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ORIGINAL ARTICLE

Porphyrin-Based Dye-Sensitized Solar Cells (DSSCs): a Review

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Abstract The current review aims to collect short information about photovoltaic performance and structure of porphyrin-based sensitizers used in dye-sensitized solar cells (DSSC). Sensitizer is the key component of the DSSC device. Structure of sensitizer is important to achieve high photovoltaic performance. Porphyrin derivatives are suitable for DSSC applications due to their thermal, electronic and photovoltaic properties. It describes some electrochemical and spectral properties as well as thestructure of porphyrin dyes used in dye based-solar cells.

Keywords Porphyrin · DSSC · TiO_2 · Solar cells

Introduction

Nowadays, the world is facing major enviromental problems such as pollution, global warming, overpopulation, natural resource depletion, waste disposal, climate changes, deforestration, ozona layer depletion, acid rain, public health issues [1]**.** People are aware and caucious about the environmental issues. One of the main problems is the depletion of natural resource that force us to think and plan for various renewable energy sources [2] – energy that is based on solar, biomass, wind power, geothermaletc [1]. Although various fossil fuel resources such as oil, coal and natural gas are the largest energy sources for our living and production, these are not renewable. Sun is direct or indirect renewable energy source. Solar energy can be used directlytoheat and light homes, generating electricity, and heatwater. Solar-to-electric energy conversion can playan important role toreplace fosil fuels [2]**.**

Sunlight is the most abundant, cleanest, cheap and safe energy source [3, 4]**.** Photovoltaic cells are used to convert sunlight into electric power. Commonly used phorovoltaic call are made of silicon (Si), cadmium telluride (CdTe), copper indium selenide/sulfide (CIS), perovskite solar cell and dye sensitized solar cells (DSSC) [1]. In 1991, Gratzel and his team developed DSSC known as Gratzel cell. In his cells, dye molecules were used as light absorber on the nanocrystalline film of titanium dioxide (TiO_2) [5]**.** DSSCs has attracted the attension of scientists as an alternativeto the conventional photovoltaic celldue to their low production costs from sun light [6, 7], high power conversion efficiency [6], simplicity of fabrication [8] and tunable optical properties [9].

In the present review, we summarized the results from literature on the use of DSSC material of porphyrin derivatives as light absorber and DSSC in four contexts:

1. Structure of DSSC
2. Working Principle of DSSC
3. Some Phorphyrine Derivative Dyes used in DSSC
4. Literature information of porphyrin derivatives for DSSC applications

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Structure of DSSC

The typical DSSC is a sandwich structure device having four major parts:

1) a photoanode composed of a nanocrystalline semiconductor film such as TiO_2 on a conducting glass substrate
2) monolayer of a sensitizer, normally a dye, adsorbed on the TiO_2 surface
3) electrolyte containing a redox couple such as I^-/I_3^-
4) a cathode

TiO_2

A porous layer of titanium dioxide (TiO_2) nanoparticles having wide band gapsuitable to generate useful voltage. Titanium dioxide (TiO_2) exits in three forms i.e. rutile, anatase and brookite. Although rutile is more stable, crystalline anataseis favoured as it is chemically more active in DSSCs [10]. The TiO_2 is a semiconductor that has a wide band gap (E_{bg} ~ 3.2 eV) [11]. It is low in cost, widely available, biocompatible, cheap, thermally stable, chemically inertand nontoxic. In atypical DSSC, the particle size of TiO_2 anatase ranges 10–25 nm with a film thickness of 5–15 μm. Figure 1 shows various semiconductor oxides have similar energy band structure as that of TiO_2.

There are several alternatives to TiO_2. Zinc oxide (ZnO) is a promising alternate to TiO_2 because of its similar band structure and relatively high electron mobility [10]. Shalini et al. prepared ZnO films on a conducting glass substrate showed an efficiency of 0.4%. Higher electronic mobility of ZnO makes it more suitable for use in DSSC, but they have lesser life time due to the degradation of organic dyes under sunlight, increasing temperature, oxygen absorption, chemical change of electrodes and interface instability [11].

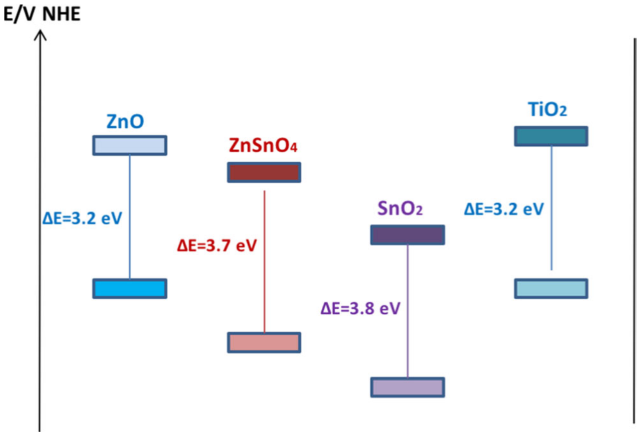


Fig. 1 Band gaps of various semiconductor oxides

Tin oxide (SnO_2) is another semiconductor oxide that has high mobility and large band gapi.e. 3.8 eV as compared to TiO_2 (3.2 eV). It creates fewer oxidative holes in the valence band under ultraviolet light thereby reduce the dye degradation rate and improve the stability of DSSCs. More positive band edge position facilitates electron injection from photoexcited dye molecules. The performance of SnO_2-based DSSCs have been observed far much less than that of TiO_2 based ones. Particles of TiO_2 that are used as a photoanode to absorb sunlight are well-known n-type semiconductor that provides more surface to adsorb dye, accept electrons from the excited dye and conducts them towards the external circuit.

