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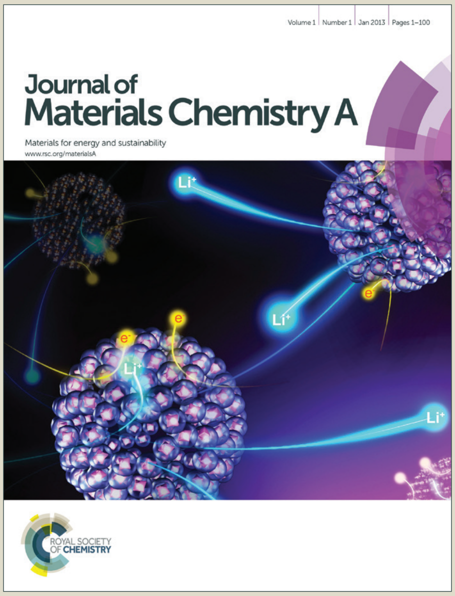

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Advances in Phthalocyanine-Sensitized Solar Cells (PcSSCs)

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Luis Martín-Gomis,[a] Fernando Fernández-Lázaro,[a] and Ángela Sastre-Santos*[a]

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Phthalocyanines are among the most promising of efficient molecules for commercial application in dye sensitized solar cells due to their extremely intense red absorbance and excellent photochemical stability. In this highlight article, we briefly review the recent progress in phthalocyanine dyes making a tour around the different strategies employed to increase their photovoltaic performance taking into consideration the crucial factors governing the dye solar cell processes, and conclude with future perspectives.

1. INTRODUCTION

The function of dye sensitized solar cells (DSSCs), mainly developed by Grätzel's group,[1] is based upon photoinduced electron injection from the molecular excited state of a given organic dye into the conduction band of a nanocrystalline metal oxide film, mostly TiO_2. Thus, photons are collected by the dye and their energy is used to facilitate the electron flow. These systems have been an attractive alternative to "all organic" photovoltaic (PV) devices because of their huge interfacial area, allowing a high load of dye, and the high electron mobility of mesoporous titania.

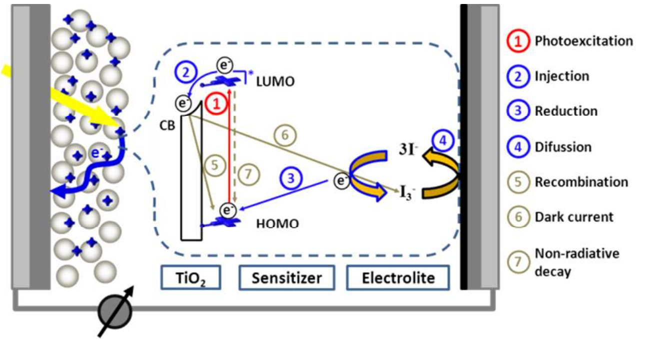

Fig. 1 Schematic representation of the composition and the operating principle of a DSSC.

Fig. 1 shows a schematic diagram revealing the operation of a typical DSSC device, which consists of a dye-sensitized mesoporous working electrode (TiO_2, anode), a counter electrode (Pt-coated, cathode) and an electrolyte (iodine-based or cobalt complexes, redox mediator) filling the space between the anode and the cathode. Upon light illumination [Fig. 1. (1) Photoexcitation], excited electrons in the LUMO level of a sensitizer are rapidly injected into the conduction band (CB) of TiO_2 [Fig. 1. (2) Injection], and then transferred to the platinized counter electrode through an external electric circuit. The holes are reduced by the redox couple, I^-/I_3^- [Fig. 1. (3) Reduction]: the oxidized dye is thereby regenerated by the I^- species to produce the I_3^- species. The diffusion of the oxidized species, the I_3^-, to the surface of the cathode completes the circuit [Fig. 1. (4) Diffusion]. Some undesirable competitive phenomena appear along the process, *viz.* recombination of injected electrons with the HOMO of the dye [Fig. 1. (5) Recombination] or with the redox couple [Fig. 1. (6) Dark current] and relaxation of the excited dye to its ground state by a non-radiative decay process [Fig. 1. (7) Non-radiative decay]. Currently DSSCs show energy conversion efficiencies over 12% and good stability, but their efficiencies have been limited by the low optical absorbance in the red/near IR region (where the solar flux of photons is maximum) of the dyes commonly used (mainly ruthenium bipyridyl complexes and porphyrins), and their low extinction coefficient in the rest of the visible region. Therefore, more efficient absorbing dyes are sought for dye-sensitized TiO_2 solar cells.

1.1 Phthalocyanines as Porphyrin Analogues

Porphyrin-based dyes possess rigid molecular structures with large absorption coefficients in the visible region, but their main advantages in comparison with Pcs are 1) their many reaction sites, i.e. four *meso* and eight β positions, available for functionalization and 2) the easy synthesis of highly unsymmetrical structures (Fig. 2a), which allow the fine tuning of the optical, physical, electrochemical and photovoltaic properties of porphyrins.[2] In particular, advances in the optimization of the device performance for a zinc porphyrin sensitizer (**YD2-oC8**, Fig. 2b), co-sensitized with an organic dye and using a cobalt-based electrolyte to enhance photovoltage of the device, obtained an unprecedented power conversion efficiency of η = 12.3%,[3] which is superior to any Ru-based device, thus stimulating investigation in the development of improved porphyrin analogues as sensitizers.

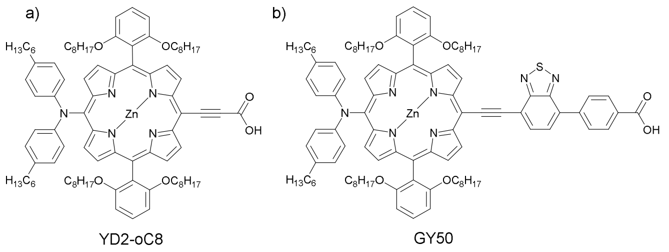

Fig. 2. Molecular structures of a) YD2-oC8 and b) Gy50 porphyrin-based dyes.

