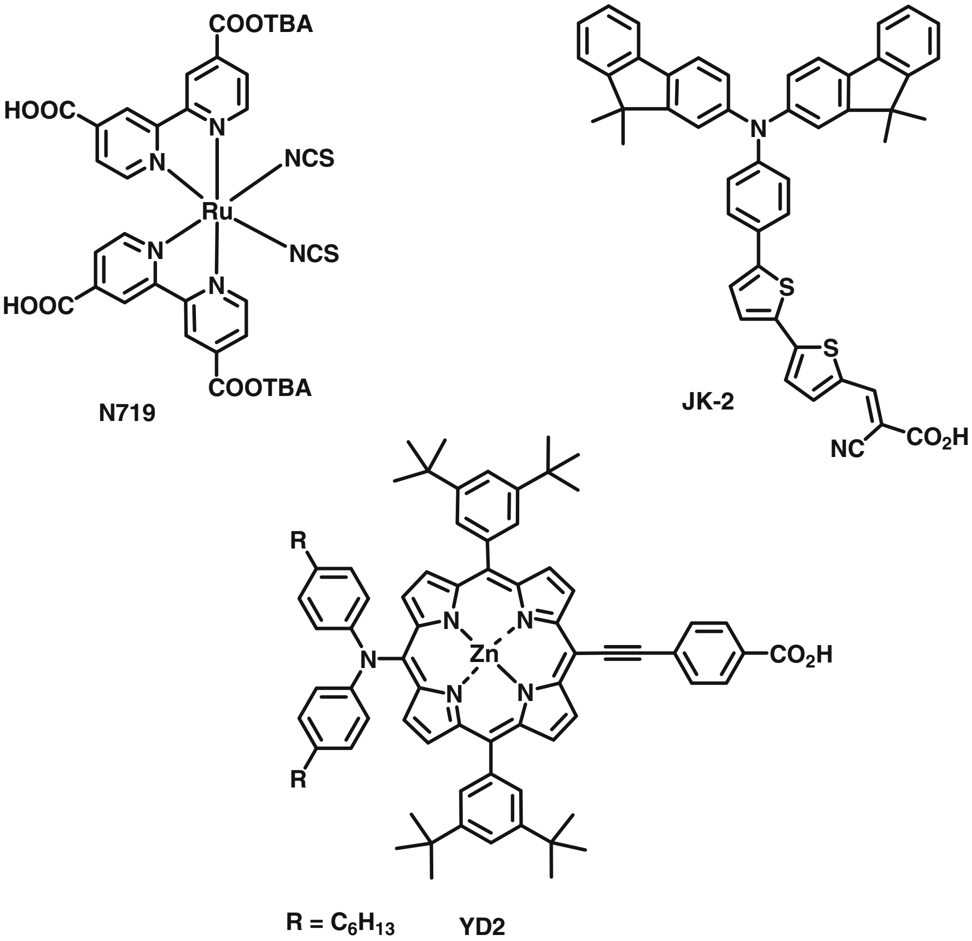
Fig. 1 Schematic diagram of DSSCs. Electron-transfer processes are indicated with *black arrows*. Unwanted back-reactions are indicated with *red arrows* including: (*1*) radiationless relaxation of the excited state of the dye, (*2*) charge recombination between dye cations and photoinjected electrons, (*3*) recombination of the electrons by interfacial electron transfer to the electrolyte

Liquid-electrolyte DSSCs which utilize an iodide/triiodide redox couple, use thick TiO_2 layers (~10 μm) optimized for maximum light absorption. The main drawbacks of these cells are their lack of long-term stability due to solvent leakage, evaporation, and corrosion [4, 5]. Moving towards totally solid-state DSSCs (ss-DSSCs) implies the use of organic hole-transporting materials (HTM) such as spiro-OMeTAD. However, difficulties found in the infiltration of the organic HTM into the mesoporous layer limit the thickness of TiO_2 films in ss-DSSCs to only about 2 μm, which decreases the light-harvesting capability and, therefore, the power conversion efficiencies [6–9].