Dye

A dye, called as sensitizer is covalently bonded to the surface of the mesoporous oxide layer to enhance light absorption [10]. The dye acts as molecular electron pump in DSSC [11] by absorbing visible light, generating excited electrons and pumping them into the semiconductor [12].

The sensitizers used in the DSSC can be divided into organic and inorganic. Inorganic dyes contains a transition metal in the structure [6]. Polypyridyl ruthenium complexes had been regarded as the most efficient sensitizers and an overall light to electric power conversion efficiency (η) of up to 11% was achieved by using N719 *(*Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II)) –based DSSCs. However, since ruthenium is a rare metal, it is expensive and enviromental issues caused by the production of ruthenium complexes limitsits applications [13].

The dye must have certain properties to be suitable for application in DSSCs e.g. strong absorption in the visible range, high photo and thermal stability [11], good adsorption onthe semiconductor's surface, that is, bonding strongly to the semiconductor surface with anchoring group, high solubility in the corresponding solvent, no toxicity, have a broad absorption spectrum in the visible range in order to capture solar radiation, a suitable high redox potential for regeneration followed by excitation [6, 14].

Many organic dyes such as porphyrine, coumarines, perylenes, phthalocyanines, triarylamines and carbazole have been paid great attention because of their modest cost, large molar absorprion coefficients and satisfactory stability [15]. Organic dyes can be classified into donor-acceptor (D-A), donor-bridge-acceptor (D-B-A) and acceptor-bridge-acceptor (A-B-A) systems that have applications as electroactive and photoactive and photoactive materials in the field of molecular electronics; mainly photovoltaic Technologies [16]. Bonding to TiO_2 surface has been achieved through functional groups such as salicylate, carboxylic acid, sulphonic acid, phosphonic acid and aclyacetonate derivatives [17]. So, the functional group of π-extended dye is vital to adsorp on the surface of TiO_2. Carboxylic acids are the most extensively studied anchoring groups in porphyrin-sensitized solar cells. They promote strong electronic coupling between the energy levels of the excited sensitizer and the metal oxide, that results in fast and efficient electron injection.

Electrolyte

An electrolyte, mostly iodide-tri-iodide, undergoes redox reaction. The efficiency of DSSCs depends on the sensitizers, photoanode and counter electrode [19]. Also elctrolyte is very important to determine cell performance. So the electrolyte is one of the key components in DSSCs. Electron injection depends on the reducing ability of the electrolyte [11, 20]. It provides internal electric ion conductivity by diffusing within the mesoporous TiO_2 layer. Electrolyte contains a redox couple (such as I^-/I_3^-) that fills the space between the two electrodes [12]**.** Based on their physical state, the electrolyte used in DSSCscan be divided into three types: liquid, quasi and solid. Liquid electrolytes could be divided into organic solvent electrolyte and ionic liquid electrolytes according to the solvent used. Iodide/triiodide-based liquid electrolyte being redox electrolyte has been the most widely used and efficientelectrolyte [21, 22].

Counter Electrode, Platinum (Pt)

Platinum (Pt) is typically used as a counter electrode to catalyze the triiodide ions that are formed in the electrolytes by the reduction of iodide ions. Although Pt has higher energy conversion efficiencies, it has few limitations such as higher cost, instability in redox electrolyte, high temperature sintering and resource scarcity. The open circuit voltage in DSSCs is determined by the energy difference between the fermi levels of the transparent conducting oxide (TCO) to the nanocrystalline TiO_2 film and the counter electrode. An ideal counter electrode (CE) should have low electrical resistance and high electro-catalytic activity towards theiodide/triiodide redox reaction, being stable and transparent [11].

Working Principle of Dye-Sensitized Solar Cells

Dye-derived nanocrystalline titania films are used as photoanod while platinized counter electrode, filled with electrolyte solution of I_3^-/I^- in organic solvent. Cell is illuminated through the TiO_2 side [20]**.**

Upon light illumination:

1. Light adsorbed by sensitizer that are adsorbed on the surface of mesoporous TiO_2 layer excites an electron. Electrons of the sensitizer are photo-excited.
2. An electron from the excited dye injects into the conduction band (CB) of TiO_2.
3. The dye molecules that loose an electron gets oxidized
4. The free electron travels through the layer of TiO_2 and flow through the external circuit to arrive at the counter electrode
5. The electron converts $I_3^-$to I^-. Then, the oxidized dye is reduced back to its neutral state electron donation from electrolyte containing usually the solution of an organic solvent or ionic liquid solvent containing I_3^-/I^- redox system.
6. The iodide is regenerated by reduction of triiodide at the counter electrode.

