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Phthalocyanines and Their Analogs Applied in Dye-Sensitized Solar Cell

Xiyou Li, Haixia Wang, and Haixia Wu

Abstract In this chapter, recent progress in the application of phthalocyanines and related tetrapyrrole metal complexes in dye-sensitized solar cell (DSSC) is summarized and analyzed. Three categories of phthalocyanines defined by the connecting positions of anchoring groups, namely symmetrically substituted phthalocyanines, asymmetrically substituted phthalocyanines and axially substituted phthalocyanines, are discussed separately. The effects of the distance of the dye molecule from the surface of the semiconductor nanoparticles, the redox potentials and the directionality of the anchoring groups on the performance of the dyes were reviewed. Porphyrins are good sensitizers to wide band semiconductors too. The performance of these sensitizers is predominantly affected by the nature, the connection position of the anchoring groups and the central metal ions. Modifications on the molecular structure of porphyrin by introducing different groups at different positions aimed at extending the absorption spectra, tuning the electronic configuration of the excited states, and inhibiting the aggregation are reviewed. The application of natural porphyrins as sensitizers in DSSCs is also discussed at the end of this chapter.

Keywords Photocurrent · Phthalocyanine · Porphyrin · Sensitizer · Solar cell

Contents

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Abbreviations

AAS	Atomic absorption spectrometry
BMII	Butylmethylimidazolium iodide
CNHs	Carbon nanohorns
DSSC	Dye-sensitized solar cell
H_2Pc	Metal-free phthalocyanine
HOMO	Highest occupied molecular orbital
IPCE	Incident-photon-to-current-conversion efficiency
LUMO	Lowest unoccupied molecular orbital
MPc	Metal phthalocyanine
M-UP	Metallo-uroporphyrins
Q-CdSe	CdSe nano particle
RRS	Resonance Raman spectroscopy
tBu	*tert*-butyl
TCPP	Tetra(*p*-carboxylic acid)phenyl porphyrin
TsPP	Tetra(*p*-sulphonic acid) phenyl porphyrin
UPS	Ultraviolet photoemission spectroscopy
XPS	X-ray photoemission spectroscopy
ZnCyt-c	Zinc-substituted cytochrome c

1 Introduction

Energy is the most important issue for mankind in the twenty-first century because of the accelerating decrease in the reserves of fossil fuels and the more and more serious environmental problems (water pollution, green house effect etc.) caused by the excessive consumption of fossil fuels [1]. Looking for alternative renewable energy source for the sustainable development of our civilization is currently an inevitable and emergent assignment for scientists. Solar energy, which is an inexhaustible power flow from the sun carried by electromagnetic radiation, has already sustained the development of our civilization for several thousands of years in the form of fossil fuels [2]. How we can take full advantage of the extraordinary amount of energy that the sun supplies us with, by changing it into a directly usable and environmental friendly form is the main focus of the scientific research in this field [2–4].

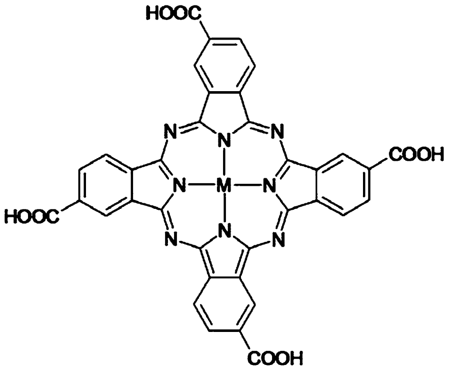
Efforts that have been made so far to change the solar energy into a directly usable energy form for our daily life include the construction of artificial photosynthesis systems [5–8], building solar cell to convert light energy directly into electricity [9–13], and synthesis of molecular machine to convert light energy into mechanical energy at the molecular level [14–17]. It is worth noting that the research on artificial photosynthesis and molecular machine has led only to hopes, not fruits so far, while the solar cell has already powered more than two million households around the world in areas where we do not have access to the central power networks [2]. The commercialized solar cells so far have been built from crystalline or amorphous silicon. There is an increasing awareness, however, that devices based on mesoscopic inorganic or organic semiconductors might show improved properties because of the interconnected three-dimensional structure. A device based on this interpenetrating network junctions has been developed by Grätzel and coworkers in the early 1990s, which demonstrated laboratory conversion efficiencies of up to 10.4% and represented a promising method for the large-scale conversion of solar energy into electricity. The key component of this device is a nanocrystalline wide-band-gap semiconductor electrode, which is associated with a sensitizer as a light-absorbing material. This device is called dye-sensitized solar cell (DSSC) or Grätzel cell [18–21].

To achieve high power conversion efficiency, the sensitizer in the DSSC should be a dye, which absorbs across the entire visible spectrum, binds strongly to the surface of the semiconductor nanoparticles, has high redox potential for regeneration after excitation, and most importantly is stable enough to exposure to sunlight for many years. The ruthenium polypyridyl complexes utilized by Grätzel come close to fulfilling these requirements, although sensitization at longer wavelength could be improved because of the low optical absorbance in the red/near IR region [22, 23]. As several chlorophyll molecules with different structure are involved in the light collection in light-harvesting arrays of photosynthesis, it is likely that better photosensitization in DSSCs could be achieved by co-sensitization of several different dyes. In addition, the ruthenium complexes are expensive because of the increasing demand in industry. Therefore, a wide variety of dyes with different structures have been developed and tested as sensitizers in the DSSCs. Among these dyes, phthaocyanine and porphyrin compounds are particularly attractive because of their similar molecular structures and photophysical properties to chlorophylls [24–26]. In the present review, we discuss on the light-harvesting and the electron-injection properties of some phthalocyanine and porphyrin compounds, which have been tested as sensitizers in DSSCs.

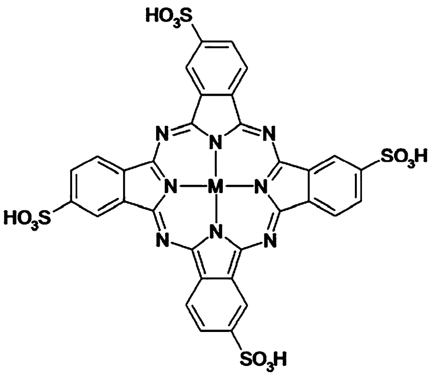
2 Phthalocyanine Sensitizers

2.1 *Phthalocyanines with Anchoring Groups at Peripheral Positions*

Phthalocyanies are well known for their high stabilities toward heat and light, large extinction co-efficient in the near IR region, the controllable redox potentials, and most importantly, the semiconducting properties [27, 28]. They were employed in the study of photo-to-electron conversion long before. For example, the research conducted by Armstrong on the photovoltaic properties of metal free, copper, cobalt, titanyl, and vanadyl phthalocyanines in the 1980s has revealed that the packing structure affects the photoelectrochemical performance of the phthalocyanine films [29–32]. Bard and co-workers had demonstrated that the behavior of the sensitized photocurrent by metal-free phthalocyanine (H_2Pc) thin films on several single-crystal n-type semiconductors correlated well with the relative positions of the energy levels of the semiconductors, H_2Pc, and the redox couples in solution. The sensitization of different metal phthalocyanines (MgPc, ZnPc, AlClPc, TiOPc, CoPc, FePc, H_2Pc) to TiO_2 and WO_3 was tested in a sandwich type cell. The efficiencies of the sensitized photooxidation of several redox couples are strongly dependent on the oxidation potential of MPc [33, 34]. All these researches revealed that phthalocyanines are promising sensitizers for semiconductor electrode in solar cell with different structures.



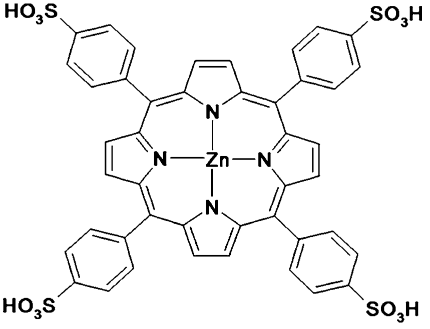
1, M = Zn, 2H



2, MTsPc M = Zn, Co, Ga, In, TiO, 2H

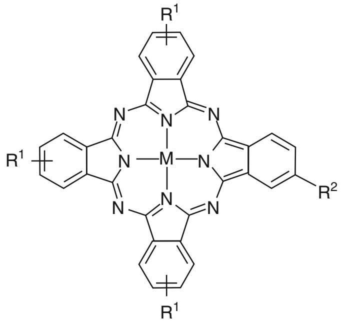
2.1.1 Symmetrically Substituted Phthalocyanines

After the invention of Gräztel cell in 1991, the importance of the binding of sensitizer on the surface of the nano-crystalline semiconductor electrode was realized and therefore phthalocyanines with anchoring groups were prepared and employed in the sensitization of nano-crystalline semiconductor electrode. The first report on the sensitization of titanium dioxide nanoparticles by phthalocyanine functionalized with carboxylic acid groups appeared in 1995 [35]. Shen and Xu prepared a zinc phthalocyanine (ZnPc) substituted with four carboxylic groups at the peripheral positions (**1**). After the adsorption of this phthalocyanine onto the surface of electrode, the absorbance of the titanium dioxide electrode was extended successfully to the visible region. At the maximum absorption band of phthalocyanine (690 nm), the incident-photon-to-current-conversion efficiency (IPCE) is about 4%, one of the highest ever reported for phthalocyanine-based photovoltaic devices. The improvement on IPCE is attributed to the fact that almost all the ZnPc molecules are in direct contact with the TiO_2 surface because of the extra large surface area of the nano-crystalline electrode. Later, the same research group modified the structure of the electrode further by introducing a layer of CdSe nano particle (Q-CdSe) onto the titanium dioxide electrode before phthalocyanine **1** was deposited. Since the optical absorption spectra of Q-CdSe particles and phthalocyanine molecules are different, a better spectral match to solar spectrum was achieved for ZnTCPc–CdSe/TiO_2 electrode. The IPCE was therefore increased to ca. 10% at the point of the maximum absorption peak at 690 nm [36, 37].



3, TsPP

Sensitization of nano-crystalline electrode by sulphonated phthalocyanine (**2**) with different central metals was also tested. Absorption spectroscopy of tetrasulphonated Zn, Co, Ga, In, TiO and metal-free phthalocyanine on a transparent titanium dioxide film electrode, which is made up of interconnected particles and pores has revealed the formation of aggregates of phthalocyanines at the surface of the electrode. Comparison of the photocurrent action spectra with the absorption spectra of the electrode reveal that the photocurrent generated only from the absorption of monomeric phthalocyanines. The aggregated phthalocyanine molecules do not contribute to the photocurrent generation. The rapid internal conversion in the molecular aggregates of phthalocyanines, which causes rapid deactivation of the excited states, hindered the electron injection from the excited phthalocyanine molecules to TiO_2 [38, 39]. In order to reduce the aggregation of phthalocyanines at the surface of the electrode, the same group has introduced a doping process for the solid films of **2** (GaTsPc) with tetrasulphonated Zn porphyrin **3** (ZnTsPP). The doping has successfully extended the absorption of GaTsPc-sensitized TiO_2 electrode and thus enhanced the light-harvesting efficiency probably because of the spectral complementarities of GaTsPc and ZnTsPP. More importantly, the photocurrent response at the Q band of GaTsPc is remarkably enhanced with 20- or 60-fold improvement, while the photocurrent response at the Soret band of ZnTsPP is markedly decreased eight-fold. This photoelectric behavior is attributed to the possible formation of phthalocyanine/porphyrin heteroaggregates during the cosensitization of the TiO_2 electrode, which prevents the formation of GaTsPc aggregates on the one hand and leads to a low-lying charge separated state between porphyrin and phthalocyanine on the other hand. The latter quenches the photogenerated charge carriers of the Soret band of ZnTsPP [40, 41].



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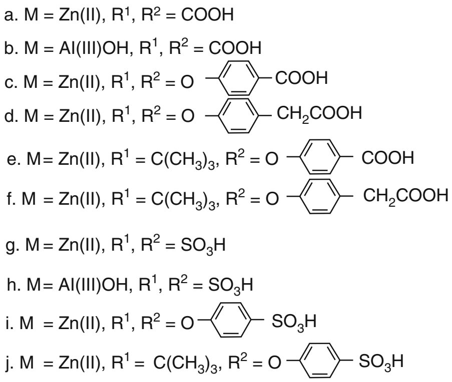
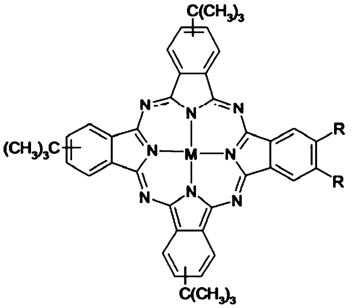
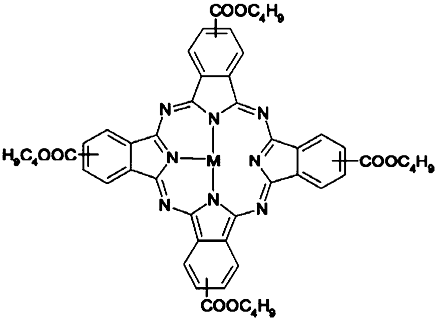


An extensive study on the sensitizing properties of phthalocyanines to TiO_2 nano-crystalline electrode was reported by Grätzel and co-workers in 1998. They connected carboxylic groups to the zinc(II) or aluminum(III) phthalocyanine ring with different linkages and prepared a series of phthalocyanine compounds which can anchor to the surface of TiO_2 nanoparticles (**4** and **5**). To get an efficient electron injection from phthalocyanines to the electrode, the anchoring groups should be connected to the phthalocyanine ring as close as possible. Both sulphonyl and carboxylic acid groups could achieve a stable binding to the surface of TiO_2, which did not present significant influence on the electron injection. The ZnPc presented peak IPCE as high as 45%, whereas aluminum phthalocyanine under identical conditions gave only 15% IPCE. This result suggested that the central metal of phthalocyanine played an important role in the sensitizing process. By introducing small organic molecules, which can coordinate to the central metal ions of phthalocyanine along the axial direction, the aggregation of phthalocyanines can be harnessed efficiently. Similarly, the aggregation of phthalocyanines on the surface of TiO_2 nanoparticles can also be reduced efficiently by introducing *tert*-butyl groups at the peripheral positions. This provides a facile way to improve the sensitizing efficiency of phthalocyanines. The most notable finding of this research is that phthalocyanines are strikingly stable on the surface of TiO_2 under continuous light exposure. It is expected that phthalocyanines could be applied in the solar cells which can transmit some visible light but absorb strongly in the near IR region [42].

