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Molecular Engineering of Sensitizers for Dye-Sensitized Solar Cell Applications

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ABSTRACT: Dye-sensitized solar cells (DSSCs) have attracted considerable attention in recent years as they offer the possibility of low-cost conversion of photovoltaic energy. This account focuses on recent advances in molecular design and technological aspects of sensitizers based on metal complexes, metal-free organics and tetrapyrrolic compounds which include porphyrins, phthalocyanines as well as corroles. Special attention has been paid to the design principles of these dyes, and co-sensitization, an emerging technique to extend the absorption range, is also discussed as a way to improve the performance of the device. This account also focuses on recent advances of efficient ruthenium sensitizers as well as other metal complexes and their applications in DSSCs. Recent developments in the area of metal-free organic and tetrapyrrolic sensitizers are also discussed. DOI 10.1002/tcr.201100044

Keywords: dye-sensitized solar cells, energy, metal complexes, organic dyes, tetrapyrrolic compounds

1. Introduction

One of the most urgent and greatest challenges to face the scientific community today is the need to meet the growing global energy demand for the future. In 2008, the global energy consumption for the entire year was estimated to be 14.4 TW, and of that amount, 81% was generated by fossil fuels.^[1] As a result a large amount of carbon dioxide was liberated in the Earth's atmosphere, causing global warming. Therefore there is a real need for the development of renewable energies. Among renewable energies solar energy is clean and abundant. The total solar energy absorbed by Earth's atmosphere, oceans and land masses is approximately 3,850,000 exajoules (EJ) per year.^[2] The energy is so vast, if we could accomplish harvesting merely a tiny fraction of the solar energy

reaching the Earth, we would solve many of our problems, not only in energy, but also global environmental and political.

A solar cell (also called photovoltaic cell or photoelectric cell) is a solid state electrical device that converts the energy of light directly into electricity. The first photovoltaic cell based on silicon was developed at Bell Laboratories in 1954, which belongs to the first generation of solar cells.^[3] Later, second-generation solar cells were developed based on thin film technology such as cadmium telluride (CdTe), copper indium gallium selenide (CIGS), amorphous silicon etc.^[4] Both first and second generations of solar cells are either cost effective or hazardous materials are used that lead to environmental pollution. For this reason, Grätzel and co-workers in 1991

developed another type of solar cells, namely nanocrystalline dye-sensitized solar cells (DSSC), which belong to the third generation of solar cells.^[5]

1.1. Device Architecture and Operating Principle

A schematic diagram of a DSSC device showing the principle of how the device operates is shown in Figure 1, as reviewed elsewhere. The typical basic configuration is as follows: At the heart of the device the mesoporous oxide layer is deposited either on a transparent conducting oxide (TCO) glass or plastic

substrate. The most commonly used substrate is glass coated with fluorine-doped tin oxide (FTO). The thickness of the mesoporous oxide layer is typically in the range of 8–12 μm . The nanoparticle size is usually in the range of 15–25 nm, which gives an internal surface area of $\sim 1000\text{ cm}^2$ substrate. Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye. On another conductive glass plate, a thin layer of platinum is deposited, which acts as a cathode. The two electrodes are held to each other by heating with a hot-melt polymer film (Surlyn, 50 μm thickness) as a space between the electrodes. A drop electrolyte (usually an

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Veerapandian Velkannan was born in Madurai in 1983. He has completed his schooling from Madurai. He obtained his B.Sc. (2003) and M.Sc. (2005) degrees from The American College and Madurai Kamaraj University, Madurai, respectively. He worked on the synthesis and physico-chemical properties of functionalised porphyrins during the doctoral program. After receiving his PhD from IIT Madras (2011), he joined the group of Dr. Giribabu in IICT, Hyderabad, as postdoctoral fellow. His research interests are in the molecular design and synthesis of tetrapyrrolic systems (porphyrins, phthalocyanines and corroles) and their applications in dye-sensitized solar cells (DSSCs).



Ravi Kumar Kanaparthi was born in 1982. After his primary and secondary education, he joined the S.V.R.M. College, Nagaram, and obtained his B.Sc in 2003. Then he joined the School of Chemistry, University of Hyderabad, as a postgraduate student and completed his M.Sc. (Chemistry) in 2005. Subsequently, he joined the same school and worked with Professor Anunay Samanta for his PhD degree. After receiving his PhD in 2011 from University of Hyderabad, he joined in Indian Institute of Chemical Technology, Hyderabad, India. At present, he is working as a Post Doctoral Fellow under the supervision of Dr. Giribabu, in the area of dye-sensitized solar cells. His research interests are in the engineering of functional fluorescent organic molecules, fabrication of organic and metal nano/microparticles, photovoltaic and optoelectronic devices, including both steady-state and time-resolved fluorescence techniques.