Phthalocyanines (Pcs) are structurally related to porphyrins but are even more conjugated macrocycles that absorb in the far visible/near-IR region. They present three different types of substitution, namely peripheral, non-peripheral and axial substitution (Fig. 3). The UV/vis of metallophthalocyanines presents a Soret band at 300-400 nm and a Q band centered around 650-700 nm (where the maximum solar photon flux occurs) (Fig. 3). The latter, with extinction coefficients over 100.000 $M^{-1}cm^{-1}$, allows an efficient photon harvesting.[4] However, Pcs suffer from a lack of absorption between 400 and 600 nm. Therefore, it might be interesting to use Pcs in combination with an appropriate dye to achieve panchromatic sensitization.

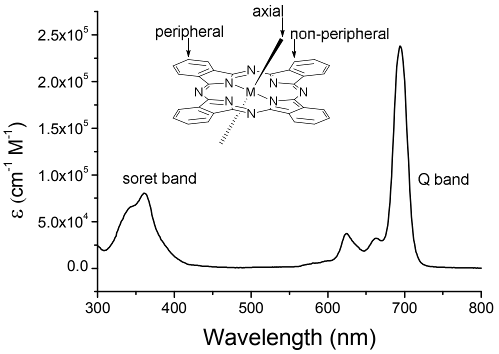

Fig. 3. Typical structure of a phthalocyanine showing the non-peripheral, peripheral and axial positions to be functionalized for phthalocyanine-sensitized solar cells, togethjer with a typical UV-vis spectrum of a metallophthalocyanine.

Although Pcs are attractive sensitizers for DSSCs,[5] due to their extremely intense red absorbance and excellent photochemical and electrochemical stabilities, their flat nature and large π-system induce in these molecules a strong tendency to stacking, which dramatically diminishes their efficiencies when used in DSSCs due to the rapid deactivation of the dye excited state [process (7) in Figure 1]. In any case, there are strategies to circumvent their aggregation tendency on the surface of the semiconductor. The control over the formation of molecular aggregates onto the semiconductor nanoparticles has been the key to achieve currently good efficiencies in Pc-based systems.

Despite the great number of phthalocyanines that have been designed and synthesized for DSSC applications and the remarkable progress obtained in this area during recent years, it is somehow frustrating to discover that porphyrins achieve much better efficiencies than Pcs (Fig. 4), even though their absorption in the red/near IR region and robustness are much lower.

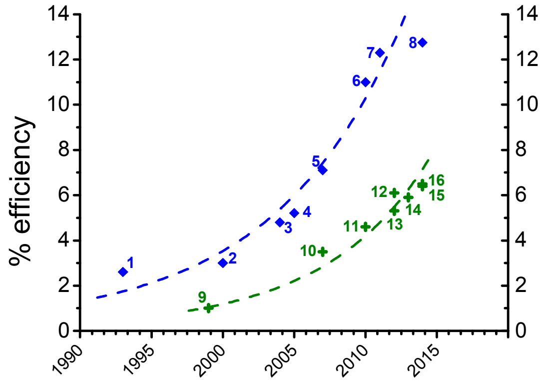

Fig. 4: Progress of the published record efficiencies, in porphyrin (◆) and phthalocyanine (✚) sensitized solar cells, from 1991 to 2014. The labelled compounds used as sensitizers, in the original publications, may have an alternative proper name or designation given by the authors: (1) Cu-2-α-oxymesoisochlorine,[6] (2) TCPP,[7] (3) 4-(trans-2′-(2′′-(5′′,10′′,15′′,20′′-tetraxylylporphyrinato zinc(II)yl)ethen-1′-yl)-1-benzoic acid (2),[8] (4) Zn 3,[9] (5) Dye 2,[10] (6) YD-2,[11] (7) YD2-o-C8,[3] (8) GY50,[12] (9) Phthalocyanine 1,[13] (10) TT1,[14] (11) PcS6,[15] (12) TT40,[16] (13) PcS15,[17] (14) PcS18,[18] (15) PcS20 [19] and (16) TT40.[20]

The evolution of the record efficiencies of porphyrin and phthalocyanine sensitized solar cells from 1991 to 2014 is shown in Fig. 4. A very promising growing trend can be inferred from the evolution of efficiencies obtained for both type of sensitizers. It is worth to highlight the 12.75% and 6.4% power efficiencies achieved using the so-called **GY50**[12] (porphyrin-based) and **PcS20**,[19] and **TT40**[20] (phthalocyanine-based) sensitizers, respectively (Fig. 5).

In this highlight, we will review the performance of phthalocyanine-sensitized solar cells (PcSSCs) featuring newly developed structures and introducing different strategies to design potentially high-efficient phthalocyanine sensitizers for DSSC applications.

2. THE FUNDAMENTAL FACTORS GOVERNING THE PERFORMANCE OF PcSSCs AND SYNTHETIC STRATEGIES FOR THEIR IMPROVEMENT.

Several factors influence the overall efficiency of a dye for DSSC, and most of them cannot be treated as singular processes, which constitutes one of the main obstacles to carry out a systematic study about the relationship between structure and sensitizing behaviour of Pcs. However, good anchoring groups and spacers for successful adsorption onto the TiO_2 surface, efficient electron injection into the TiO_2, suppression of dye aggregation in the solid state, efficient dye regeneration from the electrolyte and increase of the molar absorption coefficient of Pcs over the wide region of sunlight can be consider crucial parameters to get high efficiency PcSSCs.

2.1. Anchoring Groups and Spacers

Phthalocyanines have been repeatedly tested in the past as sensitizers of wide-band-gap oxide semiconductors.[21] However, poor incident photon-to-electric current conversion yields were obtained, remaining below 0.1% in all cases. This was attributed to the occurrence of just physisorption phenomena between the dye and the oxide, which are weaker in nature than chemisorption processes and are a consequence of the lack of a good anchoring group capable of strongly bind dye and metal oxide.