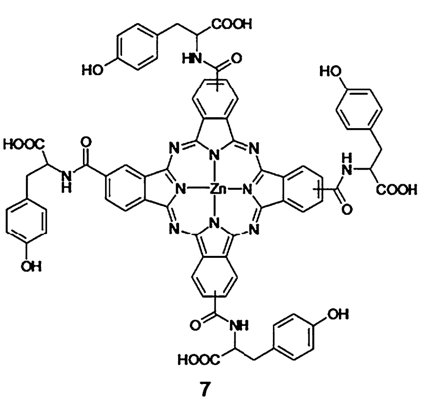


5 R = o- -SO$_3$H



6 M = Zn or 2H

Anchoring groups in the ruthenium (II) polypyridyl complexes are proven to be essential for the sensitization [20, 43]. The carboxylate groups establish good electronic coupling with the Ti (3d) conduction band orbital manifold. However, phthalocyanines with carboxylic acid groups have poor solubility in organic solvents and are difficult to be purified. Therefore, He and co-workers have developed an alternative anchoring method for phthalocyanines. This new method includes a deprotonation step of the surface of TiO_2 with $(CH_3)_3COLi$ and then followed with a reaction of ester groups of phthalocyanine with the deprotonated surface of TiO_2. With this method, He and co-workers had successfully deposited free-base and zinc 2,9,16,23-tetra(*n*-butoxycarbonyl)phthalocyanines (**6**) onto the TiO_2 nano-crystaline electrode. The IPCEs measured for the metal free and ZnPc were 0.30% and 4.3% respectively, indicating that ZnPc is a better sensitizer for TiO_2 than metal free phthalocyanine [44]. Later, He and co-workers connected tyrosine (**7**) and glycine (**8**) groups to the peripheral positions of phthalocyanine and successfully prepared a Grätzel type cell with high IPCE (24%). Incorporation of tyrosine groups makes the dye ethanol-soluble and decreases considerably surface aggregation of the sensitizer due to the steric effects and as a result improves the solar cell performance. The transient absorption spectra revealed that the electron injection from phthalocyanine to the conduction band of TiO_2 occurred in ~ 500 fs while the charge recombination happened in ~ 300 ps. Comparing with those of bipyridyl ruthenium complexes, the faster charge recombination is the dominating factor, which encumbers a better sensitization [45].



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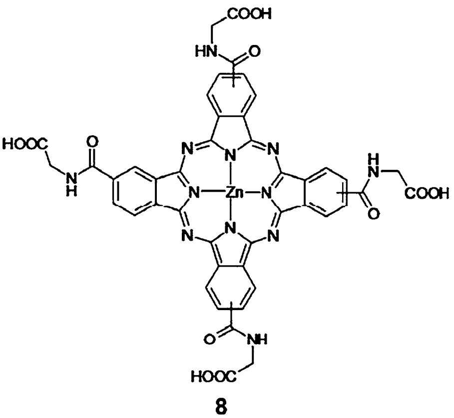

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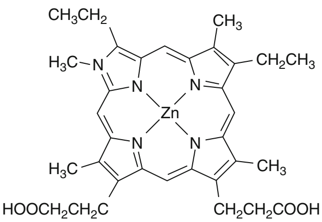
In order to clarify the electron injection and recombination process, the alignment of the energy levels at the interface between phthalocyanine **8** and TiO_2 were studied by the combination of X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) measurements. The results indicate that energy of the LUMO of **8** (0.1 eV above that of the conduction band of TiO_2) fits well with the energy requirements for efficient electron injection into the conduction band of TiO_2 from the excited state of the molecule. However, the fast charge recombination caused the low conversion efficiency. Tuning the redox potential matching between the dye and the redox couple in the electrolyte or adding electron donating groups around phthalocyanine to suppress the charge recombination process are expected to be efficient ways to improve the conversion efficiency of the solar cell [46].

With the help of transient absorption spectra, Durrant and coworkers had systematically examined the dependence of the charge recombination kinetics upon the dye oxidation potential and spatial separation of the dye HOMO orbital from the metal oxide surface. The dyes they used include a series of ruthenium bipyridyl dyes in addition to porphyrin and phthalocyanine dyes (**9**–**12**). A strong correlation is observed between the recombination dynamics and the spatial separation, which is found to be in agreement with electron tunneling theory. However, the recombination dynamics were not insensitive to the variations in redox potential of dyes because the free energy changes of the recombination reaction lying near the peak of the Marcus free energy curve. This research has pointed out for the first time that to get a better conversion efficiency, the distance between the dye and the nanoparticle surface is crucial and the shorter distance between the dye and the surface of the nanoparticle will not definitely lead to higher conversion efficiency [47].



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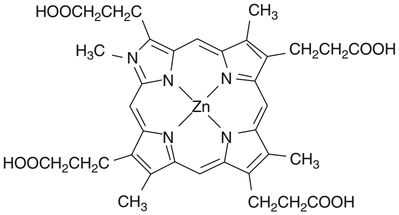

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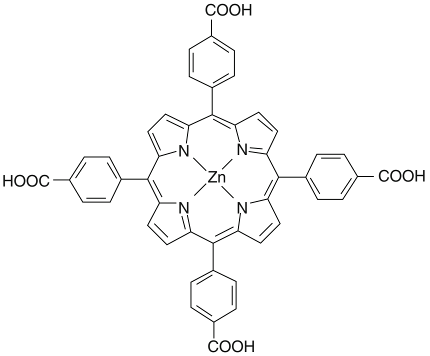

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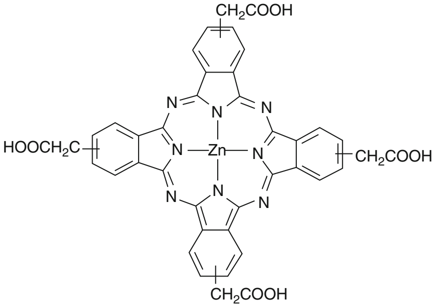

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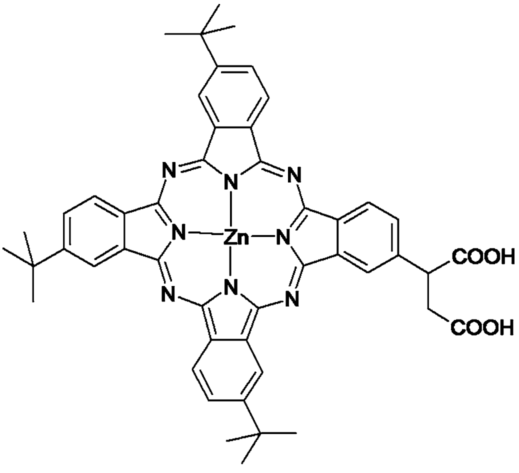
2.1.2 Asymmetrically Substituted Phthalocyanines

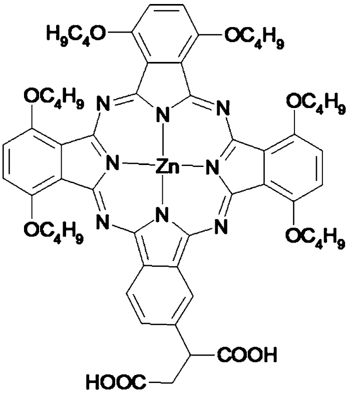
In order to achieve efficient sensitization of a nano-crystalline TiO_2 electrode, the sensitizer requires not only proper energy levels but also directionality for their excited states. The directionality should be arranged to provide an efficient electron transfer from the excited dye to the TiO_2 conduction band by good electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and the Ti(3d) orbital. The energy levels of LUMO of phthalocyanines can be tuned by incorporation of electron donating or withdrawing groups at bay or peripheral positions. The directionality of LUMO can be varied by changing the relative orientation of phthalocyanine ring toward the surface of TiO_2 nanoparticle. Therefore, the substituents around the phthalocyanine ring are endowed with two different functionalities, tuning the energy level of LUMO and the orientation of the phthalocyanine aromatic plane at the same time. This requirement leads to the development of phthalocyanine sensitizers with asymmetrically distributed substituents.

In 1999, Nazeeruddin and co-workers reported the first example of the application of asymmetrical phthalocyanine in DSSC. They have tested several asymmetrically substituted phthalocyanines (see **4** and **5** for the structures) with both alkyl groups and –COOH or SO_3H anchoring groups and zinc or aluminum central metals. But the results revealed that these compounds do not show any advantages over the corresponding symmetrically substituted compounds under identical conditions [42]. However, the continued efforts on the research of asymmetrical phthalocyanines have seen a large progress recently. Nazeeruddin designed a novel asymmetrical phthalocyanine (**13**) with three *tert*-butyl groups and one carboxylic acid anchoring group attached at the peripheral positions. The *tert*-butyl groups together with the carboxylic acid groups act as "push–pull" groups, which tune the energy levels of LUMO. The carboxylic acid groups graft the dye molecules onto the surface of TiO_2 to provide intimate electronic coupling between its excited-states and the conduction-band manifold of the semiconductor. The bulky *tert*-butyl groups can also minimize the aggregation due to the large steric hindrance. The IPCE of the standard Grätzel solar cell based on **13** is as high as 75% at 680 nm and an overall power conversion efficiency of 3.05% is achieved. The most impressive is that this compound presents high IPCEs in solid state cell as well. This research has successfully demonstrated the importance of creating directionality of the excited states in the design of new phthalocyanine sensitizers [48].



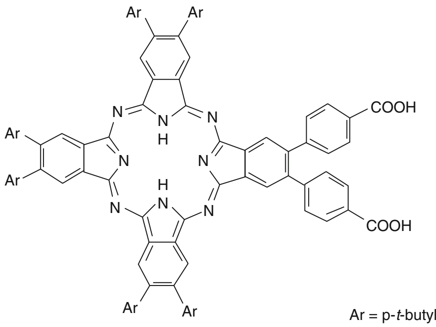
13, PCH001

On the basis of the same "push–pull" strategy, Giribabu and co-workers designed a series of phthalocyanine compounds (**14**) with electron donating groups connected at the bay positions of phthalocyanine and the same anchoring groups with that of compound **13** at peripheral positions. But the IPCE of the solar cell made from **14** is significantly smaller than that made from compound **13**. The low IPCE can be certainly attributed to a low electron-injection yield, because a residual fluorescence emission was detected upon adsorption of the dye on TiO_2. This suggests that the radioactive process competes with the electron injection, thus decreasing the branching ratio between these two deactivation channels [49].



14, PCH003

The "push–pull" strategy has also been employed in the design of a series of asymmetrical metal free (**15**) or ZnPc (**16**) with large steric hindrance. In this series of phthalocyanines, the aryl groups (phenyls) were connected directly to the peripheral positions. Since the two neighboring peripheral positions are occupied by the same functional groups, these compounds can be isolated free of regioisomers. The large steric hindrance of the phenyl groups at the peripheral positions are expected to reduce the tendency of aggregation remarkably. The carboxylic acid groups could guarantee stable immobilization of the dye molecule on the surface of TiO_2 nanocrystalline. The Grätzel cell based on **15** does not show any photocurrent response because of the low laid first excited state. However, the ZnPc **16** presents 0.57% power conversion efficiency and 4.9% peak IPCE. Introduction of axial coordination compound (chenodeoxycholic acid) do not show noticeable difference on the cell performance, indicating the aggregation of **16** has been suppressed by the large steric hindrance effectively. The performance of the cell based on **16** is not as good as that based on **13**. This could be attributed to the small driving force for the electron injection from the dye molecule to TiO_2 as well as the poor electronic coupling between the LUMO of phthalocyanine and the conduction band of TiO_2 due to the larger distance between the surface of TiO_2 nanoparticle and sensitizer molecule [50].



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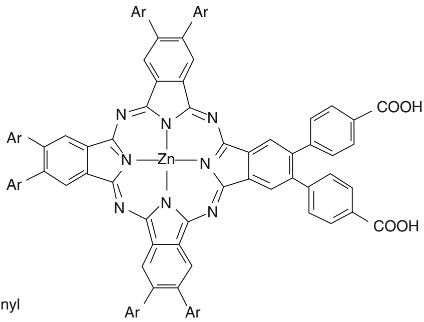
Ar = p-*t*-butylphenyl



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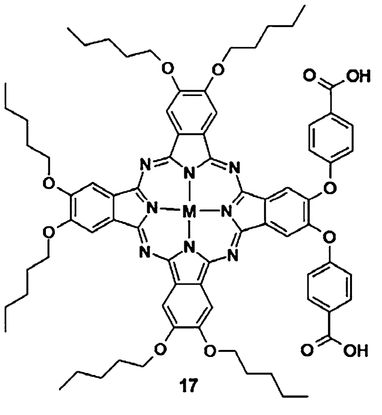
A ruthenium phthalocyanine complex with peripheral linked carboxylic groups and axial coordination (**17**) has been tested as sensitizer for TiO_2 nanocrystalline electrode. The phthalocyanine molecules were anchored onto the surface of TiO_2 with the macrocyclic plane assumed to be perpendicular to the semiconductor surface while the 4-methylpyridine axial ligand served to prevent aggregation. An IPCE of 23% at the absorption peak and overall conversion efficiency of 0.40% were recorded for the testing DSSCs. However, the Zn analog, without the axial picoline ligands, exhibited poorer efficiency and was attributed to the aggregation. This finding has revealed the high efficiency of the axial coordinated groups on reducing the aggregation of phthalocyanines and provided a promising way to improve the sensitization performance of phthalocyanines [51].



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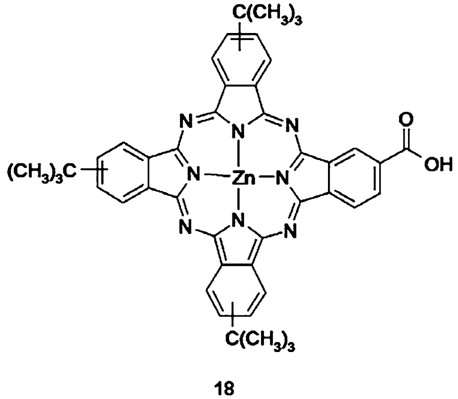

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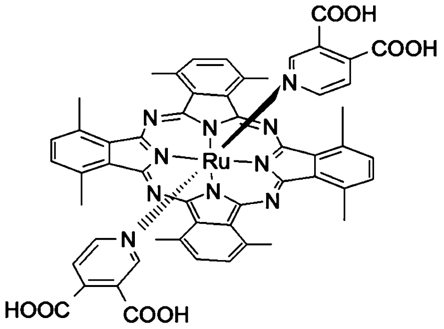
For the purpose of reducing the aggregation of phthalocyanines on the surface of TiO_2, co-deposition of asymmetrical substituted phthalocyanine with chenodeoxycholic acid has also been employed. The co-deposition of chenodeoxycholic acid with phthalocyanine **18** is expected to reduce the aggregation further and thus could improve the performance of the solar cell. The absorption spectra of the solid electrode revealed that the presence of chenodeoxycholic acid indeed suppresses the aggregation of phthalocyanine, but reduced the phthalocyanine sensitizer's load too, as observed from the absorption and IPCE data. The decrease in the load of sensitizers induced a significant drop on the IPCEs [52].