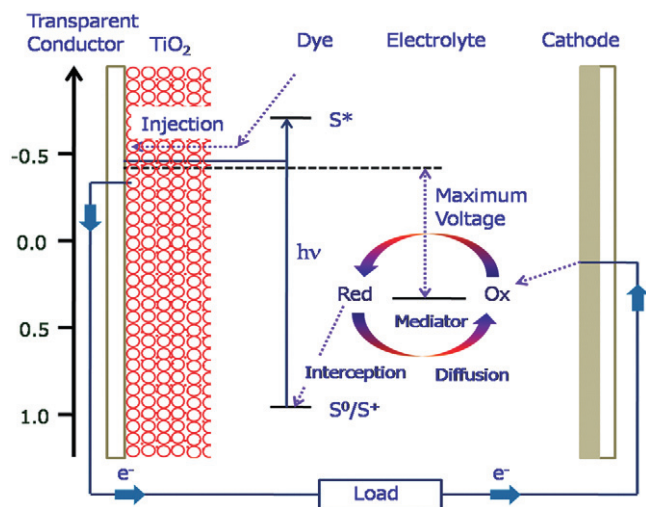


Fig. 1. Energy level diagram of a DSSC.

organic solvent containing the iodide/triiodide redox system) is injected in that space.

Photoexcitation of the charge transfer dye results in the injection of an electron into the conduction band of the oxide, leaving the dye in its oxidized state. The dye is restored to its ground state by electron transfer from the electrolyte. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The I_3^- ions formed by oxidation of I^- diffuse a short distance ($<50\ \mu\text{m}$) through the electrolyte to the cathode, where the regenerative cycle is completed by electron transfer to reduce I_3^- to I^- .

By using bis(tetrabutylammonium)-cis-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (**N719** dye) and trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (**black dye**) and I^-/I_3^- redox couple, Grätzel and co-workers have reported efficiency of $>11\%$ under AM 1.5 irradiation and stable operation for millions of turnovers.^[6] The efficiency of DSSC device is reasonably good for commercialization of technology, but durability is very low. Almost all components of DSSC devices have been further improved in order to commercialize this technology. There are a number of reviews and books on dye-sensitized solar cells.^[7] However, this account discusses about the recent trends and developments in the area of sensitizers.

1.2. Sensitizers

The sensitizer is the one of vital components in achieving high efficiency and durability of the DSSC device. For the designing of a new sensitizer, it should fulfil the following essential requirements.

1. The sensitizer should be strong with broad absorption, i.e., it cover the whole visible region and even the part of the near-IR region.
2. The molar extinction coefficient (ϵ) of the sensitizer should be high to avoid multi-layer adsorption of the sensitizer on the semiconductor surface.
3. The sensitizer should have anchoring groups such as $-\text{COOH}$, $-\text{SO}_3\text{H}$ etc. to strongly bind the dye onto the semiconductor surface.
4. The excited state life-time of the sensitizer should be a sufficiently long span (typically in the ns domain), and excited electrons of the sensitizer should be efficiently injected into the conduction band of the semiconductor (in the fs domain) to avoid the decay of the excited state dye to the ground state.
5. The excited state level sensitizer should be more positive energy than the conduction band edge of the semiconductor (n-type DSSC) so that an efficient electron transfer process between the excited dye and conduction band of the semiconductor takes place.
6. For dye regeneration, the oxidation state level of the sensitizer must be more positive (by ca. 200–300 mV) than the redox potential of the electrolyte.
7. Unfavourable dye aggregation on the semiconductor surface should be avoided through optimization of the molecular structure of the dye or by addition of co-adsorbents that prevent aggregation.
8. The sensitizer should be stable electrochemically, photochemically and thermally for longer periods.
9. The sensitizer should have good solubility in a variety of solvents, be less hazardous, and be low-cost and abundantly available.

Based on these requirements, a wide variety of sensitizers including metal complexes, metal-free organic dyes and tetrapyrrolic structures such as porphyrins, phthalocyanines, and corroles have been designed and used in DSSCs for the past two decades.

