

Are porphyrins an alternative to ruthenium(II) sensitizers for dye-sensitized solar cells?

Lingamallu Giribabu* and Ravi Kumar Kanaparthi

Inorganic and Physical Chemistry Division, CSIR–Indian Institute of Chemical Technology, Hyderabad 500 607, India

This review article reports recent advances in porphyrin-based sensitizers for dye-sensitized solar cell (DSSC) applications. The sensitizer is known to be one of the key components of the DSSC device, which plays a vital role in achieving high efficiency and durability. So far, ruthenium(II) polypyridyl complexes have been extensively used as sensitizers achieving more than 11% efficiency. The major technical disadvantages with these complexes are expensive due to rarity of the metal, tedious purification process and lack of absorption in the red region of the visible spectrum, where the light harvesting process is maximum. For this reason, porphyrins are found to be probable alternative sensitizers based on their thermal, electronic and photochemical properties. A great variety of porphyrins have been used as sensitizers in DSSC applications for the last three decades and recently, the efficiency of porphyrin-based sensitizers has crossed 12%.

Keywords: Porphyrin, pyrrole, ruthenium, sensitizers, solar cell.

DURING the last two decades, with the development of nanocrystalline films of very high surface area, the photosensitization of wide band-gap semiconductors such as TiO₂ by adsorbed dyes has become more realistic for dye-sensitized solar cell (DSSC) applications^{1–6}. In a porous thin film consisting of nanometre-sized TiO₂ particles, the effective surface area can be enhanced 1000-fold, thus making light absorption more efficient even though there is only a monolayer of dye on each nanoparticle⁷. DSSCs have attracted significant attention because of environmentally pleasant, easy to fabricate and low-cost alternatives to conventional solid-state photovoltaic devices. Historically the DSSC concept was started in 1972 with chlorophyll-sensitized zinc oxide (ZnO) electrode⁸. By using these two chlorophyll systems, photons are converted into electric current by charge injection of excited chlorophyll molecules into ZnO electrode. Since then many efforts have been made to improve the power conversion efficiency. But, a major breakthrough appeared in 1991, when O'Regan and Grätzel¹ reported a DSSC device with 7.1% efficiency.

Typically, the device composed of a porous layer of TiO₂ nanoparticles covered with a molecular dye absorbs sunlight like chlorophyll in green leaves. The TiO₂ is immersed in an electrolyte solution, above which a platinum-based catalyst is placed. Similar to a conventional alkaline battery, an anode (the titanium dioxide) and a cathode (the platinum) are placed on either side of a liquid conductor (the electrolyte). Detailed device fabrication and the working principle of a DSSC are well documented in our earlier reports^{5,6}. Since 1991 many efforts have been paid to improve the power conversion efficiency. Moreover, it did not take much time to prove that DSSCs are good alternative for the conventional first and second generation silicon and other thin-film solar cells. Interestingly, the DSSC technology works well even in the diffused light conditions, unlike in the first and second generations of photovoltaic devices.

Among various components of the DSSC device, the sensitizer is one of the key components in achieving high efficiency and durability. The most successful charge transfer sensitizers employed so far in DSSC are *cis*-dithiocyanatobis-(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (together with its various protonated forms), its modified forms (N3 and N719) and trithiocyanato 4,4'4''-tricarboxy-2,2' : 6',2''-terpyridine ruthenium(II) (the black dye), which yield conversion efficiencies up to 11% under air mass (AM) 1.5 solar conditions with liquid redox electrolyte^{1,9}. Nevertheless, studies are still needed to fill the gap between today's benchmark conversion efficiency of 32% (Shockley–Queiser¹⁰ limit predicted for a single junction cell). This can be achieved only through proper molecular designing of the sensitizer. A great variety of ruthenium(II) complexes have been reported in the literature in order to further improve the efficiency and durability of the device^{11–14}. Even though the ruthenium(II) polypyridyl complexes are more dominant in today's DSSC research, they are expensive due to rarity of the metal. Moreover, they are less durable due to the presence of two or three –NCS groups, present in ruthenium(II) sensitizers. Another important drawback is that these complexes lack absorption in the red region of the visible spectrum and also have relatively low molar extinction coefficients above 600 nm. The next challenge is that the metal complex based sensitizers involve careful synthesis and tricky purification steps. Considering these drawbacks of ruthenium(II) sensitizers, metal-free