Co-adsorption strategy has also been extended to two dye systems with the desire of expanding the responding spectra of the electrode and improving the overall conversion efficiency. A successful example was presented by Nazeeruddin and co-workers in 2007 [53]. They co-adsorbed phthalocyanine **18** and a triaryl amino dye (JK2) onto the surface of TiO_2. An astounding increase on IPCE was observed for the solar cell based on this co-sensitized electrode. The IPCE at 690 nm was recorded as high as 80% with an overall energy conversion efficiency of 3.52% under standard illumination conditions. The time resolved emission spectra revealed efficient electron injection from the excited states of the sensitizer to the conduction band of TiO_2 with very fast kinetics. The laser transient-absorption spectroscopy measurement indicates a charge recombination lifetime of 3.2 ms, which is of the same order of magnitude as that of the standard ruthenium dye used for efficient DSSC devices. Improving the conversion efficiency by co-sensitization with two or more dyes with compensated absorption spectra has been highlighted by Robertson in 2008 [54]. The co-sensitization strategy may take the overall energy transfer efficiency beyond the high of 10–11% in the near future [53, 55].

2.2 Phthalocyanines with Anchoring Groups at Axial Direction

Aggregation of phthalocyanines on the surface of TiO_2 nanoparticles always induces significant drop on the overall energy conversion efficiency because of the rapid non-radioactive deactivation of the dye excited states in aggregates. Axial coordination has been proved to hinder the aggregation of phthalocyanine efficiently. Therefore the axial ligand functionalized with carboxylic acid groups are expected not only to hinder the aggregation, but also to graft the phthalocyanines to TiO_2 in a "face-on" configuration.

Ruthenium phthalocyanine complexes have spectral, electronic, photoelectrochemical and redox properties that satisfy the requirement of a good sensitizer for DSSC and have therefore been targeted for investigation. Nazeeruddin has reported the first use of a ruthenium phthalocyanine (**19**) as a sensitizer in a DSSC in 1998. In this compound, eight methyl groups were connected at the bay positions while 3,4-dicarboxypyridine was connected at the axial direction by coordination. The carboxylic acid groups help anchoring the dye molecule on the surface of TiO_2. The resulting DSSC had an IPCE of over 60% in the near IR region (660 nm). This research established an efficient new pathway for adsorption of phthalocyanines onto the surface of TiO_2 [56].



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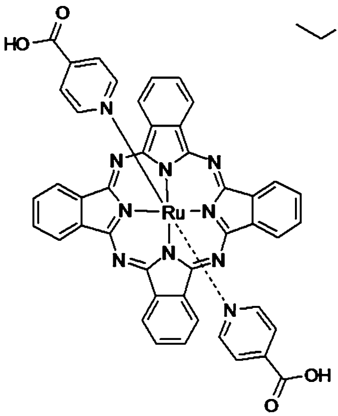
Yanagisawa had compared the sensitization properties of an axially anchoring phthalocyanine (**20**) with that of a peripherally substituted phthalocyanine (**21**) in the identical conditions. Phthalocyanine **20** with axially connected carboxylic acid groups can sensitize the TiO_2 electrode efficiently with an IPCE of 21% at 640 nm and an overall conversion efficiency of 0.61% was found for the standard testing DSSC. When pentyloxy groups were introduced at the peripheral positions and extra axial coordination groups introduced to prevent the aggregation, phthalocyanine **21** showed a less efficient sensitization to the TiO_2 electrode relative to phthalocyanine **20** with the IPCE decreased to 6.6% at 640 nm and an overall energy conversion efficiency reduced to 0.58%. The reduced sensitization performance of **21** was attributed to the pentyloxy groups at peripheral position, which may reduce the stability of the adsorption of phthalocyanine **21** on the surface of TiO_2 [57].



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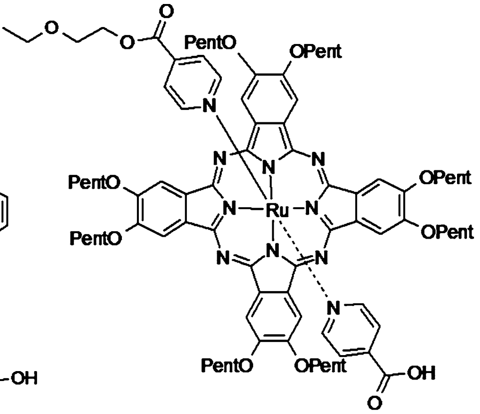

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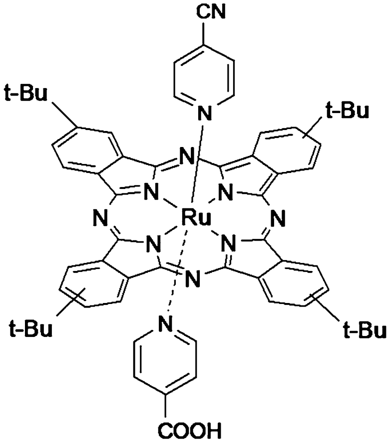
The X-ray and UV-photoemission spectroscopy study has revealed that ruthenium (II) phthalocyanine **20** has similar HOMO and LUMO energy with that of *cis*-bis(4,4-dicarboxy-2,2-bipyridine)-bis-(isothiocyanato)-ruthenium(II), $[Ru(dcbpy)_2(NCS)_2]$, the most efficient sensitizer so far. The oxidation potentials for both ground and excited states are also similar for these two complexes. The energy difference between the LUMO of phthalocyanine **20** and the TiO_2 conduction band was favorable for an efficient electron injection from phthalocyanine to TiO_2. This result suggests that ruthenium phthalocyanines, like **20**, are principally very promising sensitizers for DSSC [58].

The electron injection from ruthenium phthalocyanine with axially connected anchoring group to TiO_2 was further investigated by Durrant and co-workers with transient absorption experiments. They employed a ruthenium phthalocyanine with two axially coordinated pyridine groups (**22**). One of the axially connected pyridine bears a carboxylic acid group, which serve as a binding site, while the other one is substituted with a CN. The research reveals surprisingly that the electron injection is from the triplet states of ruthenium phthalocyanine. The long lifetime of the triplet states leads to efficient electron injection occurred in hundreds of nanoseconds and an IPCE magnitude of 45%. This finding suggests clearly that the ultrafast electron injection from the singlet states is not a prerequisite for high IPCEs. Optimizing the kinetics of the triplet states of ruthenium phthalocyanines might be a key factor to achieve a high IPCE for the ruthenium phthalocyanine-sensitized solar cell [59].



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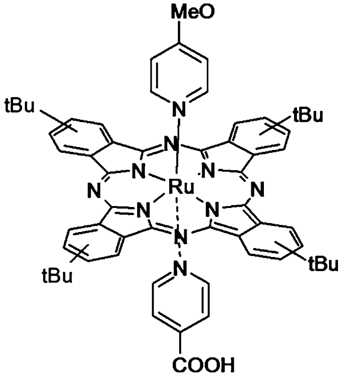
Compared with the ruthenium polypyridyl complexes (N719), most of phthalocyanine dyes used for the sensitization of TiO_2 gave significantly lower output voltages. For a deep understanding of this output voltage reducing, O'Regan and co-workers has investigated the electron injection and recombination process of a ruthenium phthalocyanine (**23**) with different axial coordinated groups at the interface of TiO_2 or SnO_2. Compared with the polypyridyl ruthenium complexes, the charge recombination processes are accelerated by the ruthenium phthalocyanine probably because of the binding of phthalocyanine with I_2 which causes significant increase on the local concentration of I_2 close to the surface of the TiO_2. This accelerated charge recombination process induces the drop of output voltage of DSSC. The problem with these ruthenium phthalocyanines is inherent in the structure and is shared with other organic dyes with large aromatic rings, including porphyrins, coumarins, perylenes, cyanines, merocyanines, and azulene. Uncovering the mystery between the structure and charge recombination rate is a key step to improve the sensitization of organic dyes to the TiO_2 nano particle further [60].



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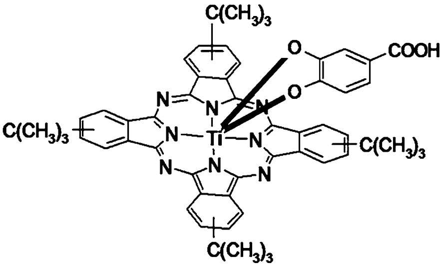
Durrant and co-workers has also prepared a novel titanium phthalocyanine (**24**) with the anchoring groups attached at the axial direction. The choice of Ti as a central metal allows axial ligation to the metal center, which is expected to reduce the aggregation efficiently. The carboxylic acid group on the axial ligand can anchor the dye to the nanocrystalline particles with the plane of the phthalocyanine ring parallel to the surface of the nanoparticle. The bulky peripheral *tert*-butyl groups help to solubilize the dye in conventional organic solvents as well as to avoid dye aggregation. Moreover, the distance between the HOMO orbital of the chromophore and the TiO_2 surface can be controlled by the axial ligation. The absorption spectra of the electrode revealed a large dye molecule loading and the absence of aggregation for the dye molecules adsorbed. The quick electron injection from phthalocyanine to TiO_2 is suggested by the strong quenching of the fluorescence of phthalocyanine and it is further confirmed by the transient absorption studies. However, the electron injection is wavelength dependent. The efficient electron injection happened after Soret band excitation, but only negligible electron injection occurred after the Q-band excitation. The observation has shown for the first time the potential of titanium phthalocyanine for the sensitization of nanocrystalline TiO_2 films. The combination of catechol axial attachment to the TiO_2 surface and *tert*-butyl peripheral groups allows efficient sensitization with no dye aggregation. These titanium phthalocyanines represent an attractive route to the development of efficient, red absorbing sensitizer dyes for DSSC [61].



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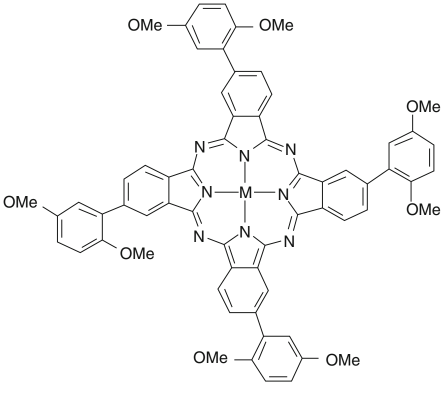
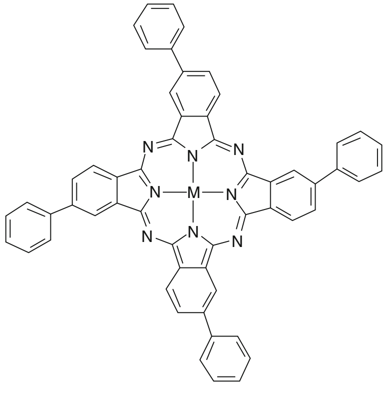
2.3 Phthalocyanines Without Specific Anchoring Groups

Although plenty of researches revealed that anchoring groups on phthalocyanine are essential for the sensitization, several phthalocyanines without anchoring groups can indeed sensitize the TiO_2 electrode with reasonable efficiency. Aranyos and co-workers have reported that a series of metal free phthalocyanines (**25**, **26**) with aryl groups connected at the peripheral positions show surprising sensitization to TiO_2 nano-crystalline electrode. Despite the absence of conventional anchoring groups in compound **25** and **26**, such as –COOH or SO_3H, the DSSC based on these compounds show reasonable IPCEs in the range of 5–9%. It is the aryl groups connected at the peripheral positions that are designated to facilitate the absorption of dyes at the surface of the nanoparticles. More interestingly, these compounds show sensitization even in aggregated states. Although without further discussion on how the aggregated phthaloycyanines inject electrons to TiO_2, one should suspect a quicker electron injection from these aryl substituted phthalocyanines than that from phthalocyanines with –COOH or SO_3H. The results also indicate that not only the directly adsorbed monolayer of dye injects electrons into the oxide, but also the molecules aggregated on top of this layer contribute to the photocurrent [62].

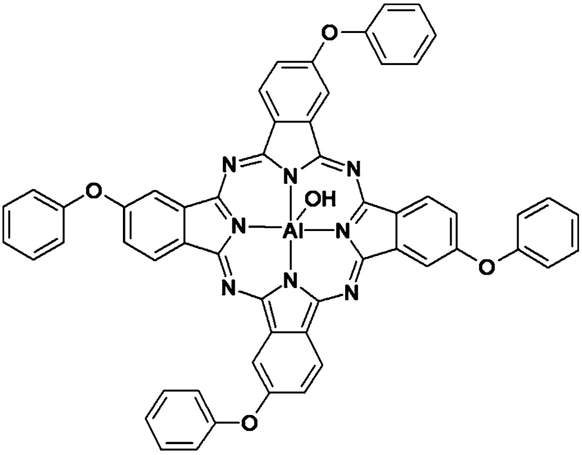


25, M = 2H, or Zn



26, M = 2H, R = H

In 2003, another phthalocyanine (**27**) with aluminum in the center but without –COOH or SO_3H as anchoring groups attached has been successfully applied in the Grätzel type cell. To prevent the aggregation of the phthalocyanine molecules on the surface of the electrode, an alkyl carboxylic acid with long alkyl chain (myristic acid) has been deposited to the surface of the electrode simultaneously. The peak IPCE of the electrode sensitized by **27** and myristic acid has been promoted for 1.7 times relative to that sensitized by pure **27**. The results indicate that the addition of myristic acid can suppress the aggregation of phthalocyanine significantly and thus improve the performance of the solar cell [63]. The successful sensitization of TiO_2 nano-crystalline electrode by phthalocyanine **25–27** strongly suggests that the aryl groups connected at the peripheral positions might be efficient anchoring groups too. Careful design on the connection position and the functionality on the aryl groups might lead to unpredictable results. More attention should be paid to these non-carboxylic acid anchoring phthalocyanines in the near future.