By this way, circuit is completed and the process can continue without permanent chemical change [6, 23]**.** These processes are competed by recombination of the injected electrons, either with the oxidized dye or the electron acceptor of the redox couple (I_3^-)**,** resulting in the dark current of the solar cell, and by relaxation of the excited dye to its ground state by a non-radiative decay process [12].

$$S_{(adsorbed)} + h\gamma \rightarrow S^*_{(adsorbed}$$
$$S^*_{(adsorbed)} \rightarrow S^+_{(adsorbed)} + e^-$$
$$2e^-_{(cathode)} + I^-_3 \rightarrow 3\ I^-_{(cathode)}$$
$$S^+_{(adsorbed)} + 3/2\ I^- \rightarrow S_{(adsorbed)} + 1/2\ \ I^-_3$$
$$S^+_{(adsorbed)} + e^-_{(TiO2)} \rightarrow S_{(adsorbed)}$$
$$I^-_3 + 2e^-_{(TiO2)} \rightarrow 3\ I^-_{(anode)}$$

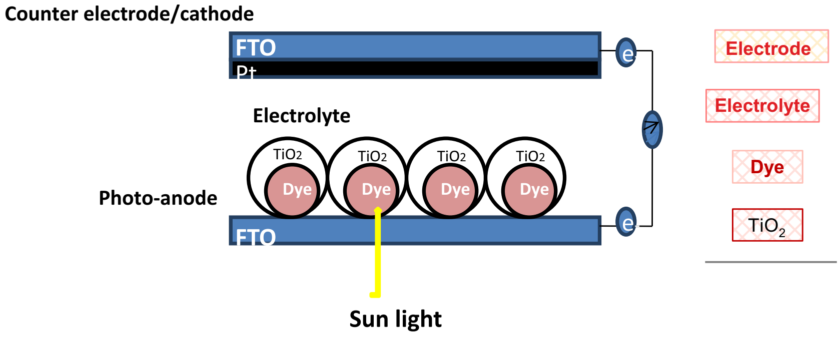


Fig. 2 Schematic diagram of a common DSSC [18]

Table 1 Absorption and emissions of 4a, b and c porphyrin based dyes

Dye	Absorption	Emission
2	432, 569	620
3	424, 566	610
4	422, 557	600

Numbers in bold represents the molecules

Some Phorphyrine Derivatives Used in Dye-Based Solar Cells

Porphyrin sensitizers have attracted a great deal of attention in solar cells as they are cheap, easy to synthesize and modify, stable [24], less toxic [25, 26], rigid geometry, the ability to coordinate metals, efficient electron transfer [27] etc. They also possess high molar absorption coefficients [28] and excellent light harvesiting potential. Porphyrins absorbsin visible and near infrared (NIR) region of solar spectrum ie. intense Soret absorption band (400–450 nm) in the blue region and moderate Q absorption bands (500–650 nm) in the red region [26, 29–33]. The energy of LUMO orbitals of porphyrin is above the conduction band of TiO_2while its HOMO level is below the redox couple of the electrolyte solution [34].

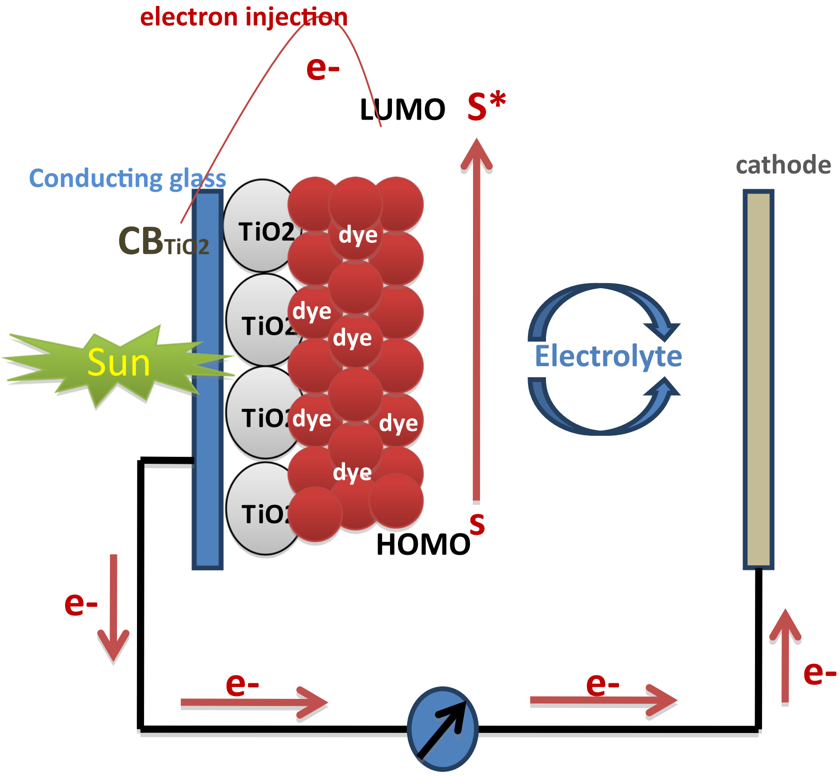
Porphyrins (Pors) are macrocycles consists of four pyrole rings fused together. They are highly conjugated systems of 20 carbons and 4 nitrogens. It has 18-Π electrons that makes them aromatic. The acidic NH protons located inside porphyrin ring can be deprotonated to yield porphyrinato anions. These rigid and planner dianion species with a central cavity exhibits remarkable ligation characteristic towards metal cations [35]. Porphyrin can be derivatize at beta and meso positions as shown in Fig. 3.

Porphyrin molecules are used in various applications such as chemical and biological sensors in addition to DSSC, transistor and organic light emitting diodes [27]. The properties of porphyrin sensitizers can be tuned by modifying their donor, Π-conjugate-bridge and acceptor [36]. Charge seperation is an important factor that affects solar cell efficiency. It is formed in photoinduced change transfer between the donor and acceptor. When the donor absorbs light energy, it injects an electron into the LUMO of the acceptor [37].