Sensitizers

Over the years, the most successful sensitizers employed in these cells have been ruthenium(II) polypyridyl-type complexes such as N719 (Fig. 2), achieving power

Fig. 2 Molecular structures of some of the most successful DSSC dyes



conversion efficiencies around 11% in the presence of a volatile acetonitrile-based electrolyte [10]. Moreover, the introduction of hydrophobic alkyl chains on the bipyridyl ligand has been a key step not only for increasing the stability towards water-induced dye desorption, but also allowing successful replacement of the solvent-based I^-/I_3^- electrolyte by a more robust ionic liquid electrolyte or eutectic mixture of ionic liquids, giving longer device stability and good efficiencies up to 8.2% under AM1.5 solar irradiation. Both features are, with no doubt, a major breakthrough in the potential outdoor applications of DSSCs [11, 12]. The need for anchoring functions to attach the dye to the semiconductor surface has been also demonstrated. In particular, carboxylate groups have shown very good electronic coupling between the π^* orbital of the electronically excited complex and the 3*d* orbitals of the TiO_2 film.

During the last decade, an impressive synthetic effort was made on the development of various types of expensive ruthenium metal-free organic dye sensitizers for DSSCs, achieving a remarkable progress in the comprehension about the relationship between the molecular structure and photovoltaic performance [13–15]. In particular, donor–acceptor organic molecules such as JK2 (Fig. 2) possessing both electron-donating and electron-withdrawing groups linked by π-conjugated linkers have shown power conversion efficiencies of up to 9.5% in liquid DSSCs. However, there is still a need to optimize these devices.

Improvement of the devices' performance has also been limited by the light-harvesting capability of the state-of-the-art dyes, which lack strong absorption in the red/near-infrared region where the solar flux of photons is maximum. Dyes like porphyrinoids which have a high molar extinction coefficient in this spectral region would allow the preparation of thinner devices, minimizing charge recombination during the transport of charges to the electrode. In natural systems, chlorophylls play the role of light-harvesting antenna, collecting the maximum number of incoming photons, which are efficiently transferred to the so-called special pair. The interest in porphyrins as an artificial antenna systems is, therefore, not surprising. These naturally occurring macrocycles are highly conjugated heteroaromatic compounds with a very intense absorption in the visible region (namely a strong Soret band centered between 400 and 500 nm and a moderate Q band in the spectral region 550–650 nm) and, therefore, are deeply colored. Many porphyrin models have been prepared in order to understand the natural system and, in many cases, as a means of developing solar energy conversion systems [16, 17]. As early as 1993, Grätzel and Kay reported efficiencies of 2.6% for porphyrin-based DSSCs [18]. The performance of these devices has been improved over the years up to 11% by rational design of the porphyrin structure [19, 20]. Thus, the push–pull porphyrin dye YD2 has been recently reported as the most efficient green dye for DSSC applications (Fig. 2).

Performances of porphyrin-based DSSCs are in general below those of the state-of-the-art ruthenium(II)-based sensitizers. The origin of the smaller η values of porphyrin-sensitized solar cells has been frequently attributed to the increased probability of exciton quenching, a consequence of the natural tendency of porphyrins to form aggregates [16]. In addition, their insufficient light-harvesting ability in the visible has been pointed out. Indeed, the extinction coefficients of porphyrin Q bands are not very large (ca. 2×10^4).

In this context, the so-called phthalocyanines (Pcs), which are synthetic porphyrin analogues, have proven to fill this gap due to their improved light-harvesting properties in the far-red and near-IR spectral region, and their extraordinary robustness [21, 22]. However, efficiency values of Pc-based DSSCs are in general below those of their porphyrin-based relatives although the reasons have not yet been rationalized.

Phthalocyanines as DSSCs sensitizers

Instead of pyrrole as in the porphyrins, Pcs are macroheterocyclic compounds which comprise four isoindole units linked by nitrogen atoms at the *meso* position. They are planar 18 π-electron aromatic compounds with a considerably large π-delocalized surface, which accounts for their unique optical properties and the strong tendency of Pcs to form π-stacked aggregates [21, 22]. Similar to porphyrins, the electronic absorption spectrum of Pcs shows two main bands, the Q band and the Soret or B band. The former, associated with π–π^* HOMO–LUMO transitions, is usually found in the region of 620–700 nm and is responsible for the deep green or blue color of these compounds [23]. These bands can be shifted or broadened depending on peripheral substitution, metallation, and aggregation of the molecules.