*For correspondence. (e-mail: giribabu@iict.res.in)

sensitizers such as synthetic organic dyes and natural dyes have been thought of as alternatives for DSSC applications. As these sensitizers do not contain noble metals, there is no concern about resource limitation. However, the metal-free organic dye-based DSSCs are not useful for rooftop applications as these molecules are not durable due to instability. For a light-harvesting system, the essential requirements are that the sensitizing dye should have broad absorbing capability, preferably one that encompasses the visible spectrum to near-IR, binds strongly to the semiconductor surface (needs to have an anchoring group), has a suitably high redox potential for regeneration followed by excitation and should be stable over many years of exposure to sunlight. Based on chemical, thermal, photophysical and redox properties, porphyrins are found to be suitable low-cost alternative sensitizers for DSSC applications, even though the synthetic protocols of the porphyrins are tedious.

Porphyrin sensitizers

Nature accomplishes enhanced light absorption by stacking chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structures that act as light-harvesting antenna¹⁵. These antenna absorb the incident light and then direct the excitation energy to reaction centres, where light-induced charge separation takes place¹⁶. Given their primary role in photosynthesis, the use of porphyrins as light harvesters on semiconductors is particularly attractive. Owing to the delocalized macrocyclic structure and strong absorption in the 400–450 nm region (Soret band) as well as two/four less intense absorption bands in the 500–700 nm region (Q-bands), porphyrins have been studied extensively and proved as promising components of molecular electronic and photonic devices^{17–19}. Numerous artificial photonic assemblies based on multi-porphyrin architectures have been designed to mimic photosynthetic solar energy transduction by converting excitation energy to chemical potential in the form of long-lived charge separation²⁰.

Anchoring groups at *meso*-position

Based on the thermal, electronic and photochemical properties, porphyrins are promising sensitizers for DSSC applications. The first porphyrin used for the sensitization of nanocrystalline TiO₂ is [*tetrakis*(4-carboxyphenyl)porphyrinato]zinc(II) (**1**; Figure 1) by Kalyanasundaram *et al.*²¹. They have studied dynamics of electron transfer from excited state of sensitizer to the TiO₂ conduction band. But, the first porphyrin that was studied by Kay and Grätzel²² in a DSSC device is the chlorophyll derivative and other natural porphyrins such as **2** (Figure 1) displayed incident photon to current conversion efficiencies (IPCE) up to 83% at Soret band region with an overall

conversion efficiency (η) of 2.6%. Since then design and synthesis of efficient porphyrin dyes for DSSCs has become one of the major topics of current research, which is evident from the research publications (Figure 2). From 1993 to date, at least 708 publications have focused on the use of porphyrins in solar cells and interestingly, the number of publications in a year is consistently growing, indicating the importance of porphyrins for DSSC applications. A variety of substituted metalloporphyrins have been studied for the photosensitization of wide band-gap semiconductors like NiO, ZnO and TiO₂, etc.^{4,23}.

The most common porphyrin sensitizers used for DSSC are *meso*-substituted benzoic acid linking groups. During the first decade (1993–2003), the efficiency for *meso*-substituted benzoic acid-tethered porphyrins has not changed much. In 2000, 5,10,15,20-tetrakis-(4-carboxyphenyl)porphyrin (**3**; Figure 1) was reported with an efficiency of 3.5% under low light intensity²⁴. Further, in the same report, the adsorption properties of **3** on TiO₂ using XPS and resonance Raman spectroscopy were studied to elucidate the binding characteristics of **3** and it is shown that the low concentrated dye (**3**) solutions (~0.1 mM) are necessary to suppress dye aggregation. In the same year, Koehorst *et al.*²⁵ and Fungo *et al.*²⁶ used heterodimers for more light harvesting; however, they failed to further improve the efficiency. Odobel *et al.*²⁷ used phosphonic acid as anchoring groups instead of carboxylic acid groups on different substitution positions of porphyrin moiety (**4–6**; Figure 1). It was observed that the effect of anchoring group on photoelectrochemical performance has little impact on the device performance. The efficiency of DSSC device using porphyrin as sensitizer having anchoring group at *meso* position had not crossed 4% till 2003, even though a variety of substitutions have been introduced on the porphyrin macrocycle^{28–31}.