2. Metal Complexes

Sensitizers based on metal complexes, in particular, ruthenium(II) complexes, have been investigated intensively for DSSC applications because of their broad absorption spectra and favourable photovoltaic properties.^[8] Generally metal complex based sensitizers consist of a central metal ion with ancillary ligand and at least one anchoring ligand. Light absorption in the visible part of the solar spectrum is due to a metal to ligand charge transfer (MLCT) process. The central metal ion is therefore a crucial part of the overall properties of the complexes. Ancillary ligands are not directly attached onto

the semiconductor surface and are typically bipyridines or terpyridines, can be tuned by different substituents (alkyl, arylheterocycle etc.) to change the photophysical and electrochemical properties and thus improve the photovoltaic performance. Polypyridyl complexes of d^6 metal ions show intense MLCT bands in the visible region and can sensitize the wide band-gap semiconductors. The energies of the MLCT states can be altered systematically by modifying the anchoring ligands as well as by changing the ancillary ligands or its substituents.

2.1. Ruthenium(II) Complexes

Ruthenium polypyridyl complexes have been intensively employed as sensitizers due to their appropriate redox, spectroscopic, and excited-state properties. In particular ruthenium(II) complexes with carboxylic pyridine derivatives are able to react readily with oxide surfaces to form the corresponding esters, presenting efficient adsorption onto the semiconductor surface and improved light harvesting efficiency, leading to fine results.^[9]

Ru complexes with carboxylated bipyridine ligands were first used for sensitization of TiO_2 single crystals in 1979.^[10] In 1985 Desilvestro et al. used a similar dye, with three carboxylated bipyridine ligands, to obtain the first reported efficient DSSC with an IPCE (incident photon-to-current conversion efficiency) of 44%.^[11] Grätzel and co-workers as well as Bignoz and co-workers have reported a trinuclear Ru(II) complex with improved light absorption properties.^[12] But, a major breakthrough came out with record efficiency of 7.1% reported by O'Regan and Grätzel using bipyridyl Ru(II) complex **N3** (Figure 2) as sensitizer and I_3^-/I^- in acetonitrile as redox electrolyte.^[5] Subsequently, in 1993 Grätzel and co-workers reported thiocyanato derivatives, *cis*-(thiocyanato)₂ bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II), coded as **N3** and **N719**, affording DSSCs with overall power conversion efficiencies of 10.0 and 11.2%, respectively.^[6] Equally and

importantly, both **N3** and **N719**, which essentially differ only in their protonation state, effect a nearly quantitative conversion of incident photons into electric current over a large spectral range. To further improve the efficiency of the DSSC, one has to improve the spectral response of the sensitizer in the near-IR (NIR) region. For this reason, Grätzel and co-workers have designed the **N749** dye, also called the '**black dye**', in which Ru centre has three thiocyanato ligands and one terpyridine ligand with three anchoring carboxylic acid groups.^[13] The MLCT band of **black dye** was red shifted. Based on this dye, an IPCE spectrum was obtained over the whole visible range extending into the NIR region up to 920 nm with an overall conversion efficiency of 10.4% under AM 1.5G. Though the molar extinction coefficient of **black dye** is lower than that of **N719**, the spectral response of **black dye** in the red and NIR region is enhanced with respect to **N719**, resulting in higher short circuit photocurrents.

Since 1997, a number of modifications have been carried out on both **N719** and **black dye** to further improve the efficiency and durability of the Ru(II) complexes. One of the drawbacks of the DSSC device is the durability due to the presence of volatile organic solvent in the redox couple and iodine. In order to improve the device durability one has to replace liquid electrolyte with either gel or hole transport materials. Grätzel and co-workers have designed a heteroleptic amphiphilic Ru(II) complex, **Z-907**, which consists of long hydrophobic alkyl chains, aiming at increased tolerance against water attack as well as to compatibility for gel electrolytes.^[14] This amphiphilic Ru(II) complex using polymer gel electrolyte (1,2-dimethyl-propylimidazolium cation has been incorporated into poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix to form polymer gel electrolyte) was reported to have an efficiency of 6.1%. The device using **Z-907** sensitizer is stable towards thermal stress and light. The same group has further extended the carbon chain on ancillary bipyridine ligand to achieve compatibility for gel electrolytes, but the efficiency is not much improved.^[15]