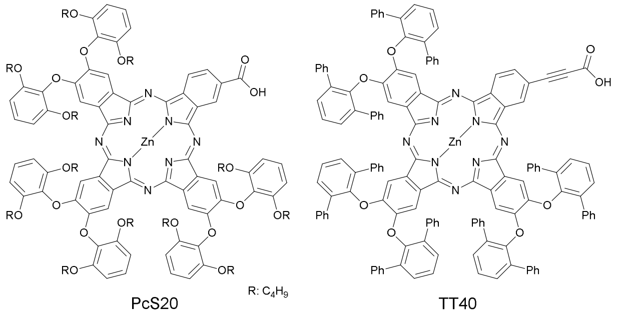

Fig. 5. Structures of the most successful DSSC dyes based on phthalocyanine (**PcS20** and **TT40**).

It seems to be clear that the point of union between the Pc core and the semiconductor surface is of vital importance if we try to obtain good efficiencies. The number and nature of anchoring groups and the spacers, if any, should play their role in the process. Attending to different published studies targeted to elucidate the importance of all the named factors,[16,22] the main features that must be fulfilled are 1) a strong binding in order to guarantee the stability of the adsorbed dye, 2) the anchoring group must be close to the semiconductor surface, in order to facilitate orbitals overlapping, and 3) the spacer should facilitate the perpendicular orientation of the dye to the semiconductor surface, and also must be conjugated to avoid decoupling between orbitals.

The COOH group has been the most important and effective anchoring group prepared so far, being Tomás Torres' group one of the most active in the field with the so-called "TT" Pcs (Fig. 6). Their first successful compound was **TT1**, bearing one carboxyl group, which displayed an efficiency of 3.51%, a record at that time.[14]

The number of the anchoring groups seems to be also important, as they are the entry gate of the excited electrons to the conduction band of TiO_2. **TT9** with two carboxyl groups directly connected to the macrocyclic ring led to a higher short-circuit photocurrent relative to **TT1**, and thus an improved 4.1% overall efficiency was obtained.[23] However, we cannot see the same trend in the comparison of carboxyethynyl asymmetric phthalocyanines **TT22** (3.13%) *vs* **TT23** (1.40%) and **TT40** (5.50%) *vs* **TT43** (3.63%).[16] The latter results may be caused by the lower energy of the LUMOs in biscarboxyethynyl derivatives, being this fact seen when conjugated spacers connect anchoring group and Pc core.

A very striking situation involves compounds **TT15**[24] and **PCH008**[25] (Fig. 6), which are actually the same molecule, a ZnPc with two carboxylic acids as anchoring groups. It is noteworthy that their published photovoltaic responses are different. Thus, a power conversion efficiency of 3.96% is described for the first one while the second one only reached 2.35%. It seems that the sun does not shine the same for all.

On the other hand, although the use of the stronger electron-withdrawing cyanoacrylic group in organic dyes has been shown to improve the photovoltaic performance, due to the superior electron-acceptor capability of the cyano group,9[,26] in the case of peripherally substituted ZnPcs no enhancement has been recorded, *e.g.* **TT7** and **TT8**[24] compared to **TT6**, their analogue without cyano group.

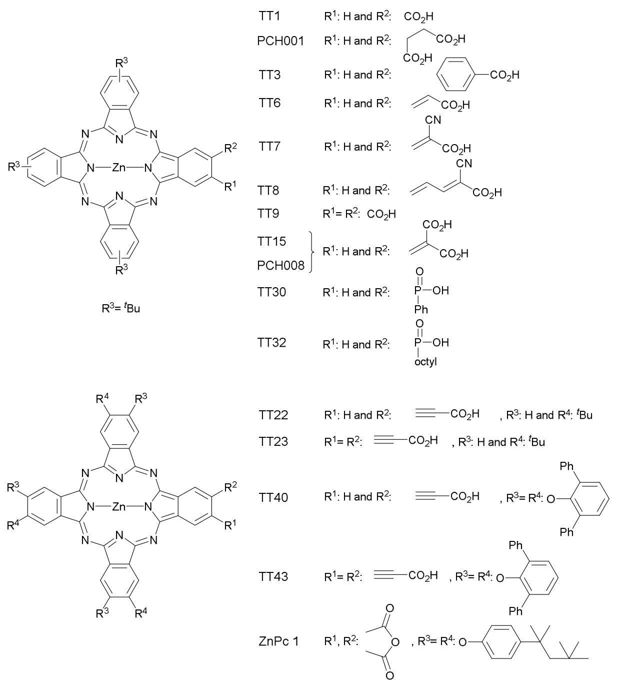

Fig 6. Molecular structures of the ZnPc-based sensitizers.

A phosphinic acid directly connected to the macrocyclic ring was also used as anchoring group in **TT30** and **TT32** (Fig. 7) pursuing a stronger bind to TiO_2 than the carboxylic acid group.[27] However, when compared to **TT1**, lower efficiencies were obtained, but with higher photostability and higher voltages.

On the other hand, the use of an anhydride directly connected to the Pc core as anchoring group has also been described by Sastre-Santos *et col.* in **ZnPc 1** (Fig. 6).[28] Although it has been pointed out that during the photosensitization process this functional group opens to a dicarboxylate, the efficiencies were lower than those of **TT9**, probably due to the higher association of the Pcs as a consequence of the lower steric hindrance of the *tert*-octylphenoxy groups in **ZnPc 1** in comparison with the bulkier *tert*-butyl groups in **TT9**.