Anchoring groups at pyrrole- β position

The electronic π cloud of porphyrin is present above and below the plane of the macrocycle and therefore it was thought that the anchoring group connected at pyrrole- β position may give better efficiency than at *meso*-positions. The use of conjugated β -substituted anchoring groups was first demonstrated in 2004 by Nazeeruddin *et al.*³², who reported a new porphyrin dye (**7**; Figure 3) with an energy conversion efficiency of 4.80% (open circuit voltage, $V_{oc} = 660$ mV and short-circuit current $J_{sc} = 9.7$ mA cm⁻²), which shows new avenues for improving the efficiency further of nanocrystalline solar cells for practical utility by engineering suitable porphyrins with smaller band-gap, capable of absorbing in the visible and near-IR regions of the solar spectrum. Later, various porphyrin sensitizers having anchoring group at pyrrole- β position were developed. In 2005, the molecular structure

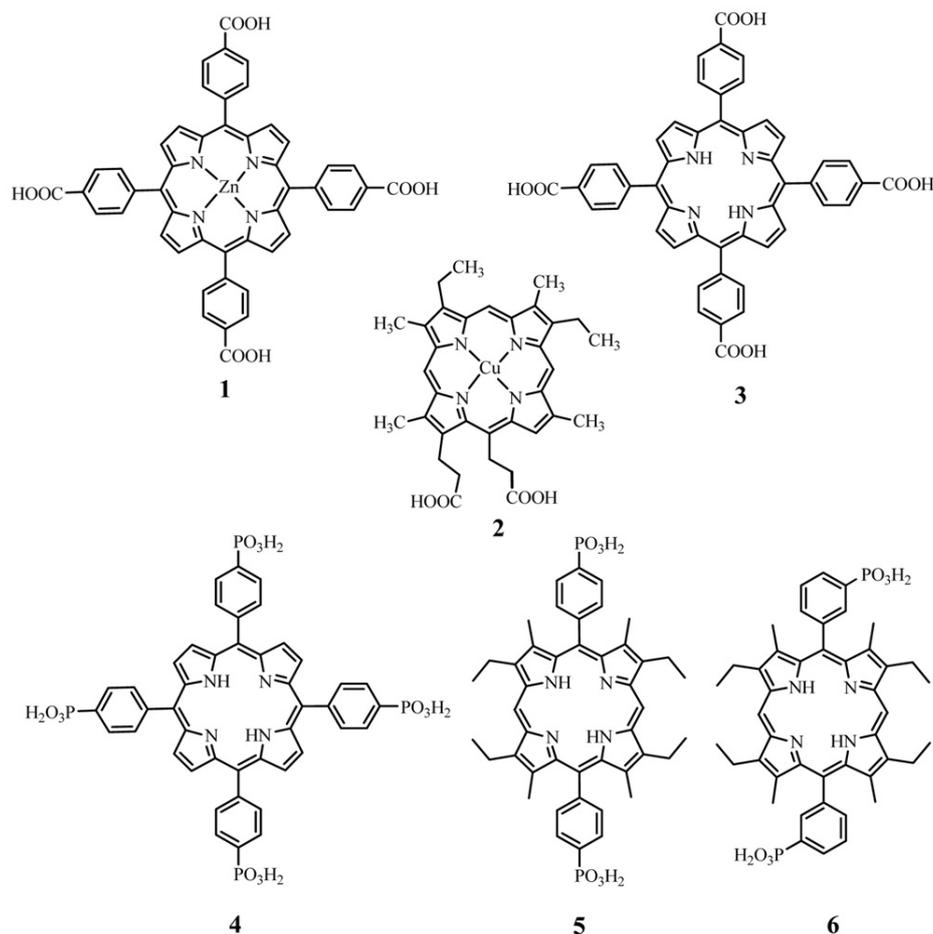


Figure 1. Porphyrins having anchoring group/s at *-meso* position.

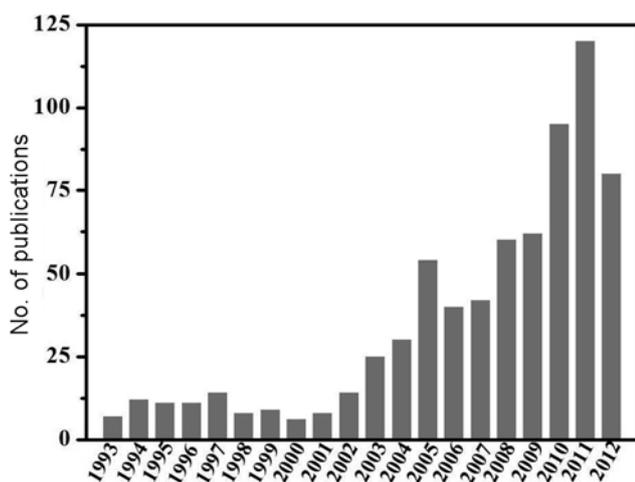


Figure 2. The number of porphyrin solar cell publications per year found via the search term 'porphyrin solar cells' in SciFinder (9 August 2012).