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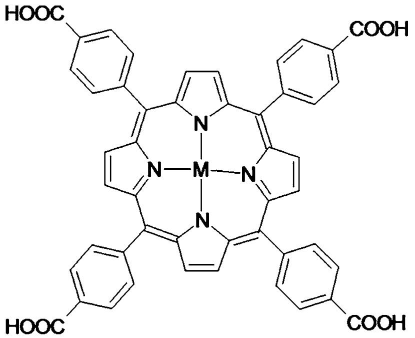
3 Porphyrin Sensitizers

The use of porphyrins as sensitizers for the nano-crystalline electrode in DSSC is particularly attractive given their important role in photosynthesis and the relative ease modification on molecular structure. Not only the porphyrin monomers, but also the large porphyirn arrays have been tested extensively as sensitizers of wide-band-gap semiconductors like NiO, ZnO and TiO_2 in the past several decades. The focus of this section is the various molecular structure modification of porphyrins for the purpose of applying as sensitizer in DSSCs.



28 M=2H, Zn

3.1 Porphyrin Monomers

3.1.1 Porphyrins with Anchoring Groups Connected at *Meso*-Phenyls

The most commonly used porphyrins in DSSC are free-base and zinc derivatives of the *meso*-benzoic acid substituted porphyrin **TCPP (28)**. Grätzel and co-workers had investigated the sensitization of **28** to TiO_2 in 1987. The energy levels of LUMOs reside right above the conduction band of the TiO_2, which ensure an efficient electron injection from the excited states to the conduction band as revealed by the steady state fluorescence and transient absorption spectra. The electron injection process was found to be very sensitive to the PH of the solution. No sensitization was observed in alkaline solution because of lack of adsorption of the anionic dye on the negatively charged surfaces of TiO_2. The electron injection can occur only from the adsorbed porphyrin molecules [64]. The efficient electron injection was further proved by the work of Fox and co-workers in 1988 [65]. In a DSSC with **28** as sensitizer, Goossens and co-workers found that the electron traps at the interface of dye/TiO_2 affected the energy conversion efficiency significantly. The electronic traps can be filled by a negative potential applied at the interface and therefore enlarge the active region where charge separation takes place, which finally leads to an enhanced collection efficiency [66].

The sensitization behavior of porphyrin with or without carboxylic acid groups was compared by Waclawik and co-workers. Their results indicate that the presence of carboxylic acid groups indeed generated higher IPCE values compared to that without carboxylic groups. The difference is ascribed to poor electronic coupling of the sensitizer without carboxylic acid groups to the titania conduction band [67].

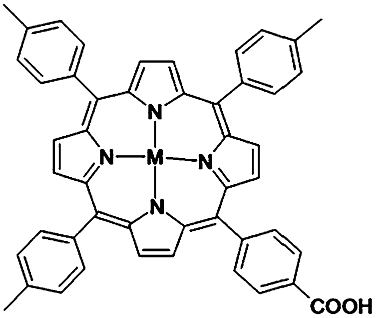
Wamser and co-workers have investigated the nature of the binding of **28** onto the TiO_2 electrodes by using X-ray photoelectron spectroscopy (XPS) and Resonance Raman Spectroscopy (RRS). The XPS spectra of TiO_2 revealed the changes of the binding energy of both O (1 s) and Ti (2p3/2) upon adsorption of **28**.

Similarly, the peaks of O (1 s) and N (1 s) of **28** were also shifted to a higher binding energy. All these changes suggest the efficient binding of **28** on the surface of TiO_2. The RRS results indicated that for cases in which **28** was adsorbed onto TiO_2 films from a much diluted solution, the porphyrin molecules interact mainly with the TiO_2 surface. Contrarily, if porphyirn were adsorbed onto the TiO_2 films from a concentrated solution, the RRS spectra were similar to that of TCPP powder, indicating the dominance of porphyrin–porphyrin interactions in this film. The optimized Grätzel cells with **28**-sensitized TiO_2 and deoxycholic acid as co-adsorbent gave good solar-energy conversion efficiencies. The IPCE was 55% at the Soret peak and 25–45% at the Q-band peaks and an overall energy conversion efficiency of about 3% [68]. The chemical adsorption of TCPP on the surface of TiO_2 nanoparticle was also confirmed by XPS, atomic absorption spectrometry (AAS), Fourier transform infrared spectroscopy (FT-IR) and UV-vis spectroscopy, etc. [69].

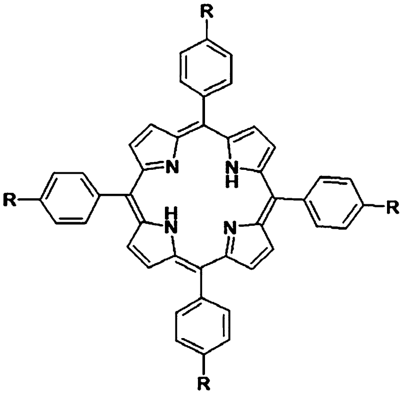
Durrant and co-workers have compared the electron injection and recombination processes of **28** or Zn-**28** with that of N3 (a famous ruthenium polypyridyl complex with very high IPCE). Their experiments revealed that the electron injection and recombination kinetic for these three dyes on the surface of TiO_2 are almost identical. The high IPCE for N3 dye probably originates from the electron transfer from the iodide redox couple to the dye cations. It is also possible that the lower efficiency of porphyrin sensitizers was caused by the annihilation of the excited states between the neighboring porphyrin molecules because of the closed proximity [70].

For the purpose of determining the ion potentials of both TiO_2 and dyes adsorbed under working conditions, Inoue measured the UV photoemission yield under an atmospheric condition by using a surface analysis apparatus. The results suggested that the adsorption of dyes on the surface of TiO_2 caused significant shift on the LUMO energy levels. This finding suggests that the energy level alignment at the interface, which is estimated from the vacuum levels or oxidation and redox potential that are independently measured, is inappropriate and these shifts must be taken into account in the discussion on the energy levels of DSSC [71]. The overall energy conversion efficiency of the DSSC sensitized by monocarboxylic acid substituted porphyrin can be improved further by doping of TiO_2 nanoparticle with Nb, Ge, or Zr. The improvement is attributed to the negative shift on the conduction band of TiO_2 electrode. The Ge-doping of TiO_2 electrode sensitized by porphyrin could promote the over all energy conversion efficiency to as high as 3.5% [72].

As the anchoring groups in the dye molecules have been proved to play a key factor on the sensitization performance, different anchoring groups with different numbers have been investigated for the porphyirn sensitizers. Ma and co-workers have compared the sensitization properties of porphyrin with only one carboxylic group (**29**) to that of the porphyrin with four carboxylic groups (**28**). Their research revealed that the number of carboxylic acid groups does not vary the binding behavior dramatically, but it indeed influences the fluorescence spectra of the adsorbed porphyrin. The IPCE and the overall energy conversion efficiency for **28** are higher than that of **29** probably because of the more stabilized adsorption on the surface of TiO_2 nanoparticles by the four carboxylic acid groups [73]. A comparison on the binding ability between carboxylic acid and sulphonic acid group has been made by the same group. Ma and co-workers have prepared a series of metal free porphyrins connected with carboxylic acid groups (**28**), sulphonic acid groups (**30**) or hydrogen respectively. The binding strength of the porphyrin on the surface of TiO_2 was found to drop following the order of –COOH > SO_3H > H while the ICPE and the overall energy conversion efficiency decreased following the same order [74].

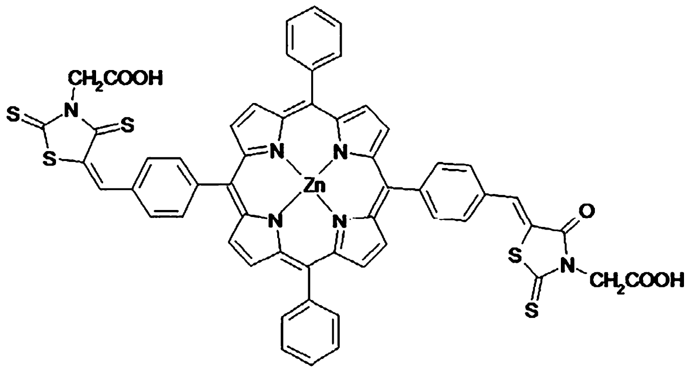


29 M=2H



30 R = SO_3H, H

Giribaru has prepared a novel porphyrin sensitizer (**31**) by connecting two rhodanine acetic acid groups at *para* position of *meso*-phenyl groups. The IPCE of the solar cell fabricated from this dye is 45% at Soret band and 20% at Q band; both of them are higher than that of the porphyrin with only one rhodanine acetic acid group. This may be due to the more stable binding of **31** on the surface of TiO_2 nanoparticle, which induces more efficient electron injection to the conduction band of TiO_2 [75].



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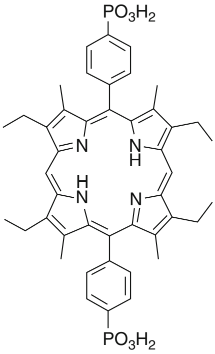

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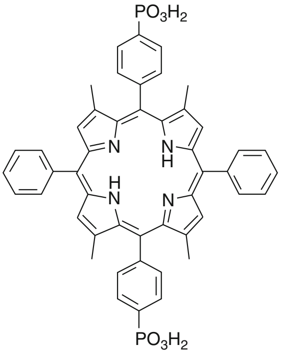

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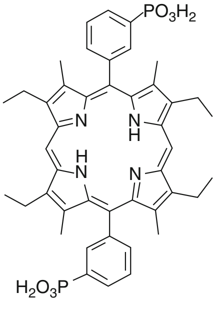

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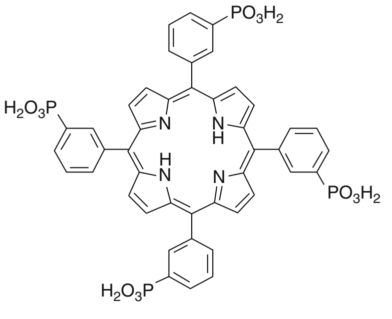

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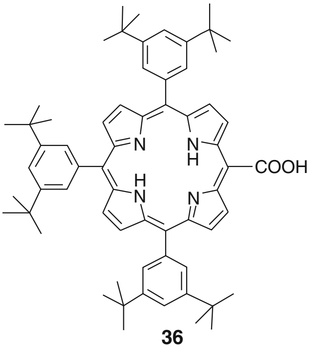
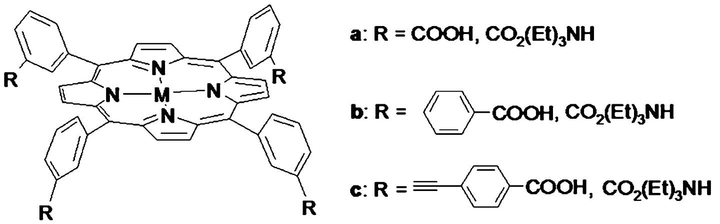


36

Odobel's research on the application of a series of new free base porphyrins (**32**–**36**) as photo-sensitizers in DSSC indicates that the anchoring groups seem to have no effect on the sensitization performance. However, the substituted position of anchoring group has great influence on the overall performance of the DSSC. This can be interpreted as due to differences in the orientation and distance of the dye molecules with respect to the TiO_2 surface imposed by the directionality of the anchoring groups, which lead to significant difference on the electronic coupling between porphyrin and TiO_2. Compared with porphyrin **32** and **33**, compound **34** presents a significant higher IPCE (21% vs. ~10%) due to the face-on configuration of porphyrin ring on the surface of TiO_2. Although porphyrin **36** and **28** exhibit quite similar excited state, oxidation potentials and similar absorption and emission characteristics, they lead to very different IPCE values in identical standard DSSCs. Porphyrin **36** bears the –COOH anchoring group directly on the aromatic core, which allows stronger electronic coupling with TiO_2 [76].

The effects of the connecting position of anchoring groups on the sensitization behavior of porphyrin compounds were further examined by Galoppini in 2007. They tested the sensitizing properties of a series of porphyrin with carboxylic acid or ammonium salt groups attached at different positions with linkages of different length. Both –COOH and $COOEt_3N^+$ H derivatives were employed for the binding studies as well as solution studies. When anchoring groups were connected at *meta* positions on the *meso*-phenyl rings (**37**), the porphyrin molecules preferred a planar binding mode to the metal oxide surfaces with no obvious aggregation.

But the porphyrin with carboxylic groups connected at *para* position on the *meso*-phenyl rings presented aggregation, suggesting close packing of the dye molecules on the semiconductor surface. Greater sensitizing efficiencies were found for the *meta*-substituted porphyrins and were explained in terms of a more efficient charge injection into the TiO_2 conduction band from rings that lie flat, and closer to the surface. The length of the bridge between the carboxylic acid groups and the porphyrin ring was found to affect the sensing efficiency significantly because it determined the distance between the porphyrin and TiO_2 nanoparticle surface. Porphyrin with two phenyl ring as bridge (**37b**) presented the highest IPCE. The longer or shorter bridge led to significant drop on the IPCEs. Ammonium salt groups were revealed for the first time to be good anchoring groups with similar binding abilities to that of carboxylic acid groups [77].



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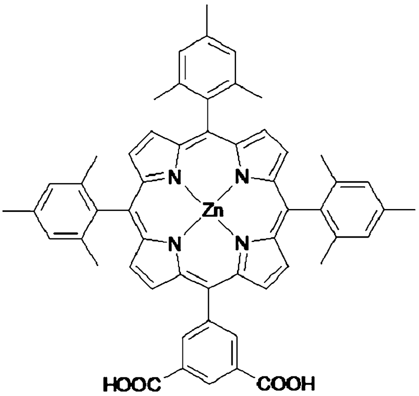

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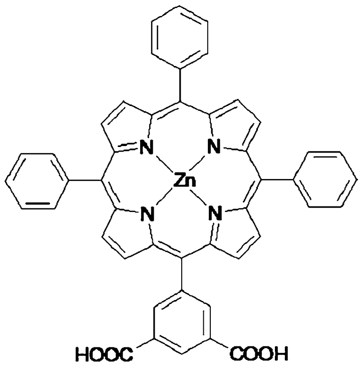

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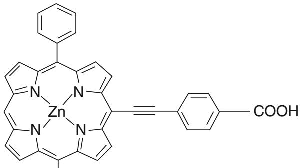
Porphyrin **37a** and **37b** have also been employed as sensitizer for a TiO_2 nanotube electrode. For comparison purpose, asymmetrical porphyrin sensitizer with two carboxylic acid groups (**38, 39**) and **28** have also been tested under identical conditions. The DSSC fabricated from these sensitized TiO_2 nanotube presents enhanced charge-collection efficiency respect to the nanoporous TiO_2 film built from TiO_2 nanoparticles. All the tested five porphyrin sensitizers exhibited efficient sensitization to TiO_2 nanotube as revealed by the photocurrent action spectra.