As probably the reader has already noted, the best spacers, when used, are the rigid ones to ensure the perpendicular orientation of the dye to the semiconductor surface. Indeed, a study carried out by Torres *et al* on tri-*t*-butylphthalocyanines showed that the efficiencies decrease in the order no spacer (**TT1**, 3.52%) > vinylphenyl (**TT5**, 3.10%, not shown) > phenyl (**TT3**, 2.20%) >> phenoxy (**TT4**, 0.67%, not shown) > pentoxy (**TT2**, 0.4%, not shown) which indicates that flexible and non-directional linkers (such as alkyl chains and oxygen atoms) reduce dramatically the efficiencies.[22] This fact together with the requirement for a conjugated nature to avoid decoupling between orbitals has directed to select vinyl, ethynyl, phenyl spacers or combinations thereof. Comparison of the efficiencies of **TT3** (phenyl, 2.20%),[22] **TT6** (vinyl, 3.28%)[24] and **TT22** (ethynyl, 3.13%)[16] clearly indicates that the phenyl group yields lower performances. However, a somehow different trend can be inferred after the work by Kimura and Mori on zinc hexa(4-methoxy-2,6-

diphenylphenoxy)phthalocyanines, which describes better PCE for phenyl (**PcS15**, figure 7, 5.3%) than for phenylethynyl (**PcS16**, 4.7%, not shown) and for the case without linker (**PcS17**, 4.6%, not shown).[18]

More elaborated linkers have very recently been described. Thus, a [7-(4'-carboxyphenyl)-2,1,3-benzothiadiazole-4-yl]ethynyl-bearing analogous of **TT40** has been synthesized, probably taking inspiration in **GY50**, although only 3.29 % efficiency was recorded, which was attributed to lower LUMO levels of the former compared to that of **TT40**.[29] On the other hand, a theoretical study has pointed out that the use of a 3-(5'-vinylthiophen-2'-yl)cyanoacrylic acid unit as spacer-anchoring group leads to the generation of the new near-IR band beyond 680 nm in the electronic absorption spectra of phthalocyaninato zinc complexes, which is very helpful for improving their charge transfer directionality as DSSC sensitizers.[30]

Recently, unusual electron withdrawing anchoring groups such as pyridine[31] or 8-hydroxyquinoline[32] have been published for different dyes This kind of groups paves the way to develop new interesting phthalocyanine molecules.

2.2. Efficient electron injection into the TiO_2

As a starting point, we can say that the key factors for achieving an efficient electron injection are, not necessarily in this order, an appropriate LUMO energetic level and its directionality and overlapping with 3d TiO_2 orbitals. Needless to say, regarding electronic requirements, that the injection process has to be thermodynamically feasible, which means that the LUMO level of the dye must lie above the conduction band of TiO_2 (-4.2 eV). This can be anticipated through a rational chemical design of the dye.

Furthermore, the need for a covalent binding of the dye to the semiconductor surface makes imperative the introduction of, at least, one carboxylic acid functionality (or a similar one that facilitates the bonding). This electronegative functionality polarizes the whole molecule, and causes the so-called "push-pull" effect, that consists in the direction of the LUMO-promoted electrons to the anchoring group (electron-acceptor moiety), thus facilitating the injection to the conduction band. **TT-1** and **PCH001** dyes (Figure 6) show intense "push-pull" directionality, due to the electron-withdrawing character of the carboxylic acid anchoring group and the electron-donor character of the *tert*-butyl peripheral chains. This feature, together with an effective, and necessary, coupling of the phthalocyanine core with the TiO_2 3d orbitals, results in effective injection and, thus, high power conversion efficiencies.

2.3. Suppression of dye aggregation in the solid state

Three strategies have mainly been employed in order to avoid this aggregation, *i.e.* 1) introduction of bulky chains in the peripheral positions of the phthalocyanine ring, 2) axial substitution (metal permitting) and 3) the addition of coadsorbents.

2.3.1 Introduction of bulky chains in the peripheral positions of the phthalocyanine ring

As the first approach, it is important to mention the breakthrough made by Torres (**TT1**)[14] and Nazeerudin (**PCH001**)[33] (Fig. 6) working independently, who published in 2007 the use of a specially designed peripherally tri-*tert*-butyl-substituted Zn (II) phthalocyanine, that efficiently sensitize TiO_2 surface giving overall efficiencies of 3.51 and 3.05%, respectively.

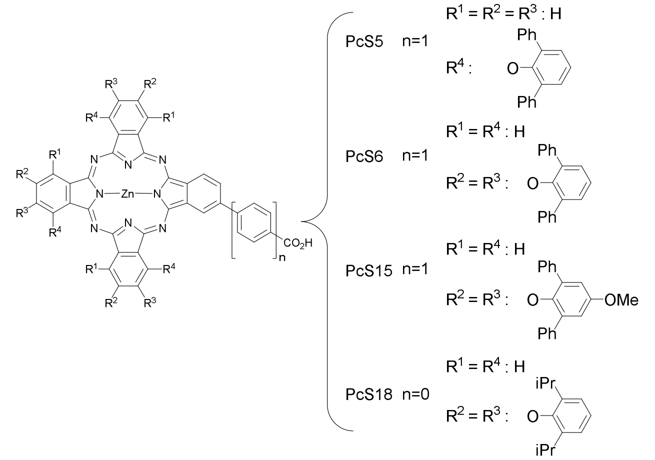

Fig 7. Molecular structures of ZnPc-based sensitizers defining "PcS series".

Since then, and thanks to that reported success, the introduction of different bulky substituents with intense push-pull effect in the peripheral positions of metallophthalocyanine-based dyes has been one of the most important synthetic strategies in order to achieve better performances in PcSSCs. In this context, we can underline the work by Mori, with the so-called "PcS" Pcs (Figure 7) who showed in 2010 how the sterically highly demanding donor 2,6-diphenylphenoxy group, strategically located in non-peripheral (**PcS5**) or peripheral positions (**PcS6**) of the ZnPc, supresses aggregation phenomena and increases the evaluated efficiency of the cell up to 4.6%.[15] The magic behind the 2,6-diphenylphenoxy group lies in its perpendicular disposition to the Pc core. This system was further improved with the introduction of methoxy groups in the position 4 of the phenoxy rings (**PcS15**) to increase the push-pull effect in the system, reaching in this way 5.3% efficiency.[17] Moreover, using diphenylphenoxy group Torres' team with **TT40** raised efficiencies till 6.01, being the difference with **PcS6** just the nature of the spacer (*vide supra*).