of **7** was slightly modified by introducing cyanoacetic acid on extended π -conjugation in the place of phenyl group (**8**; Figure 3)^{33,34}. The sensitizer has shown V_{oc} of

566 mV and J_{sc} of 13.5 mA/cm² with an overall conversion efficiency of 5.2%. The increase in test-cell efficiency was assigned to the electron-withdrawing nature of the cyano group. The molecular structure of **8** was further modified by introducing an additional extended π -conjugation, resulting in **9** (Figure 3); as a result the absorption spectrum was red-shifted with enhanced molar extinction coefficient (ϵ)³⁴. The DSSC device fabricated with this sensitizer using a hole transport material (spiro-MeOTAD) showed IPCE of 65% at Soret band region, but in the Q-band region, the highest value was only 25%. The device has shown an overall conversion efficiency of 3%.

In 2007, Campbell *et al.*³⁵ reported a 7.1% efficient porphyrin **10** (Figure 3), which consists of tetratolyl porphyrin with a conjugated bridge to a dicarboxylic acid acceptor moiety. They have reported a series of pyrrole- β carboxylated porphyrins with change in alkyl group on *meso*-phenyl group of the macrocycle. Among these sensitizers, porphyrins having 4-methyl (**10**), 4-*n*-butyl (**11**; Figure 3) and 3,5-dimethyl (**9**) on phenyl ring have crossed an efficiency of 6%. The sensitizer **10** has been used for solid-state device which shows IPCE of 63% and

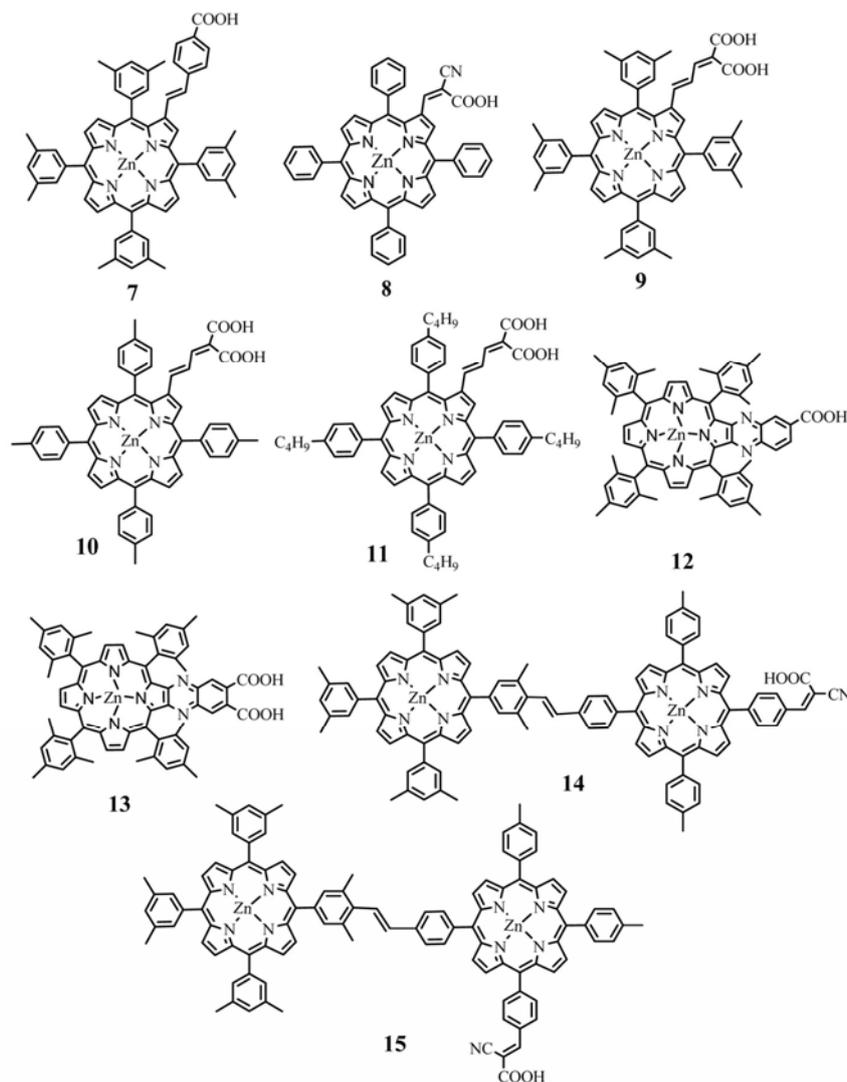


Figure 3. Porphyrins having anchoring group/s at pyrrole- β position.