Among these five porphyrin senstizers, **37b** is the best performer. The next is **39**, then **37a** and **38** behave similarly, and finally **28** is the worst performer. The better IPCE performance of **37b** with respect to **37a** was attributed to the hindered back electron transfer by the longer bridge. The lower performance of **28** could be linked to its lower extinction coefficient [78].



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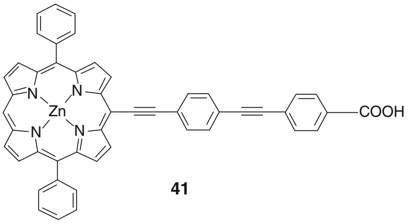

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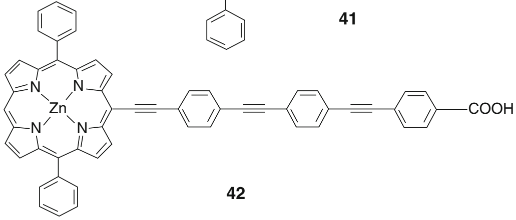

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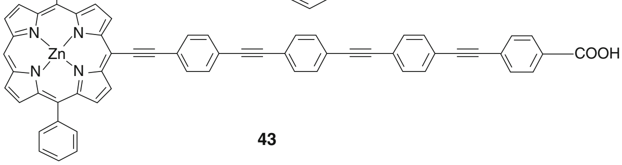

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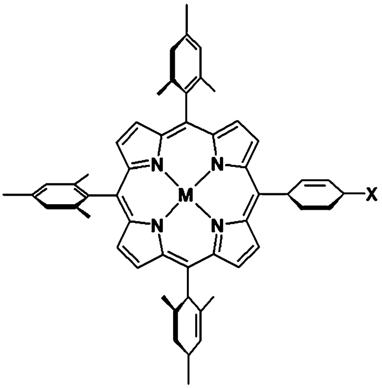
Very recently, the effects of distance between the sensitizer and the surface of TiO_2 on the sensitization process were further addressed by Lin and co-workers. They prepared a series of porphyrin compounds (**40–43**) with only one anchoring group. The anchoring group was connected with the porphyrin ring by phenylethylnyl bridges of different lengths [79]. The efficiencies of power conversion of the devices fabricated from these porphyrin dyes decreased systematically along with the increase in the length of the phenylethylnyl bridges. But the transient absorption studies revealed that the kinetics of fluorescence quenching of porphyrin was not affected by the length of he bridges, suggesting similar electron injection rate for these porphyrins. It was the back electron transfer from the conduction band of TiO_2 to the dye molecule that was responsible for the decreasing sensitization efficiency.

Meyer has tested the sensitization performance of porphyrins with only one functional group (–COOH, PO_3H_2) and different central metal ions (**44**). Methyl groups were introduced to the 2,4,6 positions of phenyl group which help to keep a perpendicular configuration for the four phenyl groups relative to the macrocycle plan. Their results indicate that all these porphyrins can anchor to the surface of TiO_2 with high stability. The photocurrent and IPCEs were found to be not affected by the nature of anchoring groups. However, they were found to be pH dependent due to the variation on the TiO_2 conduction band edge potential along with the changes of pH. The sensitization of porphyrin to TiO_2 was "turn-off" when the electrolyte pH rose above 10. This finding is important because it reveals the origin of the pH-dependent behavior of the sensitizer for the first time [80].



M = 2H, X = COOH; M = Zn, X =COOH;
M = Pt, X = COOH; M = Zn, X = PO_3H_2

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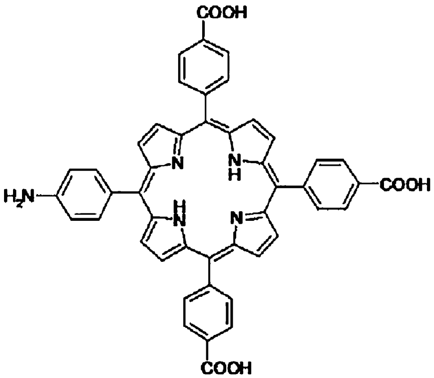

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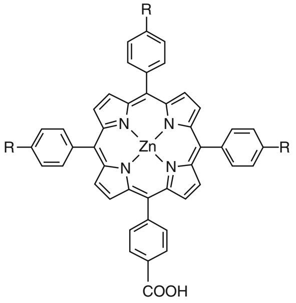
Another interesting work conducted by Wamser and co-workers in the field of porphyrin monomer sensitizers is the functionalization of tetraphenylporphyrin at the *para* positions of *meso*-phenyl with one amino group and three carboxylic acid groups. The resulted asymmetrical porphyrin (**45**) can be successfully fabricated into a modified solid Grätzel type cell with polyaniline as the solid electrolyte. The overall energy conversion efficiency of this cell is about 2% with a number of opportunities to optimize the efficiency remaining [81].

The sensitization properties of porphyrin compounds have also been improved by introducing dendron groups to the cyano substituted *meso*-stilbene moieties (**46**, **47**). The aggregation of porphyrin was efficiently suppressed by the bulky dendrons while the electron injection to the conduction band of TiO_2 was improved by the cyano groups. The overall energy transfer efficiency was promoted remarkably to 2.76% for a solid DSSC. This is an encouraging result for a porphyrin dye and it offers the potential for porphyrins as alternatives to ruthenium-based dyes in the DSSC [82].



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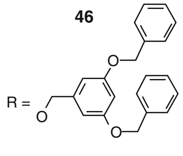

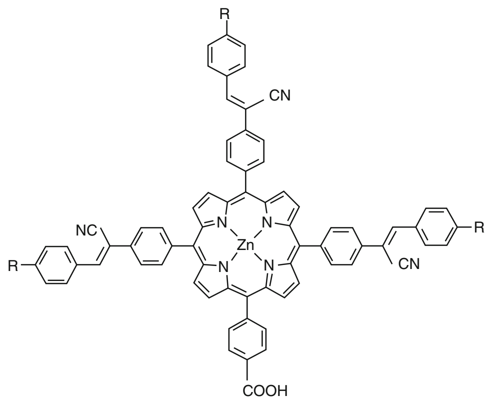

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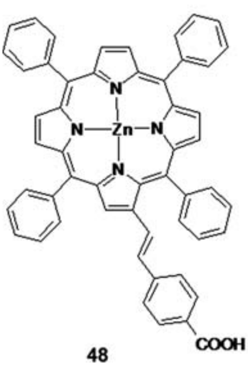
Another interesting attempt worth noting is the combination of porphyrin sensitized solar cell with a fuel cell made by Moore and Gust. The hybrid cell can realize an open circuit voltage of 1.2 V. The energy conversion efficiency of this photoelectrochemical biofuel cell can, in principle, produce more power than either a photoelectrochemical cell or a biofuel cell working individually [83].

3.1.2 Porphyrins with Anchoring Groups Connected at β-Pyrrolic Positions

Anchoring groups of the porphyrin sensitizers mentioned above are exclusively connected at the *meso*-phenyl groups. Since the directionality of anchoring groups can change the electronic coupling between the porphyrin excited states and the conduction band of TiO_2, synthetic research on connection of anchoring groups directly at different positions of the porphyrin macrocycle are attractive due to the perspective of tuning the electronic couplings. Nazeeruddin and co-workers have prepared a series of porphyrin sensitizers (**48–52**) with a benzoic acid or phenylphosphonic acid group connected at the β-pyrrolic position (2,3,7,8,12,13,17,18 positions) of porphyrin ring by a double bond. The binding of carboxylic acid group onto the surface of TiO_2 particle was confirmed by the ATR-FTIR spectra. The porphyrin with carboxylic acid group presents higher IPCEs than that with phosphoric acid probably because of the larger electronic coupling through carboxylic acid groups. The zinc porphyrins are better sensitizers than copper porphyrins as expected due to the longer lifetime of the excited state of zinc porphyirn with respect to copper porphyrin. The methyl groups at 3,5 positions also promote the IPCEs significantly by harnessing the aggregation of porphyrin molecules. The best sensitizer in this series of porphyrins was **49**, which presented IPCE at the Q band as high as 75% with an overall energy conversion efficiency of 4.8%. This finding opens up new avenues for improving further the efficiency of solar cells by engineering the structure of porphyrins [84].



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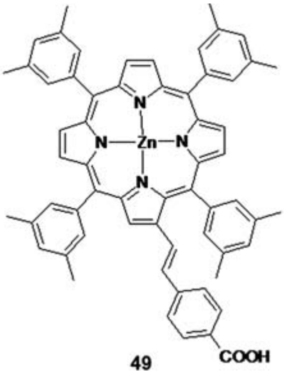

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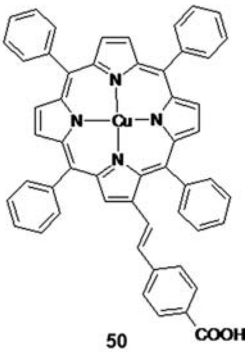

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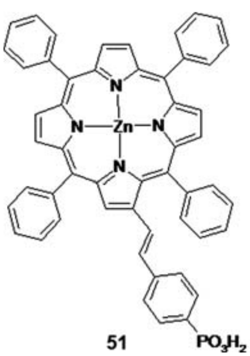

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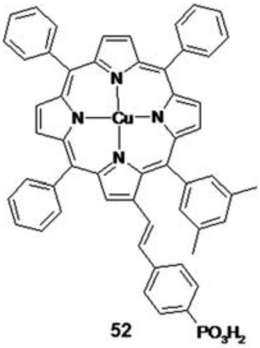
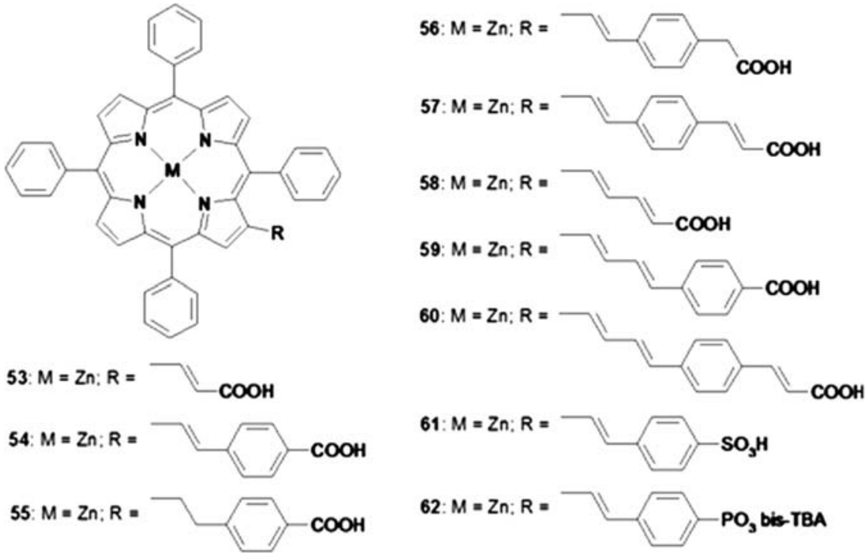
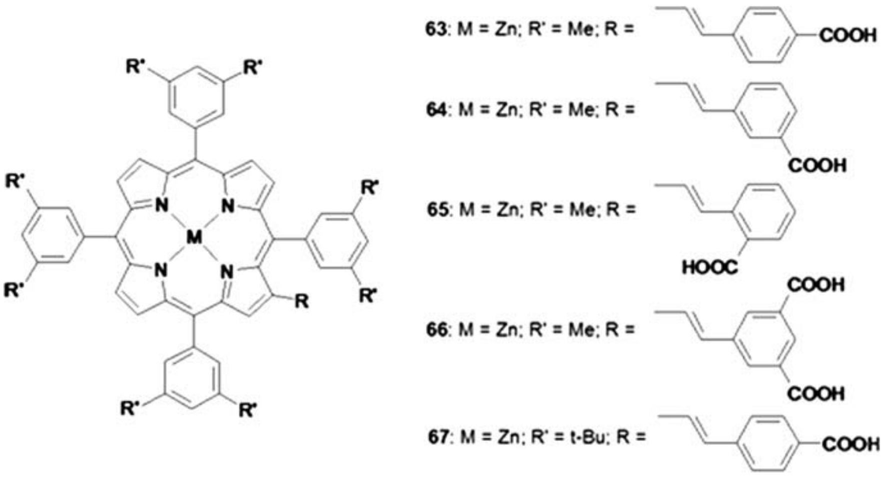


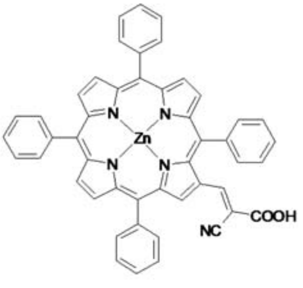
52

Systematic and comprehensive research on porphyrin sensitizers (**53–67**) with the anchoring group connected at β-pyrrolic positions have also been performed by Officer and co-workers [85]. Their results revealed that free acid form of the anchoring group exhibited the best adsorption on the surface of TiO$_2$, which is in accordance with the previous report [80]. The zinc porphyrins show more efficient sensitization than copper and metal free porphyrins. Their results also suggest that β-pyrrollic substituted porphyrin styryl carboxylic acids are superior to *meso*-aryl porphyrin carboxylic acids as light harvesters. Porphyrin **53** had been shown to be the most efficient porphyrin photosensitiser in this series of compounds with an overall energy conversion efficiency of 4.2%. Moreover, they found that the close proximity of porphyrins might not significantly diminish light harvesting. They had also demonstrated that either the sulphonic or phosphonic acid porphyrins bound to TiO$_2$ tightly, but this stable binding did not bring better cell performance. This tends to suggest that electronic coupling between the dye and TiO$_2$ surface through the binding group plays an important role in the efficiency of light harvesting. For the conjugated linkers, the number of double bonds, or the presence of the phenyl moiety, made no significant difference in overall cell performance. However, when the conjugation was interrupted, there is a significant fall in the cell performance [85].