However, the bulkier, the better? **PcS18** (Figure 7), with 2,6-diisopropylphenoxy subunits, allowed to score a 5.9% efficiency,[18] which was justified in terms of the removal of the phenyl spacer and, mainly, the higher load of dye due to its smaller size. A step beyond has been achieved with **PcS20** (Figure 5), which bears *n*-butoxy chains to 1) prevent aggregation, 2) fill the space among dyes on the titania surface and 3) increase dye adsorption density (to enhance J_{SC}). The final result is an impressive 6.4% efficiency.[19] However, this shorter chain is not enough to totally suppress aggregation of dye molecules, and some stacking could be detected.

2.3.2. Axially substituted phthalocyanines

Another synthetic approach to reduce the aggregation behavior of Pcs is the use of axial substitution. This is possible for metallophthalocyanines derived from Si, Ge, Al, Ti, Mn, Fe, Co, Ru, among many others. The introduction of this kind of compounds for sensitizing TiO_2 photoanodes in DSSC has been accomplished, mainly, with Ru (II), Si (IV) and Ti (IV) derivatives. Thus, a series of Ru (II) Pcs bearing pyridine ligands in the axial positions were prepared by Torres *et cols.* (Figure 8).[34] For the compounds bearing the anchoring group in the axial pyridine no significant photovoltaic response was obtained. On the other hand, the carboxylic acid anchoring group in the periphery of the phthalocyanine ring, *e.g.* **TT35**,[35] a Ru(II)-based analogue of **TT1**, led to a sensitizer with an efficiency of 1.01 %. Moreover, exploring the same concept, but with the addition of six peripheral pentoxy chains and two *p*-benzoic anchoring groups, afforded an efficiency of 0.40%, as reported by Sun *et cols.*[36] These low photovoltaic performances were attributed to the slow electron injection from an energetically low-lying triplet state of the RuPcs into the TiO_2 conduction band, similar to the cases of **TT23** and **TT43** (*vide supra*).

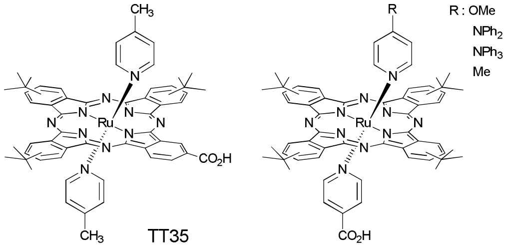

Fig 8. Molecular structure of RuPc based sensitizers.

Torres and co-workers have utilized the axial position of titanium(IV) phthalocyanines for DSSC applications using either carboxylic acid or sulfonate as anchoring groups (Figure 9a).[37] Despite these dyes are strongly adsorbed onto the TiO_2 surface, their efficiencies are very low due to poor electron injection from the LUMO of the phthalocyanine to the TiO_2 conduction band.

Turning to Si (IV) derivatives, two non-aggregated silicon (IV) phthalocyanine compounds, **SiPc 1** and **SiPc 2**, were synthesized by Sastre-Santos *et cols* (Figure 9b). The axial positions were symmetrically occupied by either two terephthalic or two 4'-carboxyphenylcyanoacrylic moieties, respectively. The measured efficiencies were 0.53 and 0.77%.[38] The higher V_{OC} and *Jsc* obtained in the case of **SiPc 2** was attributed to the presence of the cyanoacrylic moiety, acting as an electron-withdrawing unit (*vide supra*), which lead to a more efficient electron injection.

A hard lesson to be learnt from these results is that the parallel arrangement of the Pc and the TiO_2 surface induced by the presence of the anchoring groups in the axial positions leads to poor efficiencies.

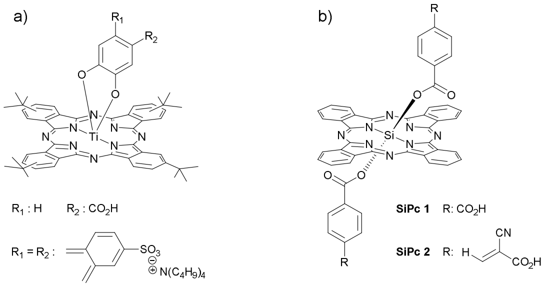

Fig 9. Molecular structures of a) Ti(IV)Pcs and b) SiPcs

2.3.3. Addition of coadsorbents

A less sophisticated but very effective strategy, in order to reduce aggregation of the dye at the semiconductor surface, is the employment of coadsorbents that strongly bind to the TiO_2 surface. These strong binding phenomena force the displacement of dye molecules from the TiO_2 surface, being therefore reduced their probability of aggregation, at the same time that shield the semiconductor particle surface, thus preventing recombination processes, causing a general (but moderate) increasing of photocurrent (J_{SC}), photovoltage (V_{OC}) and fill factor (*FF*) values. Evidently, it cannot be that simple and there must be a drawback somewhere. In this particular case, the use of coadsorbents reduces the load of dye and thus the photon harvest.