overall conversion efficiency of 3.6%. Later, they have used these pyrrole- β carboxylated porphyrins to study several aspects of solar cells, especially structure–property relationship with the cell performance. For example, they have explored the use of a post-adsorbed phosphinic acid blocking moiety to improve efficiency by minimizing recombination events at the electrode surface³⁶. The use of ionic liquid electrolytes as a replacement for volatile organic solvents in typical liquid electrolytes has also been studied³⁷. Further the V_{oc} and electron injection dynamics using β -substituted porphyrins and suggested that the reason for limitations to the V_{oc} and J_{sc} are related to reduced electron lifetime and less favourable electron injection dynamics.

β,β' -Quinoxalino porphyrins containing different numbers of carboxylic acid anchoring groups have been evaluated as photosensitizers for DSSC (**12**, **13**; Figure 3)³⁸. Both the sensitizers showed broadened, red-shifted and

amplified light absorption with the aid of extended π -conjugation. Density functional theory (DFT) calculations reveal that the HOMO–LUMO gap of these sensitizers is very low due to the substitutions onto the β,β' -edge of the porphyrins, which mainly affects the energy levels of the unoccupied orbitals of porphyrins. Photovoltaic measurements of **12** and **13** sensitized TiO₂ cells showed the power conversion efficiencies of 5.2% and 4.0% respectively. Their results further revealed that the number and position of binding/anchoring groups on the porphyrin moieties have a large impact on the photovoltaic and photoelectrochemical performances.

Mozer *et al.*³⁹ have designed a Zn–Zn porphyrin dimer comprising two efficient monomeric porphyrin dyes linked either in a linear *anti* (**14**; Figure 3) or 90° *syn* (**15**; Figure 3) fashion, representing simple building blocks of linear or branched 3D multichromophore arrays. DFT calculations show that each porphyrin dimer acts as two

non-interacting electronic entities. The Soret band of both the dimers asymmetrically broadened and the molar extinction coefficients (ϵ) of their Q-bands are nearly double to those of the monomeric units and 70% IPCE has been achieved. Surprisingly, major difference in dye uptake injection efficiency or device performance is not observed between the linear or angled dimer, suggesting that both these building blocks could, in principle, be used to construct larger 3D multichromophore light-harvesting arrays with efficient solar energy conversion. Later, many groups including our group^{40–43} have designed new sensitizers based on pyrrole- β carboxylated porphyrin, but efficiency has not crossed 7%.

D- π -A approach

As mentioned in earlier sections, porphyrin macrocycles having anchoring groups at *meso*-phenyl position, gave efficiency up to 4%, whereas anchoring groups at pyrrole- β position have shown efficiencies of up to 7%, which are relatively less compared to ruthenium(II) polypyridyl complexes. In order to further improve the efficiency of DSSC device based on porphyrin sensitizer, the design strategy of the sensitizer needs to be changed. Porphyrins have a typically intense Soret band (at around 420 nm region) and either four (free-base) or two (metallo) less intense Q-bands (in 500–650 nm region). On the other hand, porphyrins have minimum absorption in the 450–500 nm region. For further improvement of efficiency of DSSC device based on porphyrin sensitizers, one has to improve the absorption capability of porphyrin in the 450–500 nm region and/or red-shift of both Soret as well as Q-bands.

Lee *et al.*⁴⁴ have developed new porphyrins (**16** and **17**; Figure 4) based on D- π -A architecture, bearing one or two triarylamine moieties at the *meso*-position/s and studied the photoelectrochemical properties. They have used triphenylamine moiety as donor group, carboxylic acid group as acceptor and porphyrin macrocycle as π -linker between donor and acceptor. The UV-visible absorption spectra reveal that the Soret band (\sim 60 nm) and the Q bands (\sim 125 nm) were red-shifted and ϵ values enhanced due to the newly introduced substituents. The enhancement is even more pronounced in the longer wavelength region (575–725 nm) and the absorption of porphyrin **17** is higher than porphyrin **16**. Both sensitizers **16** and **17** show enhanced light-harvesting ability; however, energy conversion efficiency is found to be poor. The low energy conversion efficiency is attributed to the aggregation of the porphyrin molecules and geometry of the anchoring group.