Officer and co-workers have also successfully connected carboxylic acid groups at the β-pyrrolic position of porphyrin with one or two double bonds (**68**, **69**) [86]. Compared with the tetraphenyl porphyrin (TPP), these two compounds show red shifted absorption spectra with larger extinction coefficiency. The IPCEs of the liquid junction solar cell based on these sensitizers are 90% at Soret band and 60% at Q band. The overall energy conversion efficiency of the cell based on **68** and **69** are 2.44% and 3.0% respectively. It is worth noting that sensitizing efficiency seems not affected by the length of the linkage as also revealed in the previous research [85]. The nano-crystalline TiO_2 electrode sensitized by these sensitizers would remain transparent to the eye, while absorbing enough solar photons in the NIR region.



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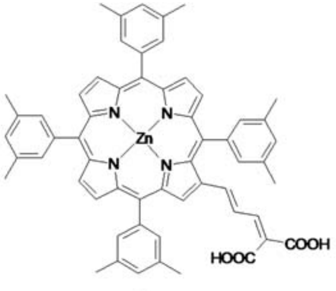

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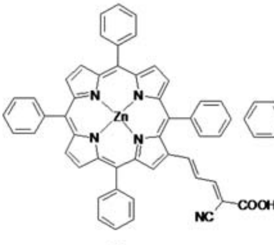

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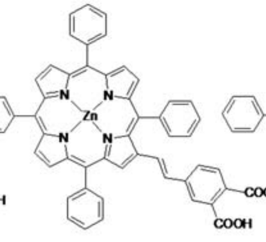

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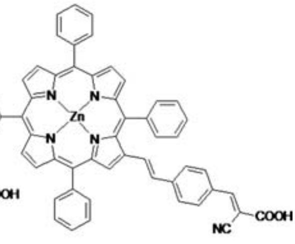
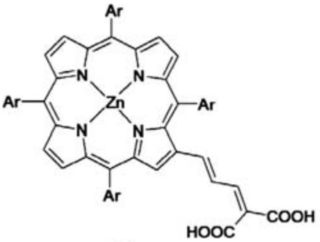


72

The same research group has also compared the sensitization properties of a series of novel green porphyrins (**70–72**) containing a β-pyrrolic substituent with that of **68** later. Because of the presence of electron withdrawing CN group at the substituent, the frontier molecular orbitals are stabilized and extended out onto the substituent by π-conjugation. The extension of the conjugation of porphyrin to the substituents provides the possibility of electron transfer from porphyrin to TiO_2 through the substituent. Significant improvement on the solar cell performance had been achieved by using these porphyrins as sensitizers. The **72**-sensitized solar cell demonstrates an IPCE close to 85% and an overall conversion efficiency of 5.6% under standard AM 1.5 sunlight [87].

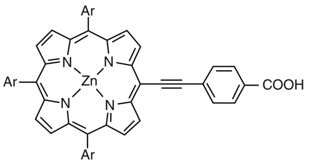


73

a Ar = Ph
b Ar = 4-methylPh
c Ar = 4-ethylPh
d Ar = 4-n-butylPh
e Ar = 4-n-octylPh
f Ar = 3,5-dimethylPh

The effects of the substituent at the *para*-position of *meso*-phenyl on the sensitization properties of porphyrins (**73**) were also examined by the same group. All these novel darkgreen porphyrins yield IPCE values of up to 75% and overall power conversion efficiencies in the range of 5.1–7.1% under one sun in a liquid electrolyte cell. **73b** presented the best performance in this series of porphyrins. More impressively, a solid-state cell utilizing **73b** as the sensitizer performed a peak IPCE value as high as 63% and overall power conversion efficiency 3.6%. These record efficiencies demonstrate the exciting potential of porphyrins as light-harvesting green dyes [88].

Very recently, the effects of the connection position of anchoring groups on the sensitization performance of porphyrins (**74–83**) were further addressed in the research of Diau and co-workers. The carboxylic acid groups were selectively connected to the *meso* or β-pyrrolic positions by different conjugated linkages. Electron donating biarylamino groups introduced onto the opposite *meso* position of the anchoring group tend to enhance the charge separation capability. The results indicate that both the position and nature of the linkages show significant influences on the spectral, electrochemical, and photovoltaic properties. However, the advantages of the β-pyrrolic position connection of anchoring groups over the *meso* position connection as revealed by the pervious research was not exhibited by these series of porphyrin sensitizers. The phenylethynyl bridge at *meso* position could efficiently red-shift the absorption spectrum. The red shift became more pronounced when a conjugated electron donating group was connected at *meso* position opposite to the anchoring group. The DFT calculation revealed that the oxidized state was stabilized by the electron donating group and thus improved the sensitization performance dramatically. An overall energy conversion efficiency of 6.0% was achieved by compound **76**, which was comparable to the performance of the famous N3 dye [89].



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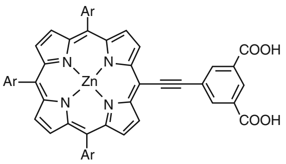

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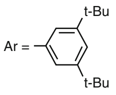

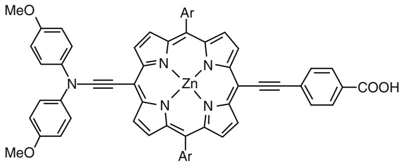

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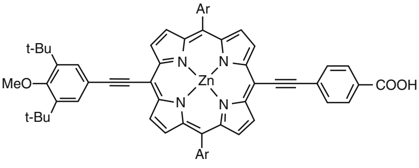

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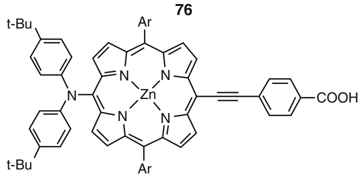

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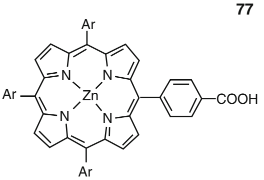

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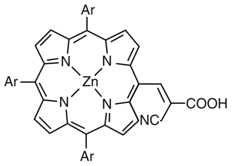

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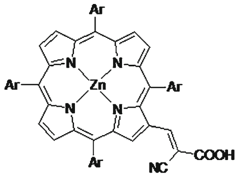

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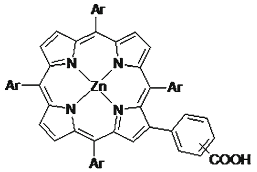
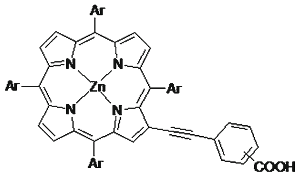


82 a *para* b *meta*

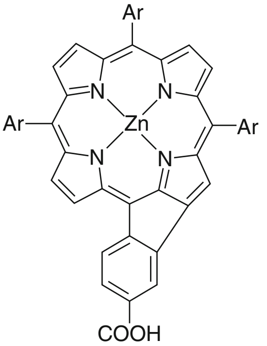


83 a *para* b *meta*

Although plenty of results support that the anchoring groups connected at the β-pyrrolic positions will benefit the sensitization of porphyrin to TiO_2, but there is also a few of researches which do not support this point. It is the overall electronic configuration of the porphyrin macrocycle that determines the coupling between the excited states of porphyrin and the conduction band of TiO_2, which then influences the sensitization performance of the dye. When the directionality of the anchoring group at β-pyrrolic position could enhance the coupling and stabilize the charge separated states, the sensitization will be promoted. In order to get a better sensitizer, the whole electronic configuration of the excited states of porphyrin must be taken into consideration.

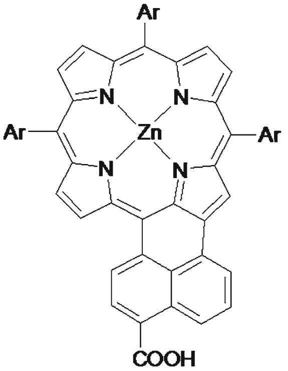
3.1.3 Porphyrins Fused with Other Small Aromatic Rings

Besides to introduce substitutents onto the *meso*-phenyl ring or the β-pyrrolic positions, modification of the molecular structures by fusing a small aromatic ring to the porphyrin ring has also been an attractive way to extend the absorption spectra and tune the electrochemical properties of porphyrins in the prospect of improving the sensitization behavior. Imahori has investigated the application of a fused five-membered porphyrin (**84**) as sensitizer in DSSC. Compared with the reference porphyrin, the fused porphyrin shows broaden and red-shifted absorption spectra as expected and the photocurrent response extends to 800 nm for the first time. The oxidation potentials of the fused porphyrin have positive shifted for about 0.07 V relative to that of the standard porphyrin. However, the DSSC with this fused porphyrin as sensitizer show significantly lower IPCE and overall energy transfer efficiency relative to that made of the reference porphyrin. This has been attributed to the insufficient driving force for an efficient electron injection for this fused porphyrin [90].



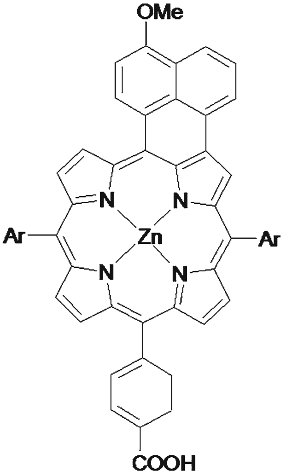
Ar = mesityl

84



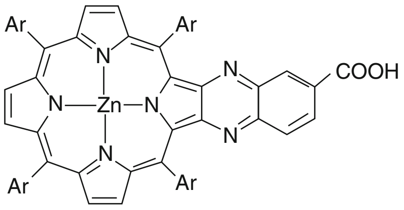
Ar = mesityl

85



86

Later, Imahori has synthesized a series of new porphyrins (**85**, **86**) fused in different ways with naphthyl moieties to improve the light-harvesting abilities in porphyrin sensitized solar cells. As the results of π-elongation with low symmetry, Soret and Q bands of the fused porphyrins were red-shifted and broadened, and the intensity of Q-band relative to that of Soret band was enhanced. The DSSC sensitized with **85** showed overall power conversion efficiency of 4.1% under standard AM 1.5 condition while the cell of **86** gave a power conversion efficiency of 1.1%. The better sensitization performance of **85** was attributed to the extension of the LUMO to the carboxylic acid group as revealed by the DFT calculation, which was not found for the LUMO of **86**. Accordingly, the larger electronic coupling between the porphyrin and the TiO_2 surface in the **85**-sensitized cell may be responsible for the high cell performance. More interestingly, the performance of the **85**-sensitized solar cell can be further improved by co-sensitization of **85** and other porphyrins with complementary absorption properties. An overall power conversion efficiency of 5% under standard 1.5 AM condition was achieved by this co-sensitization method [91].



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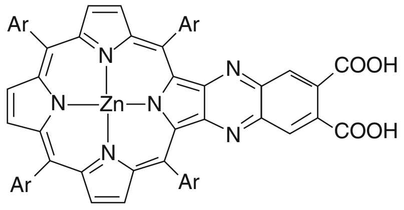


88

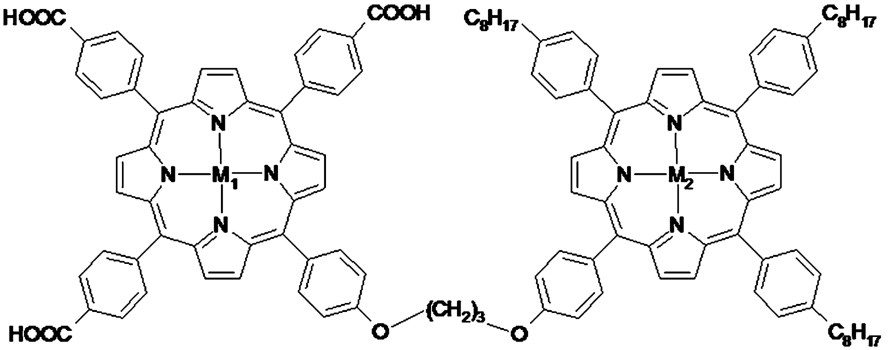
Ar = mesityl

Another important work performed by the group of Imahori is the fusing of a quinoxaline ring with one or two carboxylic acid groups to the porphyrin ring (**87**, **88**). The XPS, FTIR spectroscopy, and cyclic voltammetry studies for the adsorbed porphyrins revealed that the carboxylic acid group in **87** employed bidentate binding mode to anchor itself onto the TiO_2 surface, whereas the two binding groups in **88** utilized one bidentate and one monodentate binding modes. The photovoltaic measurements on the DSSCs sensitized by **87** or **88** have revealed power conversion efficiencies of 5.2% and 4.0% respectively. Since the absorption spectra of these two porphyrins are similar, the difference on the power conversion efficiency is dominantly determined by the binding model [92].

3.2 Porphyrin Arrays

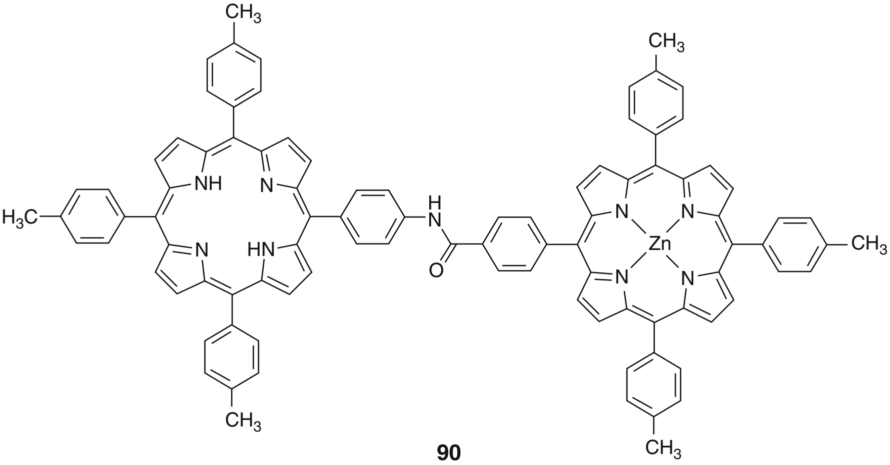
To harvest photons more efficiently in DSSCs, construction of chromophore arrays and attaching them to the semiconductor surface have been studied extensively. By connecting carefully designed series of chromophores in a branched or linear way, using appropriate spacers, the excited energy of chromophores can be tunneled to a selected chromophore, from which the electrons were injected into the conduction band of the semiconductor. The efficiency of the intramolecular energy and electron-transfer processes in chromophore arrays will depend on the bridge and the spatial orientation of individual chromophore units. The most popular chromophore arrays investigated so far are covalent bonded systems due to their high stabilities [93].