Chenodeoxycolic acid (cheno) is the most common and broadly used coadsorbent in PcSSCs preparation,[13] but there are also examples where 1-decylphosphonic (DPA)[39] or *ω*-guanidinoalcanoic[40] acids are successfully used. The convenience of using cheno as coadsorbent in phthalocyanine-sensitized solar cells was early demonstrated by Sundström *et al.*,[41] achieving an increase of 86% in efficiencies (from 0.29 to 0.54%) comparing the cell performances without and with coadsorbents in the immersion bath. The authors showed that the increase in efficiency is mainly due to an improvement in J_{SC} (from 1.27 to 2.25 mA/cm^2). They affirmed that the improvement in J_{SC}, while maintaining V_{OC} and *FF* constant, is a consequence of the minimization of the dye's aggregation on the TiO_2 surface, which leads to suppression of quenching phenomena due to energy or charge transfer processes between aggregates. Exploring the same concept, there is a published study on how different concentrations of cheno during the preparation of a **TT1** sensitized cell influence on its performance,8 and the increase was quantified in a 22% improvement in the efficiency, comparing cell performances when 1) no coadsorbent is used (2.91%) and 2) cheno is employed (3.56%). In this case, the moderate increase in the values of J_{SC}, V_{OC} and *FF*, resulting in a net improvement of the cell efficiency, can be explained by a combination of three factors, all of them caused by the competition in adsorption onto the TiO_2 surface between dye and coadsorbent molecules. Those factors are the abovementioned decrease of the dye aggregation plus an upwards shift of the TiO_2 film band edge and, finally, a shielding of the semiconductor surface against recombination processes which manifests as a long electron lifetime.

2.4. Efficient dye Regeneration

A suitable HOMO energy level of the Pc is necessary in order to have dye regeneration from the electrolyte. Until now, most of the PcSSC devices have been performed using as liquid electrolyte the iodide/tri-iodide redox couple. Some other liquid electrolytes such as cobalt(II)/cobalt(III) complexes have been integrated in the device.[19] However, the PCEs of ZnPc-sensitized solar cells based on cobalt redox shuttles were much lower than those of I^-/I_3^- redox couple. As an example, a **PcS20** cell using cobalt redox shuttles exhibits a PCE of 1.4% *versus* the 6.4% using I^-/I_3^-.[19] Moreover, solid hole-transporting molecules, such as P3HT[42] or spiro-OMeTAD[43] have been recently incorporated in solid-state PcSSCs.

The use of other electrolytes less corrosive than iodide/tri-iodide or solid electrolytes opens the door for long term stability of DSSCs, as this instability has generally been explained in terms of dye–electrolyte interactions with highly conjugated sensitizers.

2.5. Go red!

Everywhere explorers in the photovoltaic field attend to this general call as they are conscious that more than 34% of the solar photons are emitted in the NIR region up to 1100 nm (compared with only 26% in the visible).[44] However, the design of molecules able of near-infrared sensitization represents a challenging task, as their narrow band gap compels to a fine tuning of the HOMO-LUMO levels in order to allow charge injection and dye regeneration.[45]

On the other hand, moving the Q-band to the NIR has additional (technical) advantages as it enables a wide transmission window which opens the possibility for transparent devices. A near-IR dye which is transparent over the whole visible spectrum would allow visible light to pass while it converts IR solar radiation into electricity. This is of interest in solar cells for windows and tandem cells. Also, an IR dye can be used in combination with another dye to achieve panchromatic cosensitization.[46]

At least, three different strategies have been designed to push the absorption of the phthalocyanines to the red-near infrared. The first one consists of extending the conjugation by attaching some other chromophores like, for example, bisthiophene moieties (Figure 10).[47] This modification shifts the absorption maximum ca. 30 nm to the red when compared with that of **TT1**. Interestingly, the more elaborated difluorenylaminophenyl subunit pushes only 5 nm the absorption maximum of **ZnPc dye 1** with respect to that of **ZnPc dye 2**. An additional advantage of these multichromophores is the presence of a broad absorption, more pronounced in **ZnPc dye 1**, in the 400-500 nm region attributable to the peripheral substituents. There is a however to this approach, represented by an enhanced aggregation tendency, especially in **ZnPc dye 1**, leading to a decrease of the extinction coefficients of the Q-bands and considered responsible of the moderate power-conversion efficiencies (< 3%).

A second strategy has been the extension of the aromatic structure to generate benzo-fused analogues of Pcs, like the tetrabenzophthalocyanines: the naphthalocyanines (Ncs). The latter have a red-shifted absorption and eight extra positions for functionalization when compared with Pcs, although the position of their HOMO and LUMO could mismatch with the conduction band and the redox shuttle. A theoretical study has calculated that substituted tin naphthalocyanines would show Q-bands with maxima ranging from 770 to 950 nm and extinction coefficients between 2.5 and 4.5 x 10^5 M^{-1} cm^{-1}.[48]

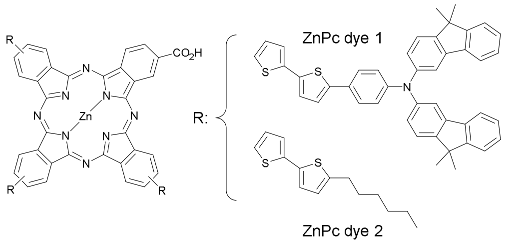

Fig 10: Molecular structures of ZnPc-based sensitizers bearing bisthiophene moieties.

In an attempt to find where the compromise lies between NIR absorption and correct alignment of the energy levels, a study has compared the performances of a silicon benzophthalocyanine (**LBG3**) and a silicon naphthalocyanine (**LBG1**) (Figure 11).[49] As expected, **LBG1** absorbs with higher intensity at higher wavelength (λ_{max} = 786 nm, ε = 3.11 x 10^5) than **LBG3** (λ_{max} = 705 nm, ε = 2.67 x 10^5). However, **LBG1** exhibited low photovoltaic performance (total efficiency 0.9%) that was rationalized by a lack of thermodynamic driving force for both the photoinduced injection of electrons into TiO_2 and the regeneration of the dye by the iodide/triiodide redox electrolyte. **LBG3**, on the other hand, exhibited high photocurrents and an excellent photoresponse at wavelengths beyond 750 nm, which led to a total efficiency of 4.5%. This was explained taking into account the decreased conjugation in **LBG3** when compared with **LBG1**, which resulted in a more negative reduction potential and a more positive oxidation potential, thus facilitating the electron injection into the conduction band of TiO_2 and a more efficient regeneration of dye by the I^-/I_3^- redox shuttle.