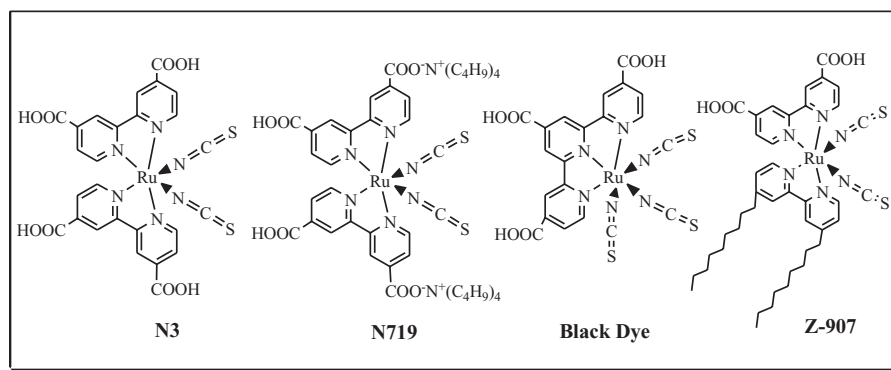


Fig. 2. Structure of **N3**, **N719**, **black dye** and **Z-907** sensitizers.

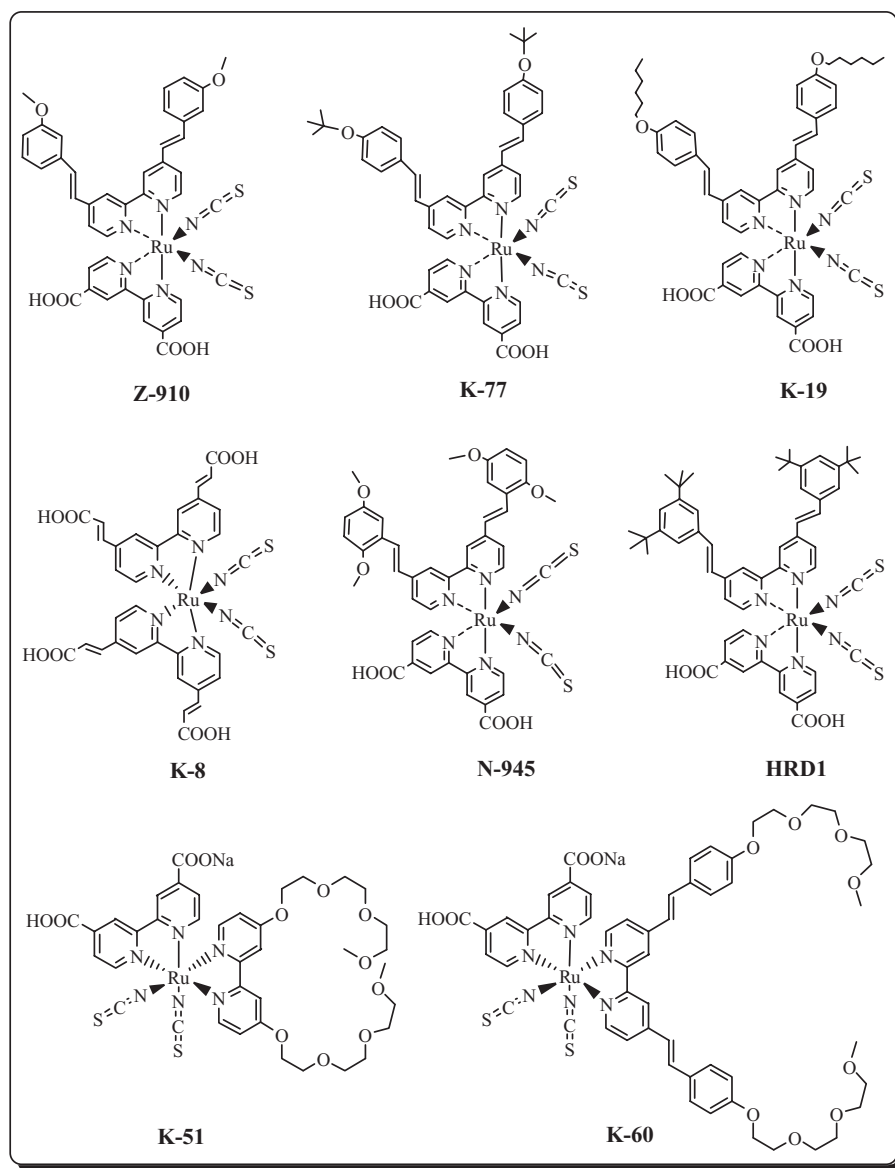


Fig. 3. Structure of Ru(II) complexes based on extended π -conjugated and ion coordination ligands.