Koehorst and co-workers had tested the sensitizing properties of a porphyrin heterodimer (**89**) to TiO_2, which represented the first example of the application of porphyrin arrays in DSSC [94]. This porphyrin heterodimer was composed of one free base porphyrin and one zinc porphyrin with one of them functionalized with carboxylic acid groups. Because of the binding of carboxylic acid groups at the surface of TiO_2, the porphyrin unite functionalized with carboxylic acid groups was in direct contact with the substrate. For the DSSC fabricated from the porphyrin dimer with the carboxylic acid groups functionalized at metal free porphyrin (**89a**), the photocurrent action spectrum reproduced the absorption spectrum, i.e., both porphyrin unites contributed to the photocurrent, indicating efficient energy transfer from zinc porphyrin to metal free porphyrin followed with efficient electron injection from the latter to TiO_2. However, when the carboxylic acid groups were functionalized at zinc porphyrin (**89b**), the photocurrent action spectrum of the solar cell presented only the contributions of zinc porphyrin. This is reasonable because the energy transfer from metal free porphyrin to zinc porphyrin was theoretically unfavorable. This result also suggested that the energy transfer from zinc porphyrin to metal free porphyrin was slower than that of the electron injection from zinc porphyrin to TiO_2. This research revealed a promising way to enhance the absorption of light and thus improve the performance of DSSC by constructing a supramolecular lighting antenna as sensitizer.



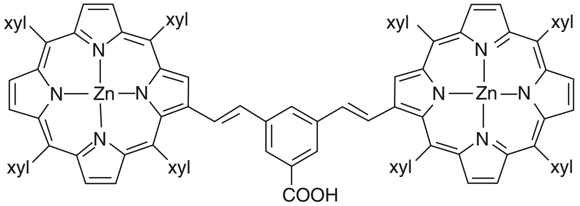
89 **a** $M_1 = 2H, M_2 = Zn$
b $M_1 = Zn, M_2 = 2H$

Sereno prepared a porphyrin dimer by connecting a metal free porphyrin to a zinc porphyrin with amid bond. The resulted porphyrin dimer was tested as a sensitizer for SnO_2 electrode. Even without anchoring groups, this porphyrin dimer showed sensitization to SnO_2 electrode with an IPCE value of 10% at 420 nm [95].



90

In a later research, Sereno and co-workers found efficient energy transfer from zinc porphyrin to metal-free porphyrin in the dyad (**90**) even in the adsorbed states. The fact that the dimer is less effective in comparison with metal free porphyrin monomer in the generation of photocurrent is explained as that the metallized porphyrin enhances the back electron-transfer process [96].



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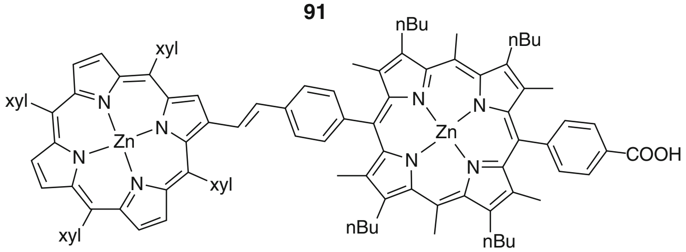

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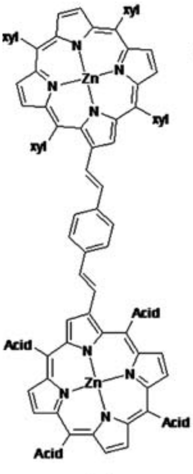

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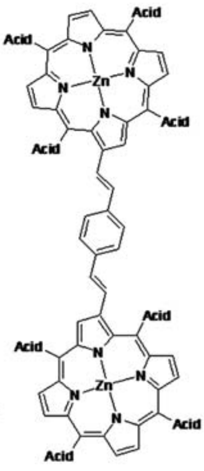

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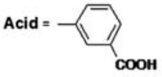

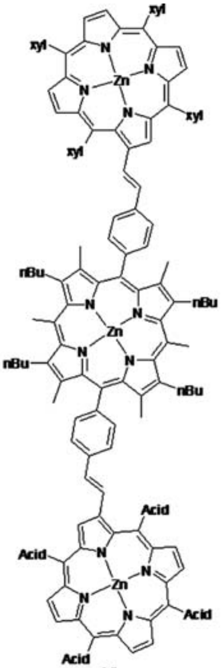

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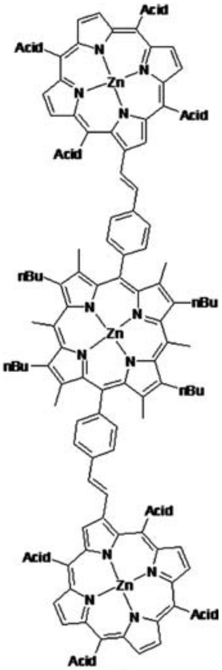

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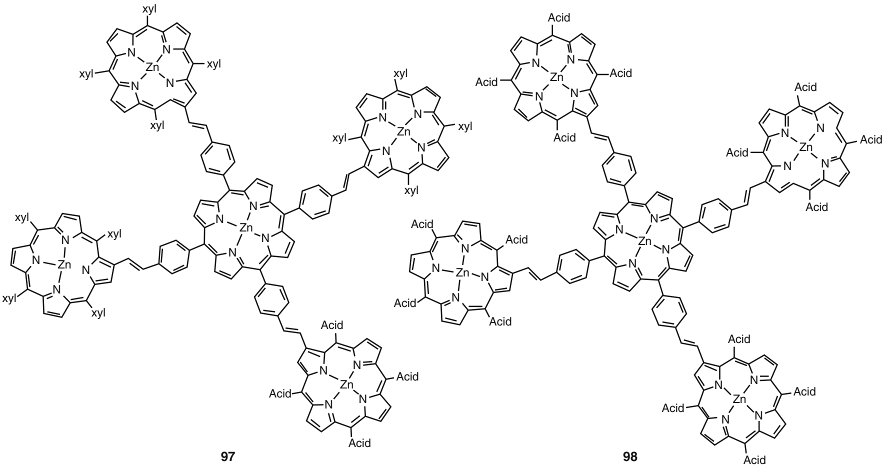
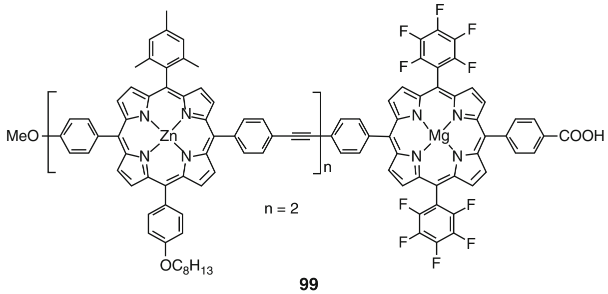


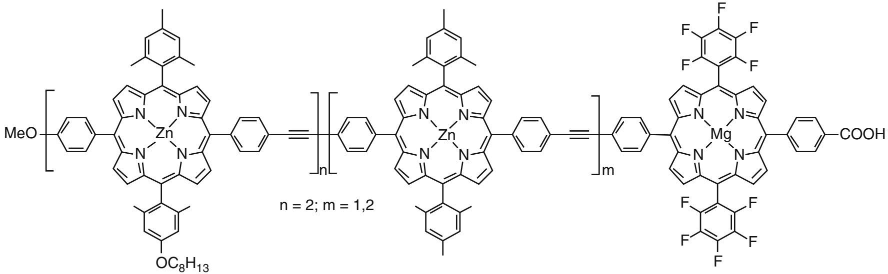
97 **98**

A comprehensive study on the photosensitization behavior of porphyrin arrays to TiO_2 has been conducted by Campbell and co-workers. The porphyrin dimers (**91** and **92**) with one carboxylic acid group as binding site present weak surface adhesion and therefore low efficiency on sensitization. The DSSC with these two porphyrin arrays as sensitizers exhibit lower IPCEs relative to that with porphyrin monomer. To strengthen the adsorption of these porphyrin arrays on the surface of TiO_2 nanoparticle, multi carboxylic acid groups were introduced to the porphyrin moieties and compounds **93–98** were prepared. The binding of these porphyrin arrays on the surface of TiO_2 is indeed enhanced and stabilized. Yet here also the monomeric porphyrin outperforms these dyes, with no apparent antenna effect observed in spite of the strong binding. This result was attributed to the lack of directionality of the binding groups in the porphyrin arrays, but it is also highly likely that the small porosity of the TiO_2 nanocrystalline layer may be preventing adsorption of these very bulky dyes [85].

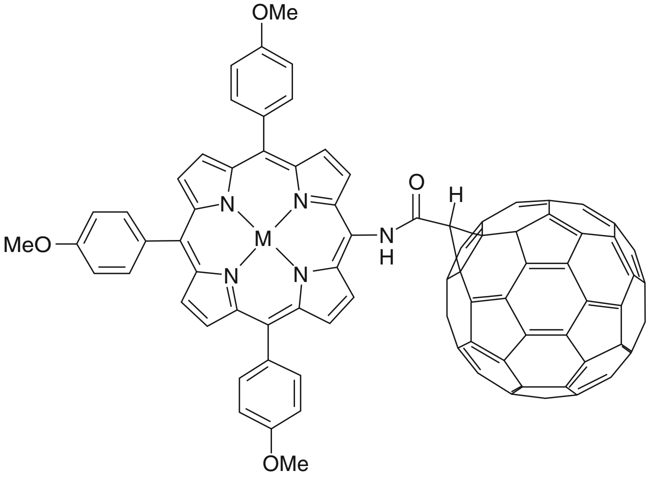
Lindsey and co-workers have prepared a series of rod like porphyrin arrays (**99**) for the DSSC application. The triad, tetrad, and pentad porphyrin arrays, each is comprised of a terminal magnesium porphyrin bearing one carboxyl group (for surface attachment); the remaining porphyrins in each array are present as the zinc chelate. The steady absorption spectra reveal weak coupling between these porphyrins at ground state, while the fluorescence spectra indicate the obvious excited energy migration along the porphyrin array to the terminal magnesium porphyrin with the efficiency as high as 99%. These design and synthesis strategies should be useful for the construction of materials for molecular-based solar cells. Unfortunately, the sensitization properties of these porphyrin arrays to TiO_2 nanoparticle electrode were not measured and no data on the photo to current conversion efficiency were reported so far [97].



99



100

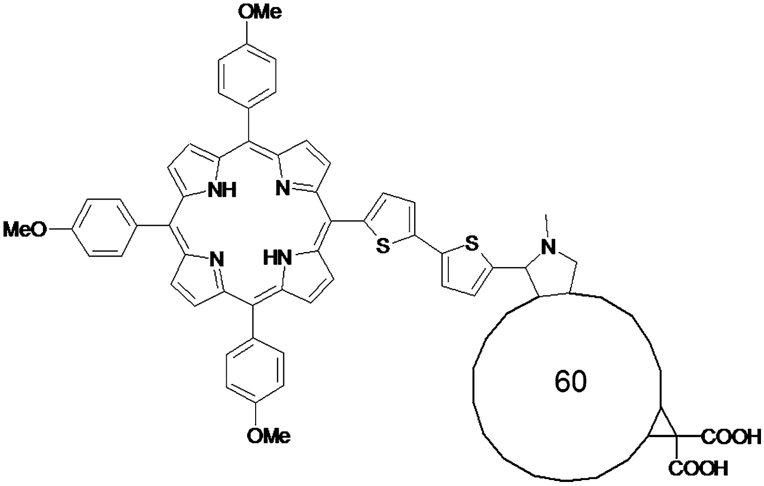


M = 2H, Zn

101

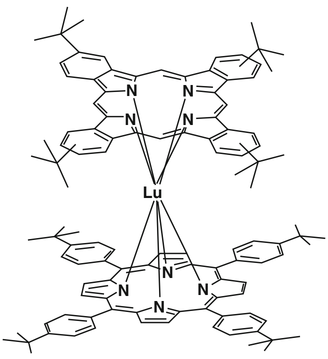
A porphyrin-C60 dyad (**101**) has been used as a sensitizer in DSSC by Durantini and co-workers in 2002. The fluorescence quenching of porphyrin was observed in the dyad, indicating efficient electron transfer from porphyrin to C_{60}. The test on the sensitization properties of this dyad to SnO_2 electrode revealed that the absorption of C_{60} contributed to the photocurrent generation. The dyad produced a higher photoelectric effect than the corresponding amidoporphyrin model. An alternative photoelectric mechanism, which involves a charge separated state, other than direct electron injection from the excited porphyrin to SnO_2, was suggested to be responsible for this improved photoelectrical response [98].

Another porphyrin–C_{60} dyad (**102**) connected by a bithiophene bridge was prepared by Shiga very recently. Carboxylic acid groups were introduced to C60 moiety as anchoring groups. The DSSC fabricated from this dye exhibited IPCEs at 420 nm larger than 40% with an overall photocurrent conversion efficiency over 0.53% at 100 mW cm^{-2}. The contribution of C_{60} to the photocurrent generation was obviously observed in the photocurrent action spectra. The introduction of C_{60} between the porphyrin unit and TiO_2 is effective in improving photosensitization [99].

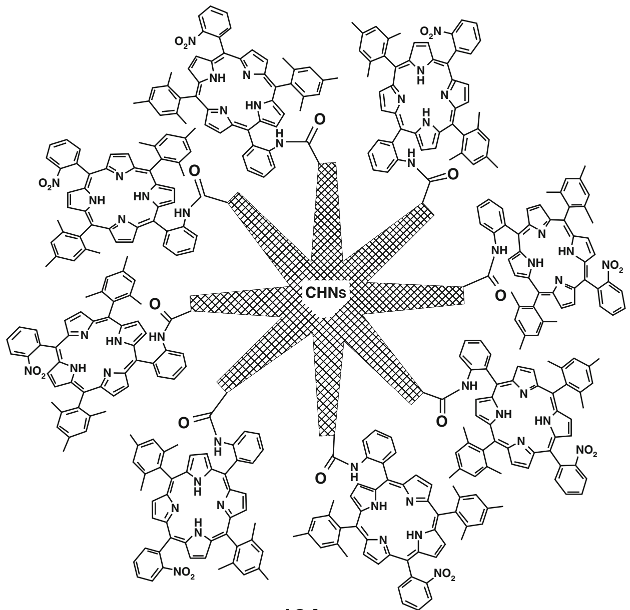


102

Liu prepared a sandwich type coordination compound (**103**) from porphyrin and phthalocyanine with the assistance of a microwave. The resulted compounds showed good solubility in conventional organic solvents. The photoelectric conversion properties have been tested with a Grätzel type cell. The results revealed that the sandwich type compound showed better photo-electric conversion efficiency than the corresponding monomeric porphyrin or phthalocyanine precursors. The short-circuit photocurrent of the solar cell with this sandwich type compound as sensitizer, was, as high as 691.31 A cm^{-2}, which was much better, than those of porphyrin or phthalocyanine monomers [100].