Mikroyannidis et al. have synthesized meso-substituted carboxylic acid Zn-porphyrin molecule (P) as shown in Fig. 1. Molecule (1) has a soret band at 427 nm and Q bands at 559 nm and 606 nm. Its absorption peak is broad and strong in the range of 300–750 nm. It is atrributed to the extended conjugation of Π-systems in the meso-positions of porphyrin. An intramolecular charge transfer (ICT) takes place between the electron donating central porphyrin core and the electron withdrawing terminal cyanovinylene 4-nitrophenyls. This group enhanced the solubility.

The LUMO and HOMO energy levels for P are −3.55 eV and −5.50 eV, respectively. The band gap value of 1 is 1.95 eV. The LUMO level of dye should be higher than the conduction band of TiO_2. The difference between that values must be higher than 0.2 eV for efficient electron injection.

Fig. 3 Working principle of DSSC



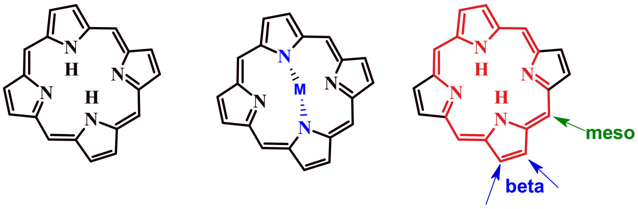


Fig. 4 Molecular structure of porphyrin (M: Zn^{2+}, Cu^{2+}, etc) [27]

The power conversion efficiency (PCE) of 1 is 2.90%. PCE has been improved up to 4.22% with addition of deoxycholic acid (DCA) to the solution of 1 for TiO_2 sensitization. Dye aggregation or close Π-Π* stacking causes the charge recombination. Also, the lower harge collection efficiency or lower incident photons to current efficiency (ICPE) is attributed to the charge recombination. IPCE is improved with coadsorption by using deoxycholic acid (DCA). Mikroyannidis et al. [26] reported that co-adsorption is necessary to break up the dye aggregates.

The structure of 1 molecule is highly conjugated that is important for red shift. Also, 1 molecule has two carboxylic acid groupsat meso positions. But at the end of conjugate system, 1 molecule has nitro groups [26].

Y. Liangs et al. [38] have synthesized three types Zn-porphyrine molecule as shown in Fig. 2. The absorption of porphyrin molecules (2, 3, 4) has measured in dichloromethane. Molecules have typical Soret and Q bands. It is observed that the absorption spectrum of 3 and 4 is slightly blue shift compared to 4a (Table 1).

The HOMO energy levels are −5.101 eV for 2, −5.135 eV for 3, −5.124 eV for 4 while LUMO energy levels are −3.117 eV for 2, −3.079eVfor 3, −3.144 eV for 4. The HOMO energy levels of all molecules are lower than that of I^{-}/I^{3-}(−4.8 eV). Y. Liangs has reported that all sensitizers can be efficiently regenerated by taking electrons from the electrolyte after photooxidation. The power conversion efficiency of the stated molecules is 4.05% for 2, 5.26% for 3 and 2.62% for 4. The PCE of 3 is greater thanthat of 2 and 4.

Molecules shown in Fig. 3 are highly conjugated and containing cyanoacetic acids. The carboxylate groups are strongly bonded to the TiO_2 surface. Synthesized porphyrin molecules have a donor- Π-acceptor (D-Π-A) system. Diphenylamine, iminodibenzyl or iminostilbene groups are introduced at porphyrin meso position as an electron donating group. The power conversion efficiency of 4b molecule is greater than that diphenylamine and iminostilbene-substituted porphyrin sensitized solar cells [39]. Dye should be strongly anchored on the surface of TiO_2 to decrease the interface resistance. Electrons in the dye molecule need be quickly seperated from holes and injected to the photoanodes before recombining [39].

Table 2 Absorption and emission of dyes synthesized by Lu et al.

Dye	Absorption	Emission
7	454, 670	688
8	459, 667	682
9	461, 468	678

Numbers in bold represents the molecules

Sharma et al. [33] have synthesized Zn-porphyrine moleculeas shown in Fig. 3. Porphyrin derivative molecule has in soret band in the 400–450 nm and two weaker Q bands in the 520–650 nm region. These bands arise from the configurational interaction of two porphyrin Π- Π* electronic transitions. The UV-vis absorption spectrum of molecule onto TiO_2 show similar absorption but broader. This is beause of anchoring of the sensitizer through its carboxylic acid groups to TiO_2.

The LUMO energy levels are −3.07 eV. It is higher than the TiO_2 conduction band edge (−4.2 eV in vacuum). The efficiently electron injection from LUMO of excited dye molecule to conductive band of TiO_2 is possible. The HOMO energy level of 5 is −5.23 eV. This value is lower than the potential of the elctrolyte redox couple I^{-}/I^{3-} (−4.8 eV). Therefore, dye regeneration is thermodynamically feasible and could compete efficiently with recapture of injected electrons by the dye radical cations.

The power conversion efficiency of molecule 5 4.72%. It is used in co-sensitization to improve the photovoltaic performance of DSSCs. Sharma used a tertiary aryl amine compound 6 with two ethynyl-pyridine substituents and a terminal cyano-acetic acid group as a co-sensitization that improved the photovoltaic performance by 7.34% [33].