The above-mentioned tendency of Pcs to form aggregates, also on the metal oxide semiconductor surface, meant that problems associated with deactivation of the excited dye became very relevant in Pc-based DSSCs. Thus, during many years efficiencies of devices made of tetracarboxy-substituted Zn(II)Pcs such as **1** persistently gave values below 1% under full AM1.5 solar light [24, 25].

Ru(II)Pcs have been seriously considered as alternatives to Zn(II)Pcs due to both their appropriate HOMO–LUMO levels and the possibility of axial coordination that avoids macrocycle aggregation. In particular, Ru(II)Pcs substituted with pyridine ligands that can additionally incorporate the requested anchoring group have been tested as dyes, demonstrating that coupling of the dye excited state to the TiO_2 conduction band can also occur through the axial pyridine ligand [26–28] (Fig. 3).

However, aggregation did not pose the only problem in achieving efficient Pc-based DSSCs, but also interfacial electron-transfer dynamics resulted in relevant phenomena affecting the final device performance. In contrast to Zn(II)Pcs, Ru(II) derivatives such as **2** (R = OMe) exhibit slower electron injection rate constants (hundreds of nanoseconds), due to more efficient injection from the Ru(II)Pc's triplet state [29]. Thus, the relaxation of the singlet to the triplet excited state by intersystem crossing is faster (100 ps) than electron injection from the RuPc singlet excited state (600 ps to 30 ns). The long lifetime of this T_1 state (200 ns) enables electron injection into TiO_2 to be slow, in competition with the T_1 decay to the ground state. Other axially substituted Pcs such as Ti(IV) and Si(IV) derivatives have been also tested, but with limited success [30, 31].

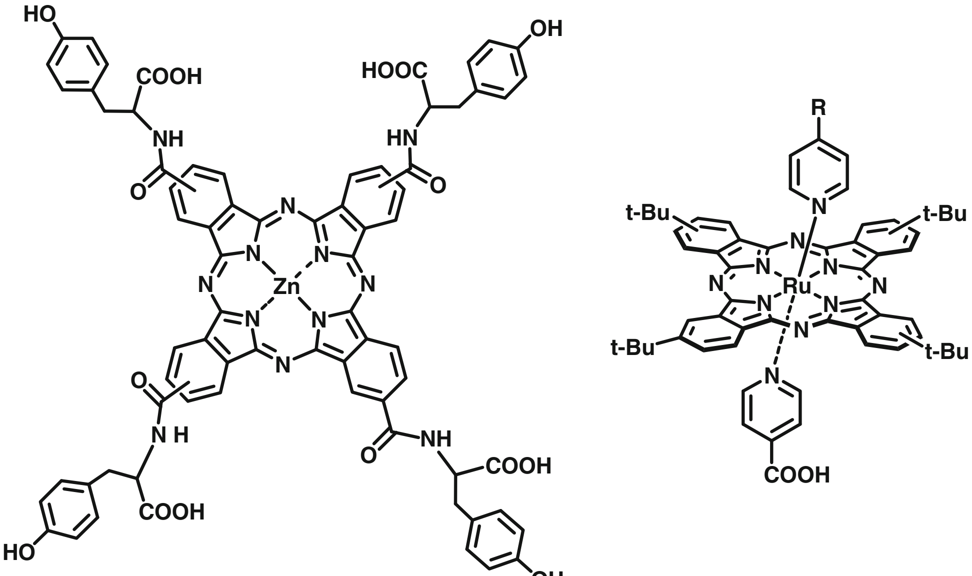
Optimization of the dye component of the cell usually requires a systematic structural modification. Besides the possibility of introducing a wide variety of transition metals at the inner cavity, chemical modifications at the macrocycle periphery can be proposed. Pc chemistry is substantially limited by the lack of solubility and methods that would allow the selective functionalization of the unsubstituted macrocycle, and the difficulty in preparing unsymmetrically substituted derivatives from already functionalized precursors [32]. In 2007, a major breakthrough was accomplished in the design and development of Zn(II)Pc sensitizers, based on the preparation of unsymmetrically functionalized A_3B-type derivatives containing three bulky *tert*-butyl groups that would help to minimize macrocycle aggregation and carboxylic acid anchoring groups to graft the sensitizer onto the metal oxide surface [33, 34]. Liquid-electrolyte cells with power conversion efficiencies around 3.5% at 1 sun and incident photon to charge carrier efficiency (IPCE) values at the Q-band maximum absorption (ca. 700 nm) of 80% were reported by the groups of Grätzel, Nazeeruddin, and Torres employing derivatives **3** and **4** (also called dye TT-1) (Fig. 4) which have low tendency towards aggregation. In particular, the TT-1 dye possesses a highly desirable "push–pull" structure with the carboxy group directly attached to the macrocycle, thus facilitating the charge transfer from the LUMO orbital of the dye to the Ti 3*d* orbital.