All three dyes **N719**, **Z-907** and **black dye** have a low molar extinction coefficient; as a result dye loading on nanocrystalline TiO_2 has to be increased for more light absorption. This in turn increases the aggregation phenomena on the surface of nanocrystalline TiO_2 . One of the ways to increase the light harvesting efficiency (also minimizing the aggregation phenomena) is to increase the conjugation length of the ligand. Grätzel and co-workers have introduced 3-methoxystyryl into the ancillary ligand to obtain a novel Ru(II) sensitizer, **Z-910**, which exhibited a prominent efficiency (10.2%) and impressive stability.^[15] The study demonstrated that enhancing the molar extinction coefficient is a good strategy to improve the

photovoltaic performance of Ru(II) sensitizers. From then onwards a number of modifications have been done on ancillary ligands to further improve optical absorption of Ru(II) sensitizers. Based on this concept, a number of dyes have been designed, synthesized, tested and demonstrated good performance in DSSCs for long-term stability.^[17] For example, Grätzel, Nazeeruddin, Zakeeruddin, Giribabu, Chandrasekharan and co-workers have developed heteroleptic amphiphilic Ru(II) sensitizers **K77**,^[17b] **K19**,^[17c] **K8**,^[17b] **N945**,^[17f] **HRD1**,^[17g] and **H112**^[17j] (Figure 3) giving DSSCs with power conversion efficiencies of 7.0, 9.0, 8.64, 10.82, 5.77 and 2.43%, respectively. **N945** sensitized DSSCs, char-

acterized by a very efficient light harvesting over a large area of the visible spectrum, and showed an energy conversion efficiency of 10.82%, surpassing **N719**. All these sensitizers have long hydrophobic alkyl- or alkoxy-substituted aromatic rings on the ethylene group of the ancillary bipyridine ligand, seeking to enhance the optical absorptivity of the sensitized TiO₂ films, and aiming at increased tolerance against water attack and, therefore, enhanced durability of the device.^[14b]

Another important aspect that influences the efficiency of DSSC devices is the presence of cations in the redox electrolyte. The influence of various cations added to the electrolyte upon the photovoltaic performance of DSSCs has been well documented in the literature.^[18] The small-sized Li⁺ ions strongly adsorb onto the surface of TiO₂. The surface adsorption results in a positive shift of the TiO₂ conduction band and consequently causes a dramatic drop in the open-circuit voltage (*V*_{OC}) of the device. Ethylene oxide can form the coordinate bonds with metal ions and thereby reduce the concentration of Li⁺ ion on the TiO₂ surface. Grätzel and co-workers have introduced triethylene glycol methyl ether on the ancillary ligand of a Ru(II) complex and reported the complex **K51** (Figure 3).^[19] They have studied the influence of Li⁺ ions using **K51** sensitizer and compared its performance with non-ion coordinating Ru(II) sensitizer, i.e., **Z-907**. Under similar test cell conditions **K51** and **Z-907** have shown efficiencies of 7.80 and 6.60%, respectively. The molar absorption coefficient of **K51** sensitizer is low, and for this reason, the same group has introduced extended π -conjugation with the ion coordinating concept and reported Ru(II) sensitizer **K60** (Figure 3).^[20] The molar absorption coefficient of **K60** sensitizer has drastically been enhanced due to the introduction of extended π -conjugation. Using non-volatile organic-solvent based electrolyte, **K60** has shown a conversion efficiency of 8.40%. The ion coordinating studies showed that the Li⁺ ions coordinate to the triethylene oxide methyl ether side chains on the **K60** sensitizer molecules.

In contrast, introduction of a heteroaromatic ring on one of the bipyridine ligands of the Ru(II) sensitizers is another way to increase the conjugation.^[21] In particular, thiophene is a π -excessive heteroaromatic five-membered ring and has been widely used in materials science. Grätzel, Zakeeruddin, Yanagada, Wang, Wu, Ko and co-workers have used thiophene for extended π -conjugation and developed a series of heteroleptic Ru(II) sensitizers: **HRS-1**,^[21a] **C101**,^[21d] **C102**,^[21d] **C104**,^[21c] **BTC-1**,^[21f] **BTC-2**,^[21m] **CYC-B13**,^[21h] **J86**,^[21g] and **JK188**^[21i] (Figure 4) giving DSSCs with overall conversion efficiencies of 9.00, 7.40, 10.53, 7.60, 9.10, 3.80, 9.03 and 9.54%, respectively. The DSSC devices that incorporate the above amphiphilic dyes display extraordinary stability under both thermal stress and exposure with light, making these cells viable for practical, outdoor use applications. In particular, DSSCs sensitized with **C101**, by utilizing either a low-volatility 3-