Lu et al. [19] have synthesized three types of Zn-porphyrine moleculebased on alkynes (7, 8, 9) as shown in Fig. 4. The absorption spectra of all molecules are similar. While the B bands involving the transition from the ground state to the second excited state are at 454, 459 and 461 nm, Q bands involving from weak transition to the first excited state are at 670, 667 and 668 nm (Table 2).

The power conversion efficiency of 9 is 8.53%, 8 is 8.20%, and 7 is 6.87%. The results of the power conversion efficiency show that long chain groups on the meso positionaffect the cell performance [19].

The carboxylic acid groups provide efficient adsorption of the dye on the semiconductor surface. Also, it promotes electronic coupling between the donor levels of the excited chromophore and the acceptor levels of the TiO_2 [17].

Zhang et al. [13] have synthesized three types of Zn-porphyrine moleculecontaining bis(phenyl hexyl) ethers (10, 11, 12) as shown in Fig. 5. The oxidation potential of 10 is 0.29 eV, 11 is 0.32 eV while 12 is 0.34 eV (Table 3). The very slightly shift of the oxidation potentials suggest minimal influence of the number of meso-substituted anchor groupand the type of anchor group on the porphyrins HOMO energy levels. The UV-Vis spectra of the porphyrin sensitizers show absorption between 400 and 650 nm due to Π-Π* transitions on the conjugated macrocycle.

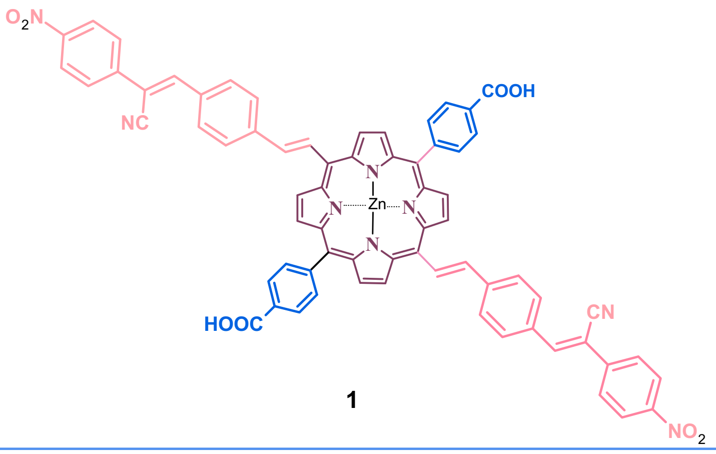


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Fig. 5 Molecule P

While the power conversion efficiency of 12 and 10 are 4.16% and 3.94%, respectively, the power conversion efficiency of 10 is 2.93%. It is probably due to the more effective conjugation of double bond in 12 with the porphyrin core than that of benzo group in 10 [13].

Three porphyrin derivatives include long alkoxy chains attached to the orto positions of phenyl ring and a phenyl carboxylate acid or acrlic acid at the meso position. All porphyrine molecules were based on Π-A-porphyrin system.

The phenyl group at meso position is conjugative linkage between the porphyrin and the binding group carboxylic acid. It is responsible to improve light harvesting performance. The double bonds at phenyl moiety are chosen as the conjugate linker.

Arrechea et al. [40] have synthesized two new porphyrine molecules that incorporate thiophene substituents (Fig. 6 13 and 14). Molecule 13 showed an intense Soret band (B band) at 471 nm and an intense intermolecular charge transfer (ICT) band at 662 nm. Also, one one the Q bands was observed at 583 nm between these bands. In 14, a new absorption band appeared at 523 nm with extension of the conjugation on the bridge by the introduction of a new thienylene-nevinylene unit. The ICT band was observed at 668 nm.

The potential energy of HOMO are −5.39 eV and −5.36 eV for 13 and 14, respectively. This values are lower than the potential of the elctrolyte redox couple I^-/I^{3-} ($E_{redox} = -4.75$ eV). The E_{LUMO} values are −3.56 for 13 and −3.54 for 14. These values show that efficient electron injection into to TiO_2 conduction band is energetically possible because of higher than the TiO_2 conduction band edge (−4.2 eV in vacuum).

Table 3 HOMO, LUMO, absorption and emission of Bis(phenyl hexyl) ethers based porphyrin dyes synthesized by Zhang et al.

Dye	HOMO Level	LUMO Level	Absorption	Emission
10	-5.09	2.83	421, 552, 591	598, 648
11	-5.12	2.91	428, 558, 594	609, 656
12	-5.14	3.00	433, 563, 611	626

Numbers in bold represents the molecules

The cell efficiency of 13 was found as 6.0% and 4.1% while 14 showed 4.7% and 5.0%. For two porphyrin molecule synthesized by Arrechea et al. where cynaoacrylate are anchoring group, thiophene substituents are spacers between the conjugated porphyrin core and the anchoring cyanoacrylate group [40].

Arteaga et al. [16] have synthesized a series of new porphyrine molecules as well as their application in dye-sensitized nanocrystalline TiO_2 solar cells (Fig. 7). The dyes exhibit strong Soret bands at 439–454 nm and weak Q bands between 574 and 664. Intramolecular charge transfer bands (ICT) occurred between the porphyrin core donor unit and the electron acceptors. An additional band around 350 nm corresponds to the Π- Π* transition was also found. The thiophene containing dyes 15–17 exhibit red-shifted when compared to the corresponding fluorene derivatives 18–20. This is attributed to the enhanced electronic coupling between the donor and acceptor entities in 15–17 due to the thiophene unit, which provides better conjugation than the fluorene moiety and lowers the energy of the charge transfer for conjugated dipolar molecules.