Effect of chemical coadsorbents on photovoltaic performance

In DSSCs, the photocurrent density (J_{SC}) is mostly governed by the light-harvesting capability and charge injection efficiency. On the other hand, the photovoltage (V_{OC}) is determined by the difference between the quasi-Fermi level of TiO_2 and the redox potential of the redox electrolyte. The introduction of coadsorbents, typically Li^+ cation and 3α,7α-dihydroxy-5β-cholic acid (CHENO) (Fig. 5), has been shown to produce an important improvement of the devices' performance [35].

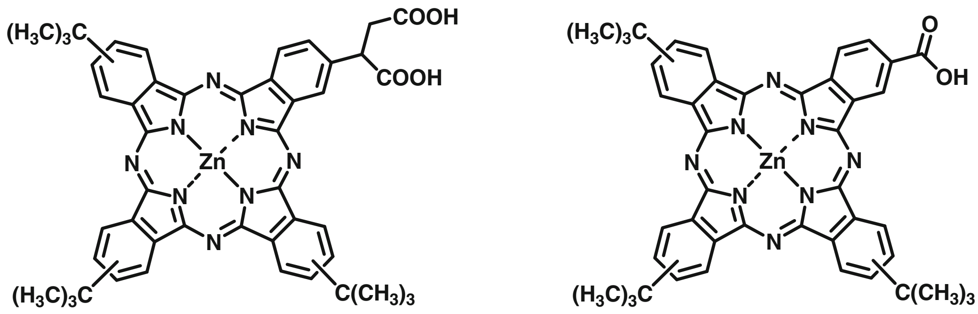
Li^+ cation acts by charging the TiO_2 surface and therefore lowering the conduction band edge of the semiconductor, accelerating the electron injection, and increasing the photocurrent in the device, although with concomitant decrease of photovoltage.

In contrast, CHENO bears a carboxylic acid functional group that allows its strong binding to the TiO_2 surface, in



1 **2**

Fig. 3 Molecular structures of some ZnPc and RuPc dyes



rac-**3**

TT-1

4

Fig. 4 Molecular structures of unsymmetrically substituted tri-*tert*-butylcarboxyZn(II)Pcs

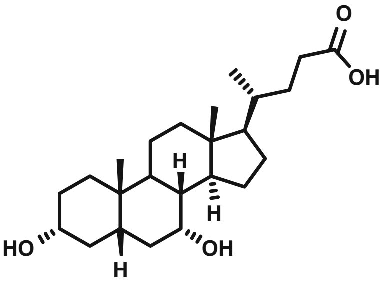


Fig. 5 Molecular structure of CHENO coadsorbent

Table 1 Photovoltaic parameters of DSSCs with different TT-1/CHENO ratios

CHENO (mM)	Thickness (μm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	η (%)
0	6	7.03	580	2.91
1	6	6.55	603	2.93
10	6	5.93	614	2.71
60	6	2.28	632	1.08
1	9	6.71	616	3.10
10	10 + 4	7.78	611	3.56

competition with the dye molecules. Therefore, the effect of adding CHENO as coadsorbent produces a remarkable increase in the photocurrent and, to a lesser extent, in the photovoltage. The increase in the photovoltage is attributed to the effect of CHENO breaking dye aggregates, thus improving electron injection into the semiconductor. In other cases, the beneficial effect of CHENO has been related to a decrease in recombination of the injected electrons with the redox electrolyte.