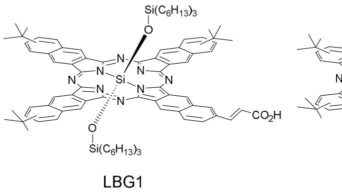

Fig 11. Molecular structures of **LBG1** and **LBG3** sensitizers.

In a step further, the influence of the electron-donating ability and the steric requirements of the substituents located onto the benzophthalocyanine ring have also been investigated. To this purpose, zinc complexes bearing *t*-butyl (**Zn-tri-PcNc-2b**) and *n*-butoxy (**Zn-tri-PcNc-3b**) substituents were synthesized (Figure 12).[50] Although the position of the Q-bands is quite similar (only 5 nm of difference) and the energies of the corresponding frontier orbitals do not differ significantly, there is a huge difference in the photovoltaic performances of **Zn-tri-PcNc-2b** and **Zn-tri-PcNc-3b**. Thus, cells sensitized with the former have efficiencies of 3.56%, while cells with the latter show only 2.20%. This fact was attributed to the greater extent of (as it couldn't be other way) aggregation in the cells using **Zn-tri-PcNc-3b**. On the other hand, the slightly higher efficiency displayed by **Zn-tri-PcNc-2b** when compared with the phthalocyanine bearing the same substitution pattern, **TT1** 3.52%,[22] was explained taking into account the redshift (20 nm in EtOH) in the absorption of their molecule, although the extinction coefficient of the Q-band seems to be higher for **TT1**.[14]

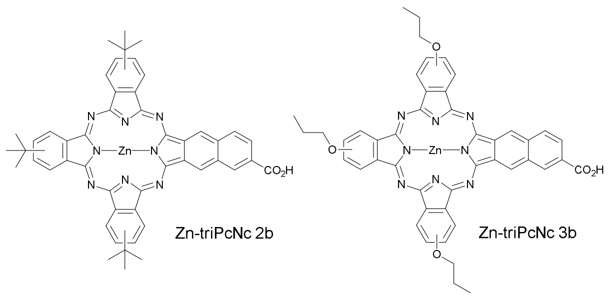

Fig 12. Molecular structures of **Zn-tri-PcNc 2b** and **Zn-tri-PcNc 3b** sensitizers.

The third strategy has been envisaged theoretically only and consists in the fusion of phthalocyanine rings. In this work, a zinc tribenzoporphyrazine and a zinc tripyrazinoporphyrazine were fused on opposite sides of a six membered-ring.[51] Computations showed that the frontier molecular orbitals show little or no contribution of the substituents, being nitro groups the only exception. The calculated Q bands are located, with few exceptions, in the 900-1100 nm range. Estimated energies of LUMO and HOMO orbitals indicated that this approach could be valid for the design of DSSCs as long as electron withdrawing substituents are avoided. Further experimental work would be needed to test the feasibility of this work line.

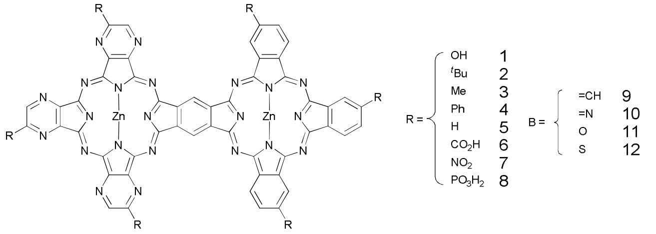

Fig 13. Molecular structures of fused ZnPc-based sensitizers.

2.6. Co-sensitization, energy relay dyes and covalent or supramolecular binding of complementary dyes: strategies to increase the light harvesting ability of PcSSCs

The enhancement of the light-harvesting ability of the dye is one of the most promising approaches for improving the efficiency in DSSCs.[52] The introduction of another different dye either as co-sensitizer or as energy relay dye (ERD) in the process has been until now the most common strategy explored for this purpose.

The use of co-sensitizers or cocktail sensitizers is a well-known strategy that consists in the addition of two or more dyes with complementary absorptions, that yields enhanced photovoltaic performances compared to the single-dye systems.[11,53] However, the dyes have to be chosen in such a way that they should broaden the absorption while avoiding inter-dye charge-transfer processes that could conduct to a decrease in the injection dynamics.[54]

Phthalocyanines have minimal absorption in the 400-500 nm region and because of that it seems to be crucial to find a co-sensitizer to enhance their light-harvesting ability in this region. Torres *et cols.* demonstrated for the first time this phenomenon in PcSSCs. Thus, the enhanced photovoltaic response of **TT1** cosensitized with **JK2** yielded an enhanced device performance, 7.7% overall efficiency,[14] compared to the individual dyes **TT1** (3.5%) and **JK2** (7.08%) The success of the increase in the performance was attributed to the fact that the high molar extinction coefficient of the dyes permitted a low dye concentration for sufficient absorption which would provide enough space on the semiconductor surface to allow adsorption of both dyes at the same time. Some other cocktail cells has been carried out by Mori co-sensitizing **PcS15** (Figure 7) with **D102** or **D131** aimed to compensate the low IPCE response of the phthalocyanine at 500 nm.[17]

The use of ERDs in the search for panchromatic response of PcSSC presents three different advantages *versus* the co-sensitizer one, *viz* 1) no need of anchoring to the metal oxide surface, 2) no affectation to the dye load and, 3) the attached dye does not participate in the charge-transfer process.