Bessho *et al.*⁴⁵ redesigned the porphyrin sensitizer **17**, resulting in **18** (Figure 4). This sensitizer has a diarylamino group attached to the porphyrin ring acting as electron donor, the ethynylbenzoic acid moiety serves as acceptor and the porphyrin chromophore itself constitutes

a π -bridge between donor and acceptor, forming the D- π -A structure. The absorption spectra shows that both Soret and Q-bands are red-shifted and the sensitizer has shown 8.8% efficiency. Interestingly, IPCE at two absorption bands has reached up to 85% (IPCE_{Soret} = 85%, IPCE_{Q band} \approx 80%, V_{oc} = 0.735 V, J_{sc} = 16.7 mA cm⁻²) on 11.5 μ m thick nanocrystalline TiO₂ surface using liquid redox (I⁻/I₃⁻) electrolyte. Although the IPCE of **18** reached 85%, this sensitizer lacks absorption between 480 and 630 nm, which hampers the efficiency of the device by reducing short-circuit current J_{sc} values. However, co-sensitization of **18** with an organic dye shows complementary spectral responses in the visible spectral range, and has an efficiency of 11% (V_{oc} = 0.77 V, J_{sc} = 18.6 mA cm⁻²) with standard AM 1.5G simulated sunlight (100 mW cm⁻²). Wang *et al.*⁴⁶ replaced donor diarylamino group of **18** with a series of organic donor groups phenylethynyl, naphthalenylethynyl, anthracenylethynyl, phenanthrenylethynyl or pyrenylethynyl in D- π -A molecular architecture. The pyrenylethynyl sensitizer **19** (Figure 4) has shown good efficiency of 10.06% (V_{oc} = 0.711 V, J_{sc} = 19.62 mA cm⁻²). This may be attributed to the broad spectral response of the sensitizer between 400 and 800 nm.

Redox electrolyte, which transports positive charge carriers from the sensitizer to the back contact of the device, is also known to play a crucial role in achieving high DSSC device efficiency. However, the use of common redox couple, iodide/triiodide system limits the attainable open-circuit potential V_{oc} to 0.7–0.8 V due to excess loss of voltage during the regeneration. Therefore, the overall DSSC efficiency is limited by triiodide high over potential for dye regeneration and by competitive light absorption^{47–49}. Moreover, the scale-up of DSSCs and the module stability are hindered by the corrosiveness of the iodide/triiodide redox couple towards most metals and sealing materials. So considering these factors, a new sensitizer (**20**; Figure 4) was developed by exploiting one-electron outer-sphere cobalt complexes as redox couples⁵⁰. As these complexes have weak visible light absorption and are less aggressive toward metallic conductors than iodine, they are expected to show better efficiency⁵⁰. The new sensitizer (**20**) is developed by a modification of **18**, by incorporating two octyloxy groups in the *ortho*-positions of each *meso*-phenyl. The octyloxy groups improved the photo-induced charge separation by reducing back electron transfer from semiconductor to electrolyte system in DSSCs using Co(II/III)*tris*(bipyridyl)-based redox electrolyte. The device based on this sensitizer showed highest IPCE values of 11.9%, which produces a V_{oc} of 965 mV, a J_{sc} of 17.3 mA/cm², and a fill factor (FF) of 0.71 under standard AM 1.5G test conditions. Further, co-sensitization of **20** with an organic dye, yielded very high efficiency of 12.3% when used in conjunction with the Co(II/III)*tris*(bipyridyl)-based redox electrolyte. The PCE even exceeds 13% under