In the case of TT-1-sensitized solar cells, adding CHENO reduces the adsorption of the Pc sensitizer onto TiO_2, but also prevents sensitizer aggregation, leading to an increase in the open-circuit voltage of the solar cells (Table 1) due to enhanced electron lifetime in TiO_2 nanoparticles coupled with the band edge of TiO_2 being shifted to more negative potentials [36]. However, a decrease in the photocurrent with increased amounts of CHENO was observed (Table 1), due to less dye molecules being absorbed. Because the CHENO coadsorbate effectively occupies the available space on the TiO_2 surface, the adequate dye/CHENO ratio has to be carefully checked until a compromise is found between suppression of dye aggregation and decrease in dye loading. Upon further increasing the film thickness up to 9 μm, the J_{SC} also slightly increased (about 3%) due to improved light harvesting. Finally, the addition of a scattering layer composed of 400 nm of anatase TiO_2 particles further increased the device photocurrent up to 7.78 mA/cm^2, reaching an optimized overall efficiency of 3.56% [36].

The effect of CHENO on the devices' performance and the photophysics of RuPc **2**-sensitized solar cells has also been studied in detail [37]. Quite surprisingly, despite the formation of aggregates being completely hindered in RuPcs–DSSCs by the presence of axial ligands, the beneficial effect of CHENO is quite evident. Indeed, the authors demonstrated that CHENO does not affect the electron injection quantum yield, but rather the cation–TiO_2 (e^-) recombination and regeneration dynamics. In particular, the slower recombination of the dye cations with the TiO_2 electrons and the faster regeneration of the dye cations by the electrolyte are the reasons claimed to be responsible for the enhanced photocurrent observed in the presence of CHENO coadsorbent molecules. A tentative explanation for that effect has been proposed to be due to changes in the dye orientation induced by the presence of CHENO on the semiconductor surface, increasing the hole–electron distance.

Influence of spacers introduced between anchoring group and Pc sensitizer

In most sensitizers, the anchoring group is usually a carboxylic acid group with electron-withdrawing character, responsible for transferring the electron from the excited dye into the TiO_2 conduction band. Moreover, electron-

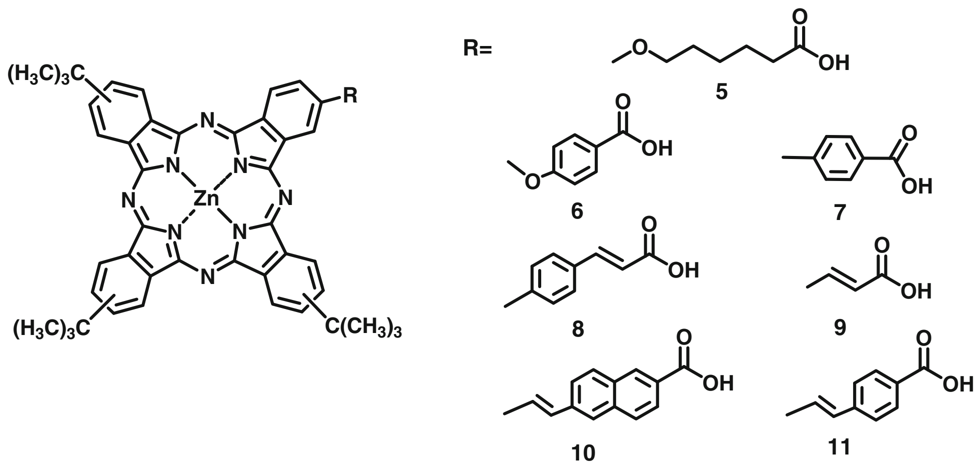


Fig. 6 Molecular structures of tri-*tert*-butyl carboxyZn(II)Pcs **5**–**11** bearing different spacers between the macrocycle and the carboxylic anchoring group