In order to achieve an optimum DSSC architecture, ERDs should present 1) a high molar absorption coefficient, 2) very high solubility in the electrolyte and 3) a high emission overlapped with the Pc Q band absorption to get an efficient Förster resonance energy transfer (FRET).[55] In this context, **TT1** has been tested with different ERDs such as perylenediimide (**PTCDI**),[56] 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (**DCM**),[57] **BL302**,[58] **BL315** or even with two dyes with complementary absorption such as **DCM** and Rhodamine B (**RB**).[59] Although in all cases the device efficiency was enhanced in the presence of the ERD, some losses in excitation transfer efficiency were found due either to energy transfer to the desorbed sensitizing dyes or to the quenching by molecular aggregation of the ERD. A more detailed study of the ERD is still open to better understand the processes involved.

On the other hand, it has also been demonstrated the possibility to do it the other way, *i.e.* to incorporate Pcs as ERD in DSSCs. Zinc tetra-*tert*-butylphthalocyanine has been used as ERD of the ruthenium dye **N719** achieving a four-fold increase in the external quantum yield in the red region of the spectrum.[60]

Another elegant strategy to improve the light-harvesting ability of the sensitizer is the binding, either covalent or supramolecular, of a complementary chromophore with a phthalocyanine to make a π-elongated macrocycle able to undergo efficient energy or electron transfer to the injecting system. The design of an adequate dyad would avoid the competition between the dyes for the binding sites on the conducting metal oxide.[61] Very recently this proof of concept has been demonstrated by supramolecularly binding a zinc phthalocyanine to a perylenemonoanhydridemonoimide (Figure 14) obtaining much higher power conversion efficiency (PCE = 2.3 %) and incident-photon-to-current-efficiency (IPCE = ca. 40 %) than the devices made of individual dyes.[62] The covalent version was demonstrated with a hybrid sensitizer obtained by binding a tin (IV) tetra-*tert*-butylnaphthalocyanine and the ruthenium-based **N719** dye. The IPCE curve covered indeed a wavelength range from 300 to 950 nm. Besides the improvement in the IPCE, SnO$_2$-based cells stained with this sensitizer showed an increase in the *Jsc* compared with cells dyed only with **N719**.[63,64]

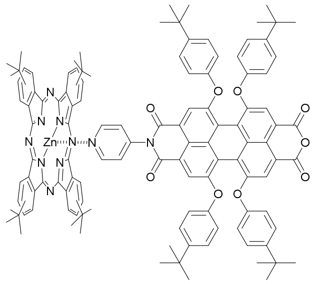

Fig. 14. Molecular structure of self-assembled zinc phthalocyanine-peryleneimide dyad

SUMMARY AND FUTURE PERSPECTIVES

Table 1 summarizes the evolution over time of the PcSSCs photovoltaic parameters. At the current stage, the devices fabricated using the push–pull **TT40**,[20] and **PcS20**,[19] have attained unprecedented efficiencies (under standard AM1.5G solar irradiation) of 6.01 and 6.4%, respectively, which is still far away from the 12.7 % obtained by the zinc porphyrin **GY50** on a TiO_2 film and using a cobalt electrolyte.[12]

Table 1

Sensitizer	Year	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)	Ref.
Pc 1	1999	5.4	416	0.49	1	13
TT1	2007	7.60	617	0.75	3.5	14
TT3	2009	4.80	610	0.74	2.20	22
TT5	2009	6.80	613	0.70	3.10	22
PcS2	2010	5.3	580	0.74	2.3	15
PcS5	2010	4.8	580	0.77	2.1	15
PcS6	2010	10.4	630	0.70	4.6	15
TT35	2010	3.64	522	0.51	1.01	35
TT6	2011	7.37	609	0.74	3.28	24
TT7	2011	5.88	587	0.75	2.55	24
TT8	2011	6.80	576	0.69	2.64	24
TT15	2011	9.15	600	0.72	3.96	24
TT9	2011	9.37	605	0.73	4.10	23
PcS15	2012	12.8	610	0.68	5.3	17
TT22	2012	7.01	610	0.73	3.13	16
TT22	2012	0.70*	564*	0.78*	3.26*	16
TT23	2012	3.70	520	0.73	1.40	16
TT23	2012	0.35*	455*	0.75*	1.24*	16
TT40	2012	12.3	638	0.70	5.50	16
TT40	2012	1.31*	585*	0.76*	6.13*	16
TT43	2012	8.77	584	0.71	3.63	16
TT43	2012	0.85*	521*	0.76*	3.54*	16
TT30	2012	7.07	563	0.75	2.97	27
TT32	2012	7.67	559	0.76	3.24	27
PcS18	2013	13.7	613	0.70	5.9	18
PcS20	2014	15.1	600	0.71	6.40	19
TT40	2014	13.9	621	0.70	6.01	20
TT40	2014	1.45*	568*	0.75*	6.49*	20

All the measurements have been performed under simulated solar irradiation of 1 sun (100 mW/cm^2 1.5 air mass global) except * 0.095 sun

Towards the design of the perfect Phthalocyanine for DSSC

It remains clear that a perpendicular arrangement of the dyes on the TiO_2 surface, in combination with one or two carboxylic anchoring groups and bulky peripheral substitution, are crucial parameters for a good PcSSC design. The spacer between the anchoring group and the Pc must be rigid to induce directionality and conjugated to allow orbital overlap. Functional chromophores such as anthracene, pentacene, fluorene, pyrene, BODIPY and perylene anhydride, which have been linked to porphyrin derivatives, might also play a role to improve the light-harvesting ability of the phthalocyanine. Fused Pcs also will be potential good candidates going far to the red for good photon absorption. But, there is no doubt, that the synthesis of push-pull ABCB substituted Pcs, would have all the adequate characteristics to be good DSSC photosensitizers. However, these unsymmetrically substituted Pcs, due to the synthetic difficulty, still remain as an exciting challenge that the best synthetic phthalocyanine groups should pursue. It is fully expected that with a larger number of researchers in the field, a high efficiency in PcSSC will be reported in the not-too-distant future.

We believe that this highlight provides a complete overview of the state of the art in this particular field and will serve as guidance for strategies to design efficient phthalocyanines and donor–acceptor phthalocyanine systems towards much improved DSSCs.

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