The HOMO energy levelof the dyes have potentials ranging from 0.73 to 0.76 V, which are higher than that of the redox couple (~0.40 V). The LUMO energy levels of the dyes range from −1.07 to −1.20 V, lower than the energy level of the CB (conductive band) of TiO_2 (~− 0.5 V), with the energy gap of 0.57–0.70 V. It is well know thatan energy gap of 0.2 eV is necessary for efficient electron injection.

DSSCs based on the dyes bearing a cyanoacrylic acid acceptor group showed the best photovoltaic performance and corresponds to an overall conversion efficiency of 5.56 and 4.13%, respectively. DiphenylamineZn(II) porphyrin behaves as core electron donor unit whilethe cyanoacrylic acid, rhodanine acetic acid, and dicyanorhodanine are acceptors.

Fig. 6 Y. Liangs et al. have synthesized three types Zn-porphyrine molecule

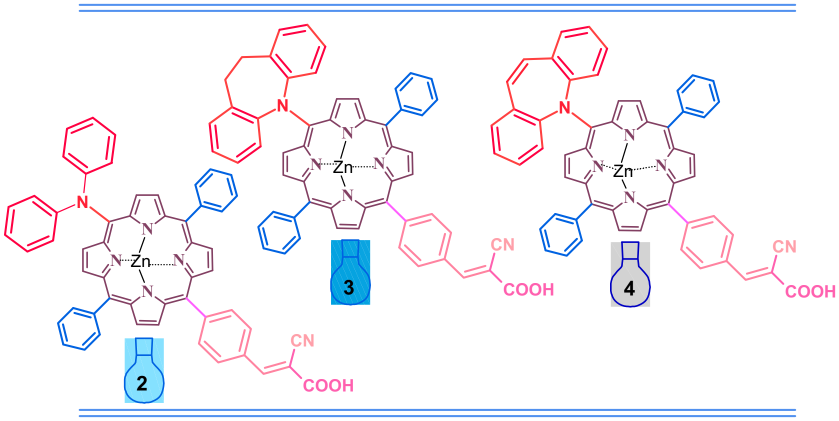


Fig. 7 Porphyrin derivative synthesized by Sharma et al. consists of a Zinc-metallated porphyrin unit covalently linked with a 1,3,5-triazine group and two terminal carboxylic acid groups of glycin

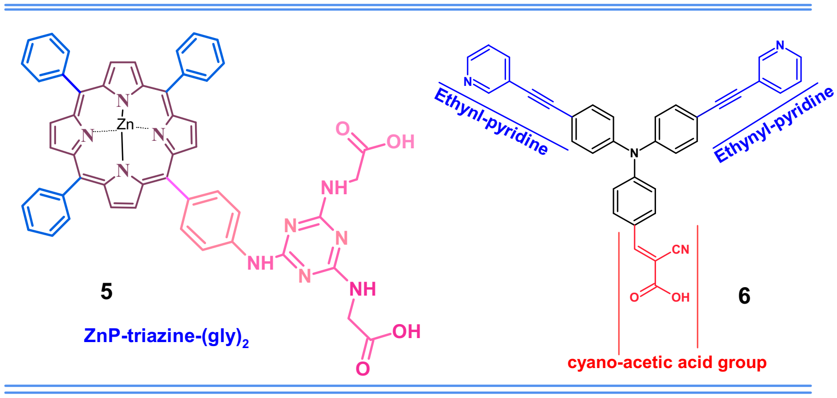
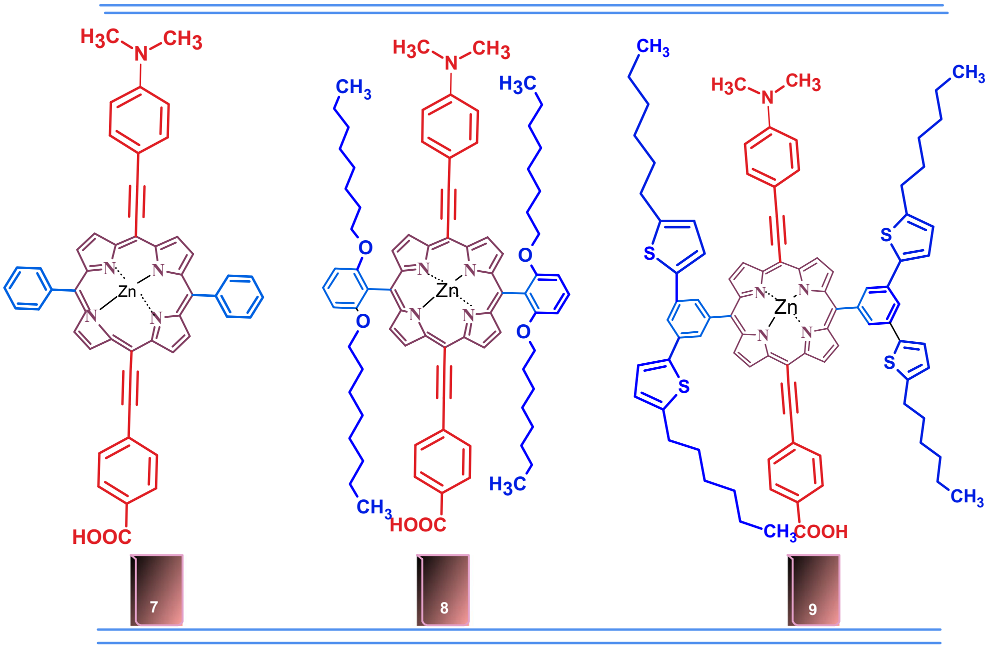


Fig. 8 Alkyne based dyes synthesized by Lu et al.