donating groups, connected to the anchoring group through π-conjugated fragments, such as ethenyl, ethynylphenyl, or bisthienyl, are quite recurrently employed in the organic dye skeleton to facilitate directional intramolecular charge transfer from the donor to the acceptor moiety of the dye, and subsequently to the semiconductor [13–15]. In this way, the cationic charge formed upon photoexcitation of the dye would be effectively delocalized and physically separated from the TiO_2 surface, restricting the recombination between the injected electrons and the oxidized dye. This donor–acceptor or "push–pull" concept has also led to successful designs of porphyrin sensitizers [19].

In the case of Pc sensitizers, Torres, Nazeeruddin, and Palomares have reported a series of monocarboxylic acid Pc derivatives (**5**–**11**) and systematically checked their performance in DSSCs compared with Pc sensitizer TT-1 in which the carboxy group is directly attached to the macrocycle (Fig. 6; Table 2) [38–40]. As expected, the IPCE values dramatically drop to less than 1% overall efficiency when the carboxy anchoring group is separated from the Pc by insulating alkoxy or aryloxy spacers, i.e., using Pc **5** and **6**. In contrast, rigid π-conjugated bridges do not interrupt the electronic coupling between the Pc and the semiconductor surface, rendering devices made of derivatives **7**, **10**, and **11** average power conversion efficiencies of 2%. Similarly to porphyrin derivatives [17], conjugation of the carboxy anchoring group through an ethenyl spacer to the dye led to superior photovoltaic responses in DSSCs. Thus, derivative **8**, bearing a π-conjugated phenylenevinylene spacer, showed higher performance than Pc **11**, which has an opposite arrangement of the ethenyl and phenylene groups. In spite of this, the better results obtained with Pc **3** suggest that the anchoring group should remain as close as possible to the chromophore to maximize the coupling between the Pc and the TiO_2.

Table 2 Comparative photovoltaic data of tri-*tert*-butyl carboxyZn(II)Pc dyes bearing different spacers between the Pc and the carboxy group

Sensitizer	TT-1	**5**	**6**	**7**	**8**	**9**	**10**	**11**
η (%)	3.52	0.40	0.67	2.20	3.10	3.28	2.20	1.87

Influence of binding group and light-harvesting efficiency

The binding of monocarboxylic acid-functionalized dyes to the TiO_2 surface is frequently quite weak. Although more acidic sulfonic and phosphonic groups produce a stronger binding to the metal oxide, carboxylic acid derivatives typically show significantly superior solar cell sensitization, therefore implying good electronic coupling between the carboxylic acid function and the TiO_2 surface.

In the case of porphyrin sensitizers, the use of an α-cyanoacrylic anchoring unit produces an enhancement of the light-harvesting properties and concomitant photovoltaic performance in comparison with the acrylic acid derivatives [41, 42]. This structural modification has also been applied to Pc sensitizers **12** and **13** (Fig. 7) although with reduced success due to an increase in their aggregation tendency [40]. However, the incorporation of two carboxylic acid functions in Pcs **14** [43] and **15** has finally led to beating the record that TT-1 has held for 3 years within this family of good performance tri-*tert*-butyl ZnPc sensitizers [40] (see Table 3; Fig. 7) mainly due to an enhancement in the photocurrent response as a consequence of its broader spectrum coverage. In conclusion, the optimization of this particular family of Pc sensitizers is a delicate matter, in which the most important parameter is the choice of an appropriate π-conjugated binding segment, able to electronically connect the Pc dye and the TiO_2 surface and at the same time improve to the maximum the

Fig. 7 Molecular structures of tri-*tert*-butyl carboxyZn(II)Pcs **12**–**15** bearing different carboxylic-based anchoring groups