methoxypropionitrile electrolyte or a solvent-free ionic liquid electrolyte, show >9.00% and ca. 7.40% conversion efficiencies, respectively, and retain over 95% of their initial performance after 1000 h full sunlight exposure at 60°C.^[21d] In another study, a DSSC using **104** and a volatile electrolyte showed 10.53% overall conversion efficiency; under similar test cell conditions **Z-907** showed an overall conversion efficiency of 9.00%.^[21c] Ko and co-workers have introduced either unsymmetrical indeno[1,2-b]thiophene (**JK-188**) or fused dithiophene group (**JK-189**) in the ancillary bipyridine ligand to increase the molar absorption coefficient.^[21i] Under similar experimental conditions **JK-189** and **N719** showed efficiencies of 9.54% and 9.00%, respectively, using volatile electrolyte. Mishra et al. have replaced the 4,4'-dicarboxy bipyridine ligand of **Z-907** with 5,5'-(2,2'-bipyridine-4,4'-diyl)-bis(thiophene-2-carboxylic acid) as an anchoring ligand and reported a heteroleptic Ru(II) complex **BTC-2**.^[21m] The complex **BTC-2** shows red-shifted absorption with increased molar extinction coefficient. **BTC-2** shows an overall conversion efficiency of 9.10%.

One of the reasons for the lower durability of Ru(II) complexes is a charge recombination process. In order to minimize the charge recombination process of Ru(II) sensitizers, one has to introduce hole transport organic molecules in heteroleptic Ru(II) complexes and efficiency is not much improved.^[22]

All these Ru(II) complexes have either two –NCS (**N3**, **N719** etc.) or three –NCS groups (**black dye**) in its molecular structure. The –NCS groups not only dictate the properties of the complexes but also cause the instability. The instability of champion dyes (**N719** and **black dye**) in the DSSC is caused primarily by desorption of the dyes from the surface and/or liberation of the –NCS ligands from the metal centre.^[23] Chemical strategies for avoiding the labile Ru–NCS bond have been realized recently. These NCS-free Ru(II) sensitizers (cyclometalated Ru complexes) have shown remarkably high efficiency.^[24] The first cyclometalated Ru(II) complex for DSSC was reported by van Koten by replacing three –NCS groups of **black dye** with an another terpyridine ligand.^[24a,e] The molar extinction coefficient of cyclometalated Ru(II) complexes was increased, but the absorption maximum was blue shifted. The overall conversion efficiency of the DSSC device is very low. Grätzel and co-workers have replaced two –NCS groups of **N3** sensitizer with 2-(2,4-difluorophenyl)pyridine and reported a complex **Ru-1** (Figure 5).^[24b] TDDFT calculations show that the HOMO is located mostly on ruthenium and the cyclometalated ligand, and the LUMO is on the 4,4'-dicarboxy-2,2'-bipyridine ligand. This sensitizer in the DSSC has shown an efficiency of 10.10%. Chou and Chi et al. have reported a series of cyclometalated Ru(II) sensitizers by using 2-pyridyl pyrazolate ligands. The molar extinction coefficient of the complex **TFRS-2** (Figure 5) has increased two-fold, when compared to **N719** with an overall conversion efficiency of 9.54%.^[24d]