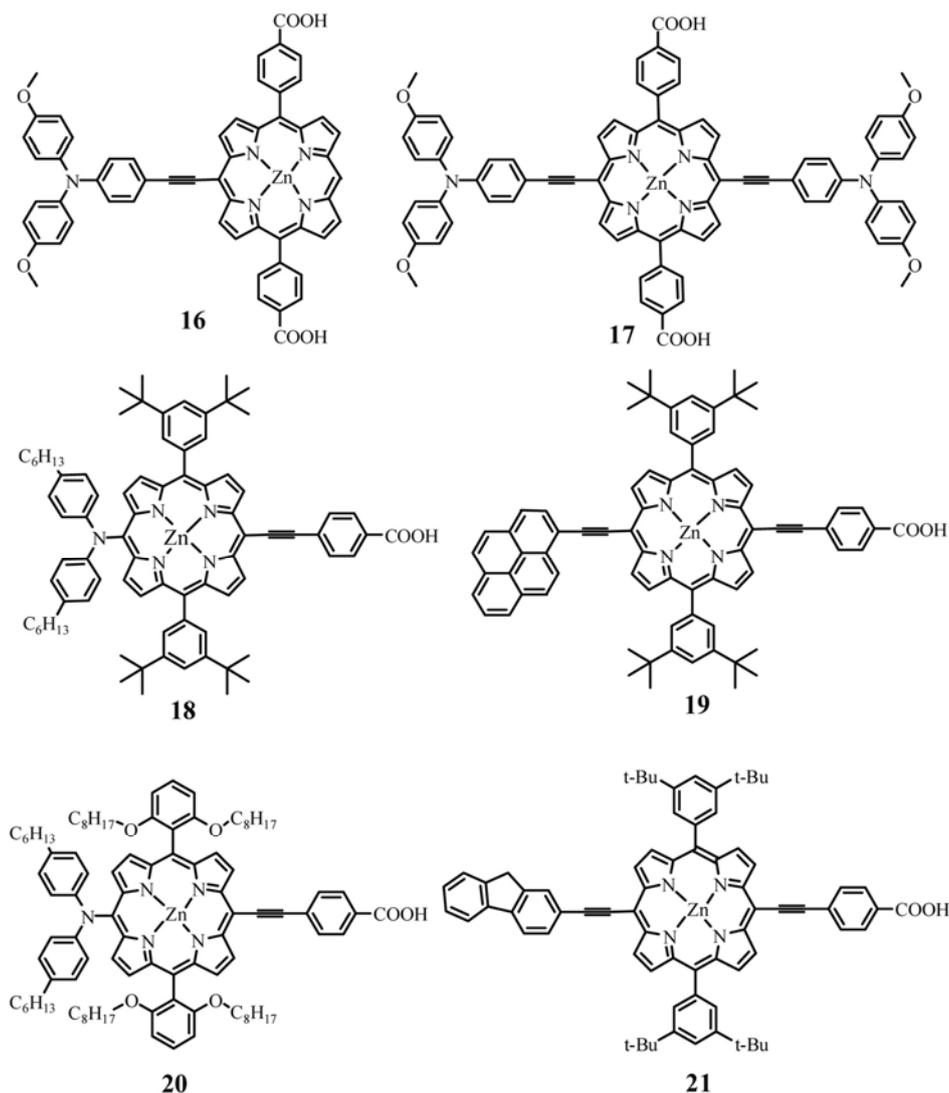


Figure 4. D- π -A porphyrin structures.

AM 1.5G solar light of 500 W m^{-2} intensity. This is really a breakthrough in DSSC research, because the highest efficiency of Ru(II)-based sensitizer (11.57%) is taken over by the porphyrin-based sensitizer⁵¹. Usually, porphyrin-based dyes exhibit less V_{oc} values compared to the ruthenium dyes due to more recombination processes⁵². However, the V_{oc} of **20** (965 mV) is found to be higher than any one of the ruthenium-based sensitizers reported so far. By elegant modification on the molecule **20**, Grätzel⁵⁰ and co-workers succeeded in improving the V_{oc} . The octyloxy groups placed at *ortho*-positions of phenyl rings and near the porphine macrocycle greatly reduced the recombination losses as well as aggregation, and thus helped improving the overall efficiency. Perhaps, a similar kind of strategy may be adopted while designing new porphyrin-based sensitizers in order to get higher V_{oc} values.

Interestingly, after this report, the research on porphyrin-based sensitizers has increased dramatically. For exam-

ple, Wang *et al.*⁵³ prepared a series of zinc porphyrins modified with polyaromatic or heterocyclic substituents. Photovoltaic measurements suggested that the fluorene-modified porphyrin, **21** (Figure 4) is an efficient sensitizer for solar harvesting and gave an overall efficiency of 8.1%, which is about 90% that of the Ru(II) sensitizer, N719 solar cells under similar conditions. The superior performance of **21** results from higher J_{sc} and V_{oc} , and stronger and broader photovoltaic responses from 350 to 750 nm. Further their results suggested that rigid molecular structure and high fluorescence quantum yield of a sensitizer can be important factors for designing an efficient photo-sensitizer. Wu *et al.*⁵⁴ have further redesigned the porphyrin sensitizer architecture, but the efficiency has not crossed the record efficiency. Warnan *et al.*⁵⁵ reported a new series of push-pull diketopyrrolopyrrole-porphyrin dyes for DSSCs. By placing diketopyrrolopyrrole (DPP) between the porphyrin core and the anchoring