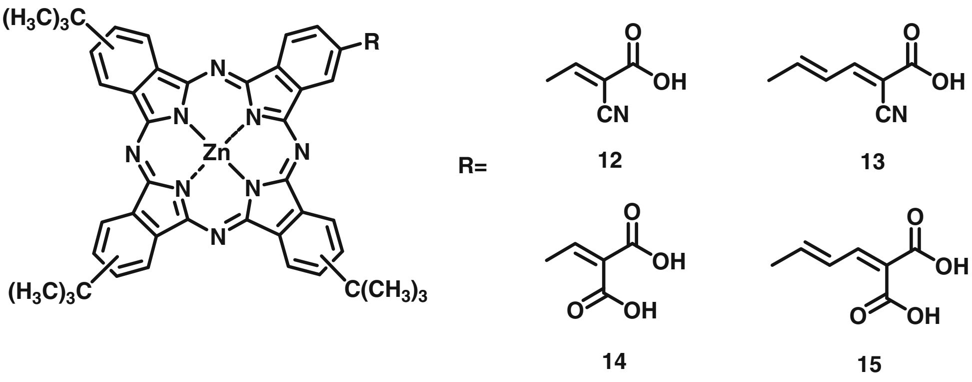


Table 3 Comparative photovoltaic data of tri-*tert*-butyl carboxyZn(II)Pc dyes bearing different binding groups

Sensitizer	TT-1	**12**	**13**	**14**	**15**
η (%)	3.56	2.55	2.65	3.96	2.87

light-harvesting efficiency without altering the aggregation properties of the macrocycle.

Changes at phthalocyanine peripheral and non-peripheral substituents

The introduction of different substituents at the peripheral or non-peripheral positions of Pcs produces, among others, important changes in the Q-band absorption and the aggregation properties of these macrocycles, and modification in the HOMO–LUMO levels. However, these structural modifications should be carefully analyzed because both properties can change at the same time.

For instance, counterintuitively, the substitution of the three *tert*-butyl substituents in Pc dye **3** by six stronger electron-donating α-butoxy groups in Pc **16** (Fig. 8) leads to remarkably lower overall device efficiencies (ca. 1.1%) [44]. Because this new Pc sensitizer did not show any particular strong tendency to form aggregates, a possible explanation for these results is a lower electron-injection yield in consequence of the modification of the dye HOMO–LUMO levels. However, studies confirming this hypothesis were not published.

On the other hand, Pc **17** (Fig. 8) bearing six bulky *t*-butylphenyl groups at the peripheral β position was also considered as a sensitizer in which aggregation phenomena would be considerably suppressed [45]. However, the corresponding cells displayed only a 0.57% conversion efficiency, demonstrating, once again, that suppressing Pc aggregation is not enough to achieve good performance solar cells. Considering previous results reported by Torres et al. [38], the disappointing results could be this time attributed to the inefficient coupling between the Pc dye and the conduction band of TiO_2 through an inefficient phenylene spacer.