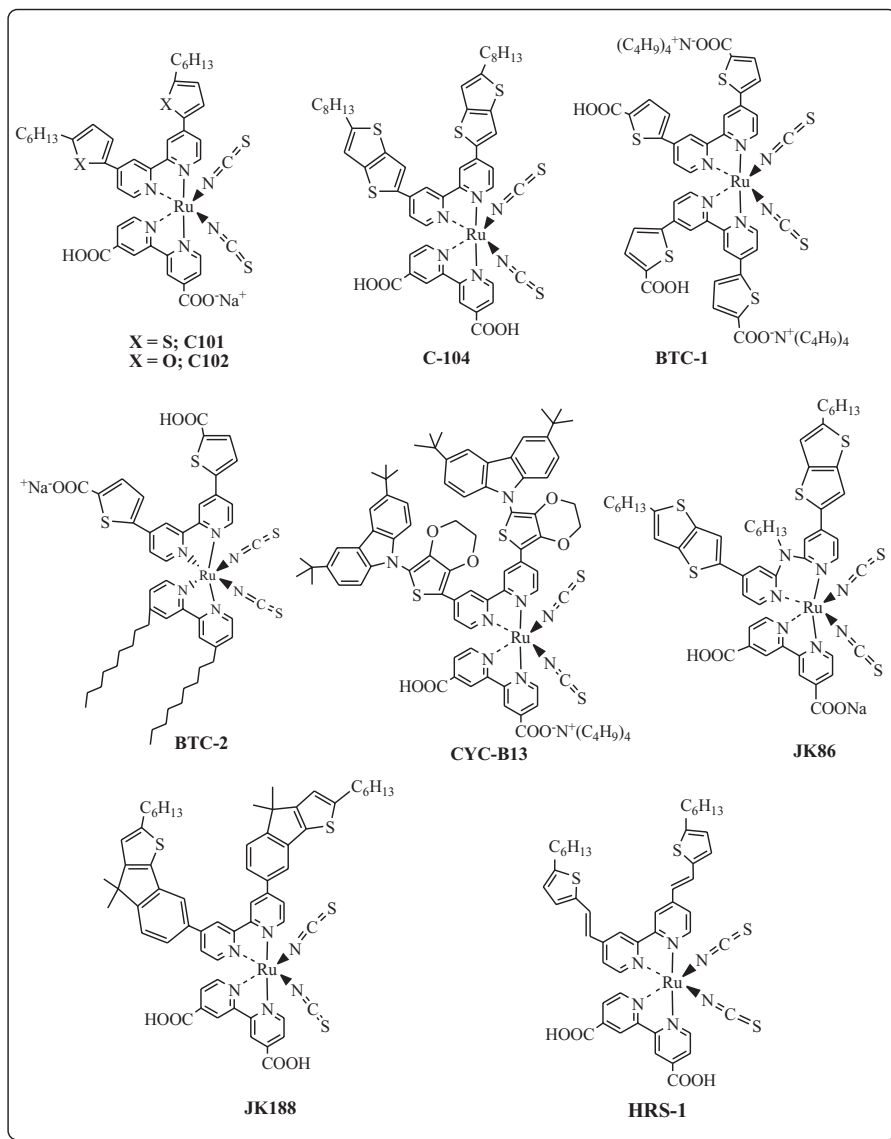


Fig. 4. Structure of Ru(II) complexes based on heteroaromatic ligands.

Kisserwan et al. have replaced three $-\text{NCS}$ groups of **black dye** with 6-phenyl-2,2'-bipyridyl ligand bearing a thiophene moiety, **T66** (Figure 5).^[24f] The absorption maximum of **T66** is blue shifted with increased molar extinction coefficient. Using ionic liquid electrolyte, **T66** has shown an efficiency of 5.70%. In order to broaden the absorption of Ru(II) sensitizers, Grätzel and co-workers have introduced a triphenyl group on one of the terpyridine ligands and reported Ru(II) sensitizers **Ru-2** (Figure 5). Absorption spectra reveal intense and broad absorption bands arising from a collection of MLCT and TPA-based intraligand charge-transfer (ILCT) transitions that extend up to 800 nm. The sensitizer **Ru-2** has shown an efficiency of 8.02%;

under similar test cell conditions **N3** has shown an efficiency of 8.65%. Giribabu and co-workers have reported Ru(II) complexes by replacing two $-\text{NCS}$ groups of **black dye** with bipyridine ligand.^[25] The anchoring groups are either on the bipyridine ligand (**m-BL-5**) or on the terpyridine ligand (**m-BL-1**, Figure 5). Under similar test cell conditions, **m-BL-5** has shown a better efficiency than **m-BL-1**.

2.2. Other Metal Complexes

The main drawback of Ru(II)-based sensitizers is the cost due to the rarity of the metal in earth's crust. Several attempts were