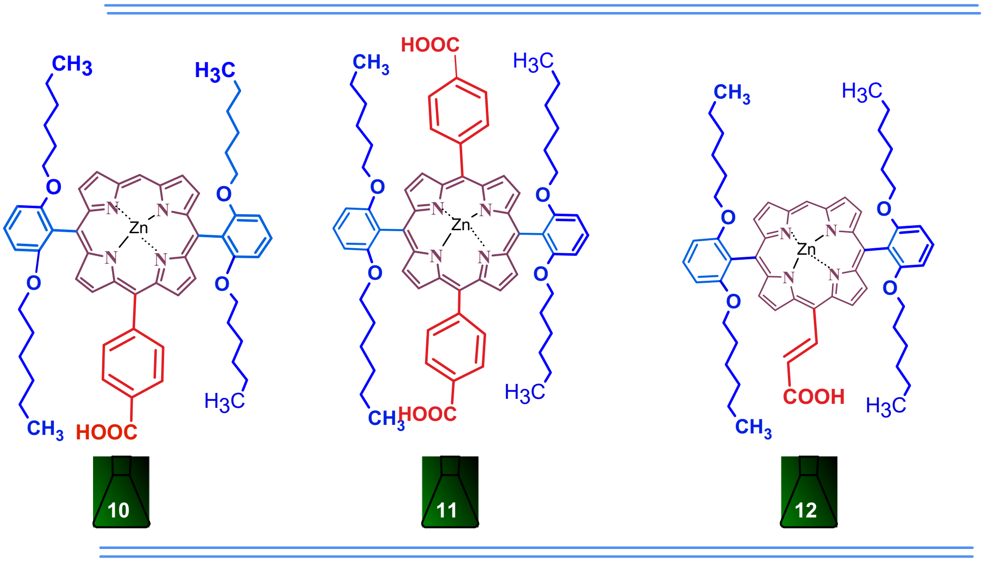


Fig. 9 Bis(phenyl hexyl) ethers based porphyrin dyes synthesized by Zhang et al.

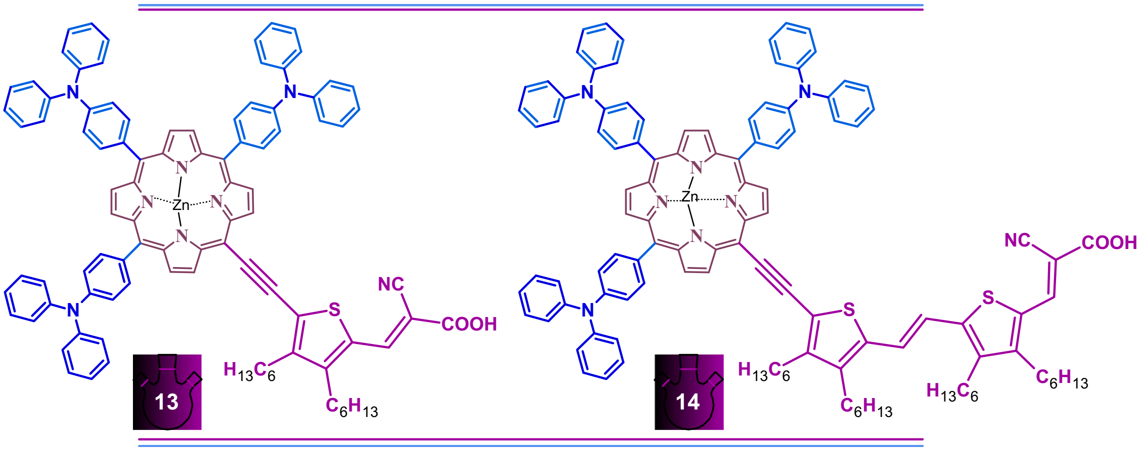


Fig. 10 Thiophene incorporated porphyrin based molecules synthesized by Arrechea et al.