group, the photoactivity of the dyes at around 500 nm was enhanced. However, the efficiency was very poor (2.55%) due to high cathodic oxidation potential, which makes the regeneration reaction particularly inefficient and subsequently limits the charge-collection efficiency and the short singlet excited-state, that may reduce the electron injection quantum yield. Kang *et al.*⁵⁶ synthesized two push-pull Zn(II)-porphyrin dyes with an electron-donating bis(3,3-dimethylfluorenyl)amine group at the *meso*-position. One of dyes having a strong electron-accepting cyano-acrylic acid substituent shows relatively high overall energy conversion efficiency (7.22%) compared to the other dye which has only -COOH group. These dyes show enhanced conversion efficiencies in the presence of co-adsorbents. A similar kind of zinc porphyrin sensitizer based on D- π -A architecture was later reported by incorporating triphenylamine as a donor moiety, but its efficiency is less⁵⁷.

He *et al.*⁵⁸ reported a simple zinc porphyrin having an acrylic acid at the *meso*-position shows an energy conversion efficiency of 5.1%. Warnan *et al.*⁵⁹ doped a zinc porphyrin sensitizer with antenna molecules such as borondipyrromethene and diketopyrrolopyrrole, which are held axially by metallo-supramolecular interactions. Although the cocktail sensitizer showed panchromatic response⁵⁹, its light-harvesting efficiency remains below 5%. Ripolles-Sanchis *et al.*⁶⁰ synthesized three push-pull molecules and the dye having simple -COOH acceptor group showed better efficiency (8.61%) than the other dyes. In another study it was found that the number and position of thienyl and *p*-carboxyphenyl substituents at *meso*-position of a zinc porphyrin dye significantly affect the performance of the device⁶¹. Zhou *et al.*⁶² have synthesized two novel dyes by modifying porphyrin with alkyl-thiophene and 2,1,3-benzothiadiazole moieties. With the introduction of low-band-gap chromophore in the porphyrins, the absorption spectra of the two porphyrin dyes broadened and the maximum wavelength was red-shifted compared with tritolylporphyrin. Under standard global AM 1.5G solar conditions, the DSSC fabricated from one of the dyes showed 5.46% efficiency and monochromatic IPCE reached 65% with a broad respondent region of 350–800 nm (ref. 62). Recently, a new series (push push-pull pull) of two A₂B₂ type porphyrins has been synthesized and characterized as photosensitizers for DSSCs applications⁶³. These dye molecules contain a porphyrin unit as a π -spacer, two *N,N'*-dimethylphenyl groups as electron donors and two phenylcarboxylic acid moieties as anchoring groups. Under photovoltaic measurements, overall IPCEs of 3.80% and 4.90% were achieved, which were further improved up to 4.83% and 6.07%, when chenodeoxycholic acid (CDCA) co-adsorbent was employed in the device fabrication. These results further suggested that the electron lifetime was improved by the co-adsorption of CDCA because of the improvement in both V_{oc} and J_{sc} .

Very recently, few more articles related to the porphyrin DSSCs have been reported in the literature^{61,64,65}. However, their efficiency is not further improved.

Conclusion

The record efficiency of porphyrins opens a new debate – can we consider porphyrins as an alternative to the classical ruthenium(II)-based sensitizers? This can be answered by looking at the pros and cons of both ruthenium(II) and porphyrin sensitizers. The porphyrins have certain advantages over ruthenium sensitizers. Porphyrin sensitizers can be conveniently synthesized by well-established protocols. Unlike ruthenium counterparts, these sensitizers are inexpensive, stable and durable. The porphyrins derivatives showed relatively higher molar absorption coefficients; in other words, they are good harvesters. So, considering these advantages and the remarkable efficiency (12.3%) we can say that porphyrins are indeed a good alternative to the ruthenium dyes. In future one expects that this record efficiency can be broken by designing appropriate porphyrins having broad absorption starting from the visible to NIR region, and linear response of the photocurrent to full sunlight. However, further developments are needed to replace the volatile electrolyte by nonvolatile ionic liquid-based systems and solid-state hole transporting conductors. It is also necessary to develop new sensitizers which have reasonable absorption between the Soret band and Q-band region.

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