103



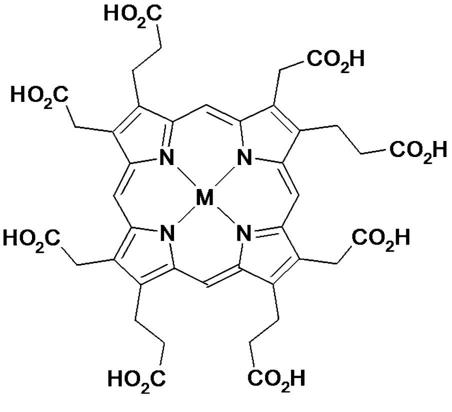
104

Very recently carbon nanohorns (CNHs) covalently functionalized at the conical tips with metal free porphyrin moieties (**104**) were tested as sensitizer in a photoelectrochemical solar cells. A nanostructured SnO_2 electrode deposited with porphyrin functionalized CNH exhibited an IPCE of 5.8%; it is greater than the one observed for the sum of the single components. The fluorescence lifetime measurement reveals that photoinduced electron transfer from porphyrin to the nanohorns takes place followed by the direct electron injection from nanohorns to the conduction band of SnO_2. The results obtained demonstrate the potentiality and applied utility of CNHs in directing efficient charge transport in photoelectrochemical devices [101].

Controversial results have been deduced from the researches of different groups on the sensitization behavior of porphyrin arrays as mentioned above. Some of them revealed that porphyrin arrays have advantages over porphyrin monomers in the sensitization of wide band gap semiconductor while the rest showed the opposite results. The porphyrin dimer composed of a metal free porphyrin and a zinc porphyrin seems the most successful porphyrin array sensitizer so far. Programing the photoinduced energy and electron-transfer sequence in a porphyrin array is the key step toward a good porphyrin array sensitizer.

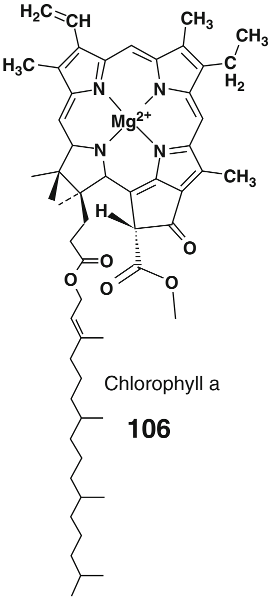
4 Natural Porphyrin Sensitizers

The important role of chlorophylls in photosynthesis inspired people looking for ways to apply these natural porphyrins in DSSC as light harvesting sensitizers. The use of zinc and antimony metallo-uroporphyrins **M-UP** (**105**) as photosensitizers for TiO_2 colloid was investigated by Kalyanasundaram et al. The flash photolysis studies revealed that the electron injection to TiO_2 conduction band happened from both singlet and triplet excited states of Zn uroporphyrin [102].



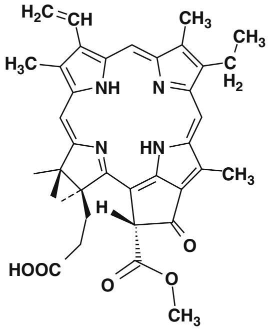
105

Grätzel has investigated the sensitization behavior of chlorophylls and related natural porphyrins to nano-crystalline TiO_2 electrode. The natural porphyrins they employed include chlorophylls (**106**), Pheophorbids (**107**), H_2–, Zn–, or Cu–chlorin–e6 (**108**), Cu–2–a–Oxymesoisochlorine e4 (**109**) and H_2–, Zn–, Cu–Mesoporphyrin IX (**105**). The photosensitization of colloidal TiO_2 electrodes by these chlorophyll derivatives gave high IPCEs, approaching the unity efficiency of primary charge separation in natural photosynthesis. More interestingly, even the nonfluorescent Cu chlorophyllin present efficient sensitization to TiO_2 colloid electrode due to the fast electron injection from the excited states of Cu chlorophyllin into the conduction band of TiO_2. However, the realistic application of these chlorophyll derivatives is limited because of the low efficiency of the overall energy transfer as well as the low stability of these compounds [103]. The study on the mechanisms of the photosensitization by electrochemical and transient absorption studies revealed that the electron injection to the conduction band of TiO_2 happened from singlet excited states for the fluorescent chlorine e6 and from triplet states for the non-fluorescent copper 2α-oxymesoisochlorin e4. The recombination of the injected electron with the oxidized dye is relatively slow and leads to a high charge separation yield [104].

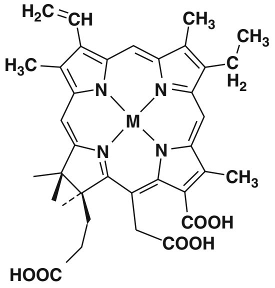


Chlorophyll a

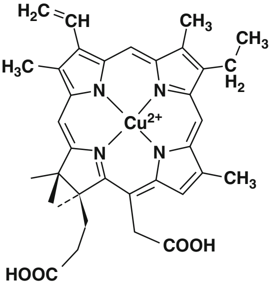
106



107 Pheophorbid a



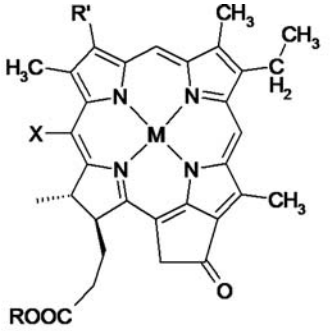
108
M = H2 H2-chlorin e6
M = Zn Zn-chlorin e6
M = Cu Cu-chlorin e6



Cu-2-a-Oxymesoisochlorin e4

109

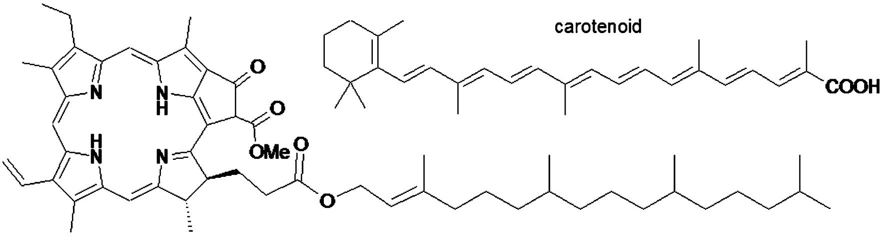
The sensitization of H_2-chlorine e6 (**108**) was also tested by Amao and co-workers. Their results indicate that chlorine–e6 present efficient sensitization to TiO_2 with an overall energy transfer efficiency of 0.40% under light intensity of $100\,\text{mW cm}^{-2}$ [105, 106].



BChl-c: M = Mg R' = $CH(CH_3)OH$ X = CH_3 R = stearyl, etc.
BChl-d: M = Mg R' = $CH(CH_3)OH$ X = H R = farmesyl, etc.
1 : M = Zn R' = CH_2OH X = H R = CH_3
2 : M = H_2 R' = $CH{=}CH_2$ X = H R = CH_3
3 : M = Zn R' = $CH{=}CH_2$ X = H R = CH_3
4 : M = Zn R' = CH_2OH X = Cl R = CH_3

110

Tamiaki prepared a series of zinc chlorine with methyl carboxylate groups. The sensitization of these compounds to carbon past was investigated. The experimental results revealed surprisingly that the aggregates of zinc chlorine on the carbon past were responsible for the photocurrent generation, and even more surprising, the sensitization of chlorine aggregates was more efficient than that of zinc chlorine monomer. This result was opposite to most of the others obtained from porphyrin or phthalocyanines. O_2 was suggested to get involved in the photocurrent generation [107].

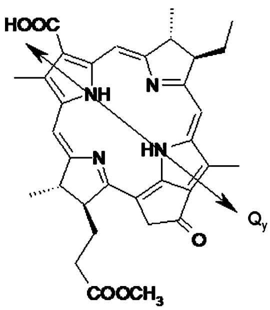


111

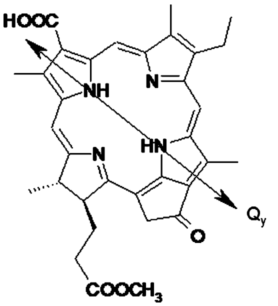
pheophytin

Polívka had investigated the co-adsorption of carotenoid and pheophytin (**111**) on the surface of TiO_2 electrode and the photophysical properties of pheophytin in this film. The results demonstrated that the fluorescence of **111** was efficiently reductive quenched by carotenoid in this co-assembled film, suggesting similar mechanisms to that in the natural photosynthetic systems. The radical anion of **111** formed during the electron transfer recovered to the neutral state quickly before the charge recombination between carotenoid cation and pheophytin anion took place. It is suspected that the electron injection from the pheophytin anion to the conduction band of TiO_2 was responsible for this quick recovery. This result indicated that such a "self-assembling" strategy may be also considered for novel DSSC constructions [108].

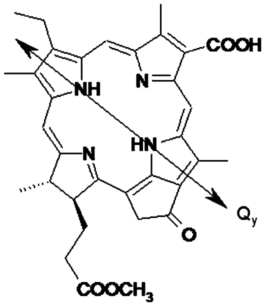
Durrant have investigated the photoinduced electron-transfer reactions of zinc-substituted cytochrome c, ZnCyt-c, immobilized on the surface of nanocrystalline TiO_2 electrodes. Efficient electron injection from the triplet state of ZnCyt-c into TiO_2 electrodes is revealed by transient absorption studies, which resulted in a long-lived charge separated state. The previous research on the light-induced electron injection into TiO_2 electrodes has typically focused on achieving strong electronic coupling between TiO_2 nanoparticles and the dye molecules, this leading to fast electron injection into the conduction band of TiO_2 from the singlet excited states of the dyes. In this ZnCyt-c sensitized system, the protein matrix acts as a spacer between the Zn-porphyrin and the nanoparticle surface, which hindered the fast electron injection from the singlet excited states. Due to the high efficiency of the intersystem crossing from singlet to triplet states of ZnCyt-c, the relative slow electron injection from the triplet states of ZnCyt-c presents a high efficiency too. This sensitization pathway requires only relatively weak electronic coupling between the sensitizer and the electrode surface and may be a promising way to improve the energy conversion efficiency in DSSCs [109].



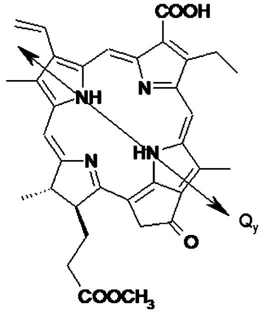
112 (BPhe a)



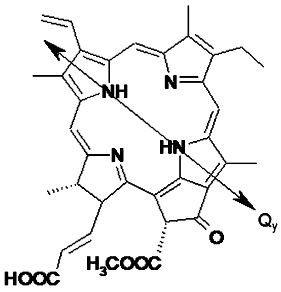
113 (Phe a)



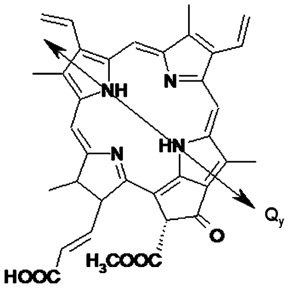
114 (Phe x)



115 (Phe b)



116 (Phe c_1)



117 (Phe c_2)

Koyama has examined the sensitization behavior of a series of pheophorbide sensitizers (**112–117**) with similar structure. The results indicate that the short-circuit current density as well as the overall solar energy-to-electricity conversion efficiency increased with the increasing Qy absorption and with the decreasing one electron-oxidation potential. Two empirical models are built based on the experimental results. One model suggests a parallel electron injection from both excited and ground states to the conduction band of TiO_2 whereas the other one supports an electron injection via the excited state only, in which both the Qy absorption and the Qy-state one electron-oxidation potential can contribute [110].

5 Conclusion

Both phthalocyanines and porhyrins are very promising sensitizers for wide band gap semiconductors. DSSCs fabricated from these kind of sensitizers present overall power conversion efficiency as high as 7%, which is still smaller than that achieved by the ruthenium polypyridyl complexes though, but higher than most of other dyes. The multiplicity on the molecular structure modification of these compounds provides a great potential for further promotion on their sensitization properties. The research in this field is still far from systematic and comprehensive and quantitatively much less than the researches on polypyridyl ruthenium complexes. But from the limited researches as mentioned above, several important aspects should be taken into account during the design of novel sensitizers.

1. To achieve an efficient sensitization of TiO_2 nanocrystaline electrode, anchoring groups connecting with phthalocyanine or porphyrin are necessary. The anchoring groups help not only to immobilize the dye molecule on the surface of the semiconductor electrode but also to keep a strong coupling between the excited states of the dye molecules and the conduction band of the semiconductor.
2. The electron injection from the excited states of the dyes to the conduction band of the electrode is predominately affected by the oxidation potential of the dye molecules as well the distribution of the LUMO over the whole molecule. Tuning the redox potentials and the LUMO distribution by functionalizing the aromatic ring asymmetrically with different groups at different positions seems a promising way towards a better sensitizer.
3. Aggregations of the porphyrin or phthalocyanine molecules on the surface of the nano-crystalline electrode always induce massive non-radioactive decay of the excited states and thus reduce the efficiency of the electron injection. Therefore, preventing the aggregation of the dye molecules on the electrode surface will be a foremost issue during the design of new sensitizers, which can be achieved normally by axial coordination, bulky substituents at peripheral positions or the co-adsorption with other materials.
4. Although with some disagreements, sensitization with two kinds of co-adsorbed dyes or with molecular arrays of different chromophores has proved to be advantageous to the overall power conversion efficiencies of DSSCs. New molecular arrays based on porphyrin or phthalocyanine molecules with carefully programed photoinduced electron or energy transfer sequence are expected to be promising candidates for good sensitizers in DSSC.

The application of phthalocyanine or porphyrin analogs as sensitizers in DSSC has been explored for more than 10 years up to now. From the point of overall power conversion efficiency, these tetrapyrolle macrocyclic compounds are not as successful as polypyridyl ruthenium complexes. However, the recent great improvement on the performance of the phthalocyanine- or porphyrin-based DSSCs and the deeper understanding on the sensitization mechanisms revealed large potentials for further development for this kind of sensitizers. Given that many new porphyrin or phthalocyanine compounds exhibit excellent light-harvesting properties in artificial photosynthetic systems, we anticipate that many new sensitizers based on phthalocyanine or porphyrin will be forthcoming.

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