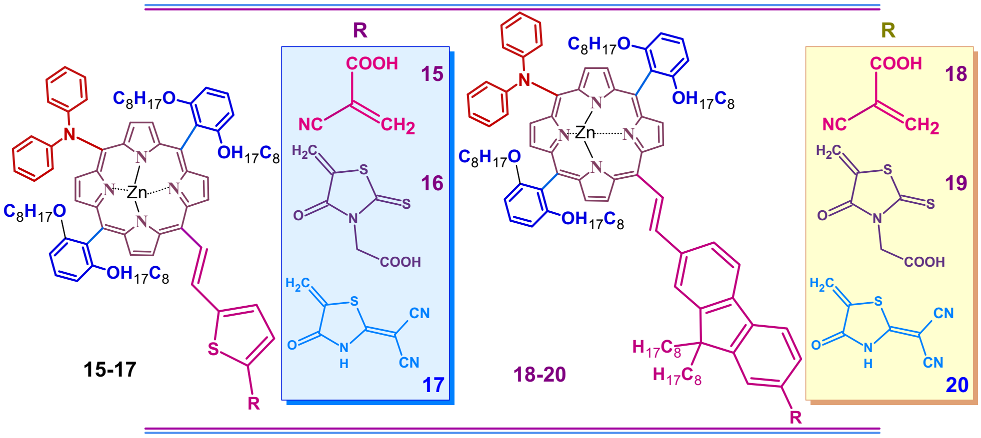
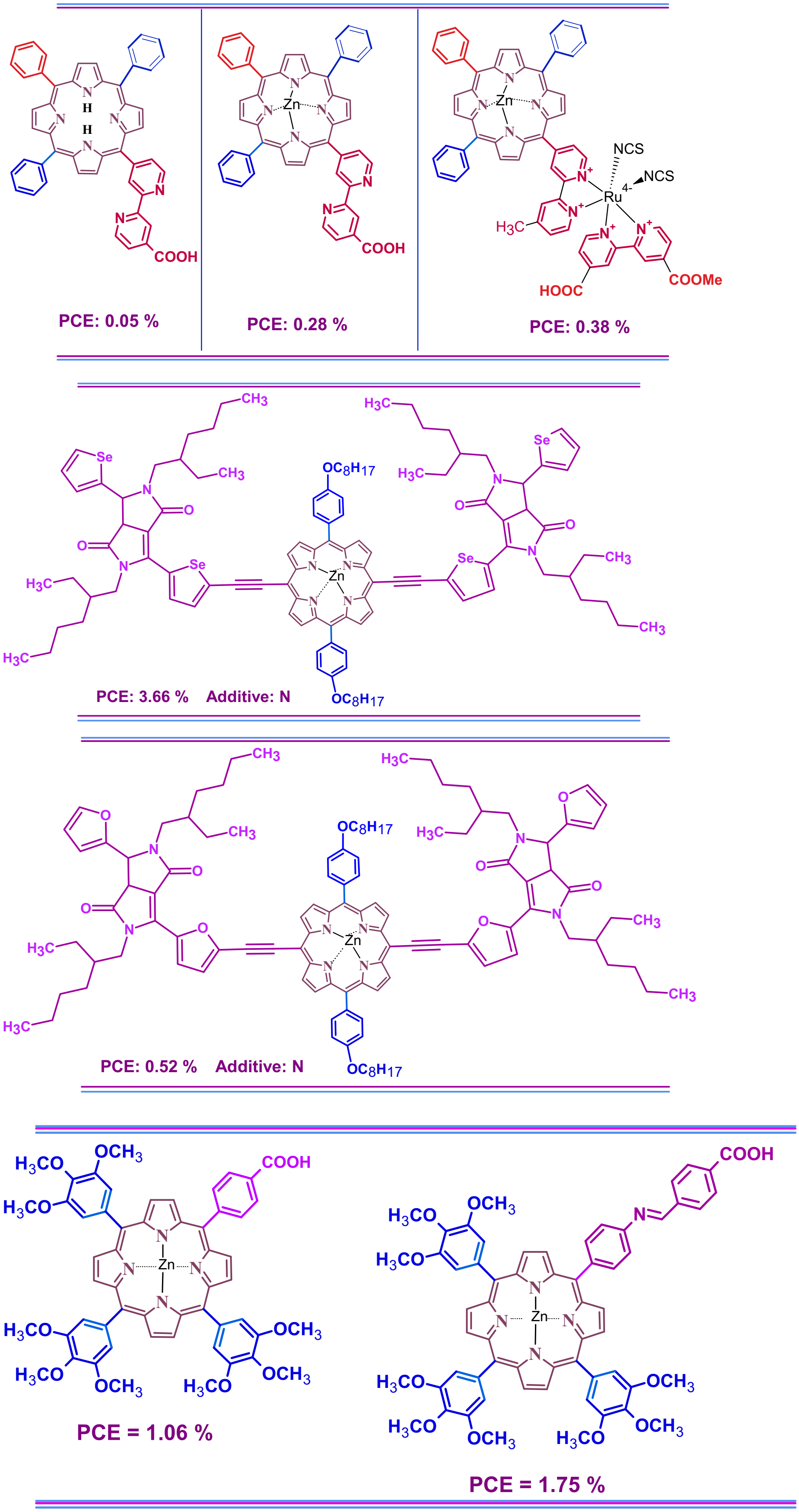


Fig. 11 Porphyrin derivatives synthesized by Arteaga et al.

Fig. 12 Molecular Structure and photovoltaic performance of some porphyrine derivatives



These electroactive units are linked by either vinyl-fluorene or vinyl-thiophene spacer units [16].

Few porphyrine-based porphyrins and their photovoltaic performance are shown in Fig. 8, 9, 10, 11 and 12 [41–43].

Conclusion

Various porphyrins, especially zinc complexes, have been used in DSSC preparation. Their LUMO energy levels are above the conduction band of the TiO_2 while HOMO energy levels are below the redox couple in the electrolyte solution. These require for charge seperation at the TiO_2/dye/electrolyte surface. Metal free-porphyrin has low photovoltaic conversion efficiency than zinc-porphyrins. Porphyrins generally show lower performance due to the limited light absorption, poor matching to solar light distribution and consequently posses a low value of short circuit current. Generally, two methoda are used toincrease their performance ie. elengating the Π system and lowering the symmetry of the macrocycle, which can lead to a significantly broadened Soret band and red shifted Q band absorptions. DSSC devices using porphyrin sensitizers with the linker and anchor units functionalized at the β-position is reported to show a value as high as 7.1%.

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