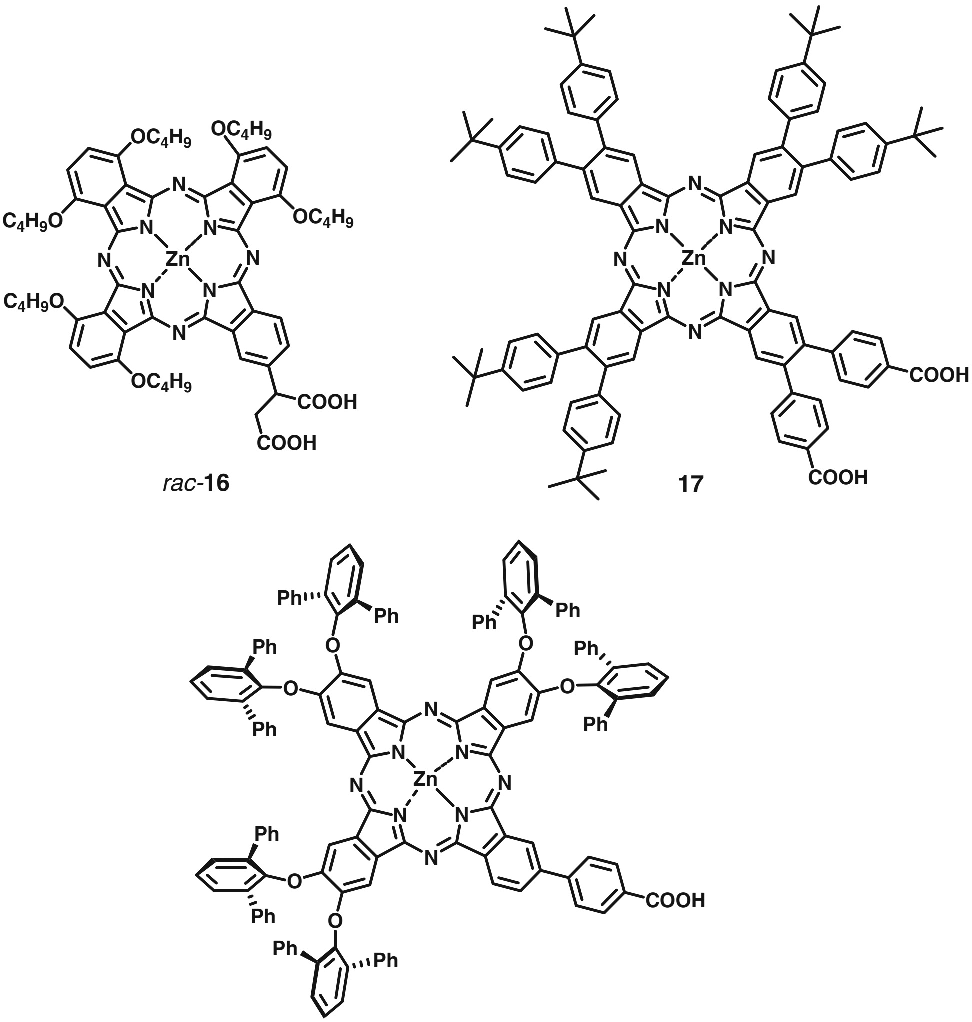
In contrast, very recently, the efficiency values of Pc-based DSSCs reached 4.6% by employing derivative **18** (Fig. 8) carrying peripheral highly bulky 2,6-diphenylphenoxy groups, which completely suppress macrocycle aggregation when anchored to the TiO_2 film, but also carrying a phenylene spacer to connect the Pc with the carboxylic anchoring group [46]. For the first time, Pc-based solar cells resulted in a higher efficiency without using CHENO as coadsorbent. In this case, the bulky groups are acting by avoiding macrocycle aggregation and maybe blocking the interactions between the Pc aromatic surface and the I_3^- electrolyte [47], reducing the dark current.

Perspectives

The application of Pcs in the field of DSSC is rapidly growing.

In the near future narrowly absorbing, stable, near-infrared Pc dyes with absorption at wavelengths higher than 750 nm, low tendency to aggregate, high internal quantum efficiency, and large open-circuit voltages should be developed. On the other hand, while further optimization of the dye structure is achieved, new strategies for the construction of highly efficient devices are emerging. Thus, the combination of Pcs with other dyes with complementary absorbing spectra is an appealing strategy to achieve panchromatic sensitization of TiO_2 films. Pc dyes offer optical windows in the visible region that make these molecules very appealing components of cosensitizer blends [34]. On the other hand, the use of long-range Förster resonance energy transfer (FRET) has been proposed as A new concept for increasing light harvesting in DSSCs using Pcs in combination with energy relay dyes (ERDs) as cosensitizers [48, 49], or Pcs as luminiscent dyes, unattached to the TiO_2, dissolved in a liquid electrolyte [50]. Last but not least Pcs are also finding

Fig. 8 Modification of the peripheral and non-peripheral positions of Pc sensitizers



rac-**16** **17** **18**

application in inorganic *quantum dot*-based solar cells [51] and in solid-state excitonic solar cells [52, 53], via resonant energy transfer and cascaded charge transfer from a secondary absorber. All these new physical approaches developed parallel to the optimization of the dye structure by synthesis chemistry will pave the way to new Pc-based colorful macroheterocyclic sensitizers for DSSCs.

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