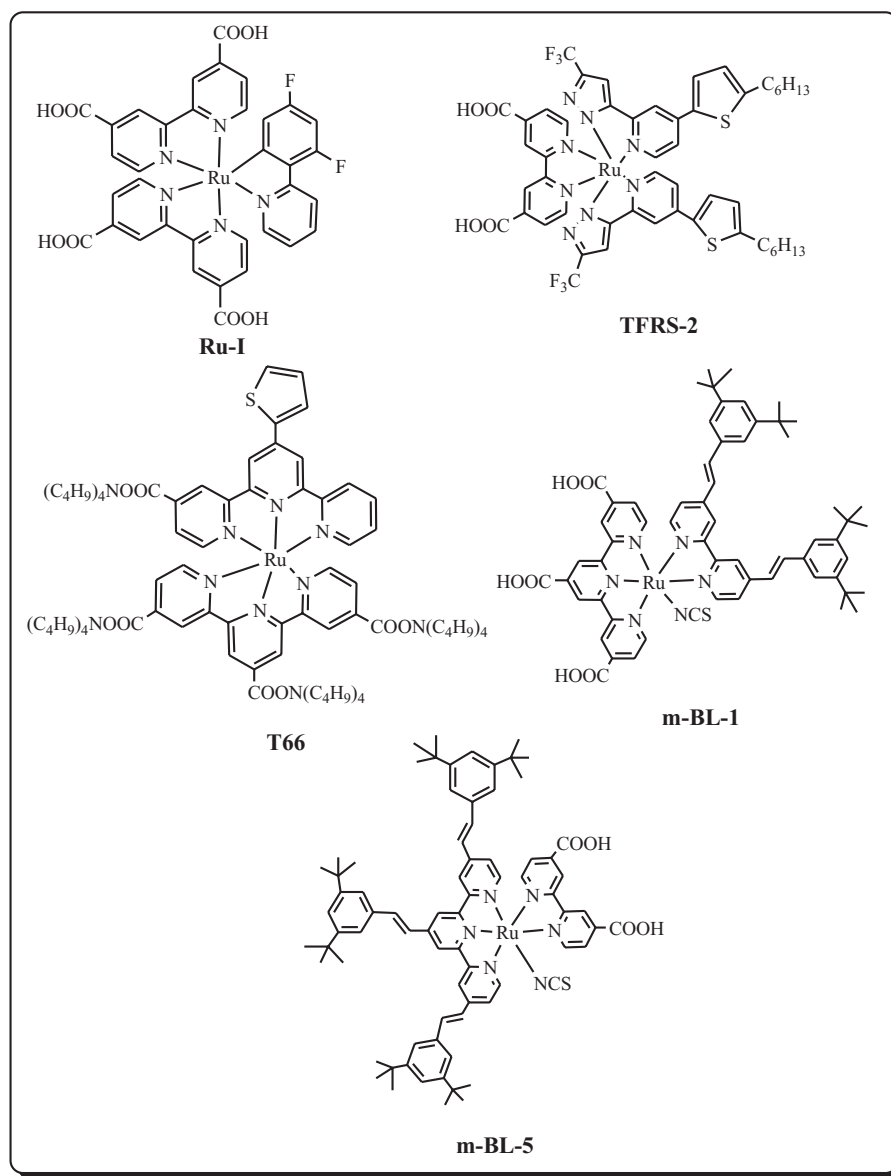


Fig. 5. Structure of cyclometalated Ru(II) complexes.

made to replace Ru with other metals such as Fe^{II} , Ni^{II} , Cu^{I} , Zn^{II} , Os^{II} , Pt^{II} , and Re^{I} (Figure 6) and these are summarized below.

Iron and ruthenium belong to the same group in the periodic table and iron is a low-cost element. Ferrere and Gregg first reported substantial photosensitization effect of an iron(II) bipyridyl complex, *cis*-[$\text{Fe}^{\text{II}}(2,2'$ -bipyridine-4,4'-dicarboxylic acid) $_2(\text{CN})_2$] (**Fe-1**).^[26] This complex exhibits two MLCT bands at 430 and 635 nm, with an extremely short-lived, non-emissive excited state. This dye produced a short-circuit photocurrent (J_{SC}) of $290 \mu\text{Acm}^{-2}$ and V_{OC} of 360 mV under approximately one sun. Further, Ferrere examined the influ-

ence of bpy ligand structural changes on photosensitization yields for **Fe-1** complex as well as solvatochromism of iron(II) complexes.^[26b,c]

Cu(I) complexes were introduced into DSSCs by Sauvage and co-workers because of their similar photophysical properties to Ru(II) complexes.^[27] They reported a DSSC device using Cu(II) phenanthroline complexes (**Cu-1**) as sensitizers with poor photovoltaic performance. Sakaki and co-workers changed the position of the anchoring groups ($-\text{COOH}$) and reported several derivatives for DSSCs.^[27b] The sensitizer **Cu-II** has an IPCE of 30% under AM 1.5 G. Grätzel and co-workers have reported Cu(I) based sensitizers.^[27c] They found that the

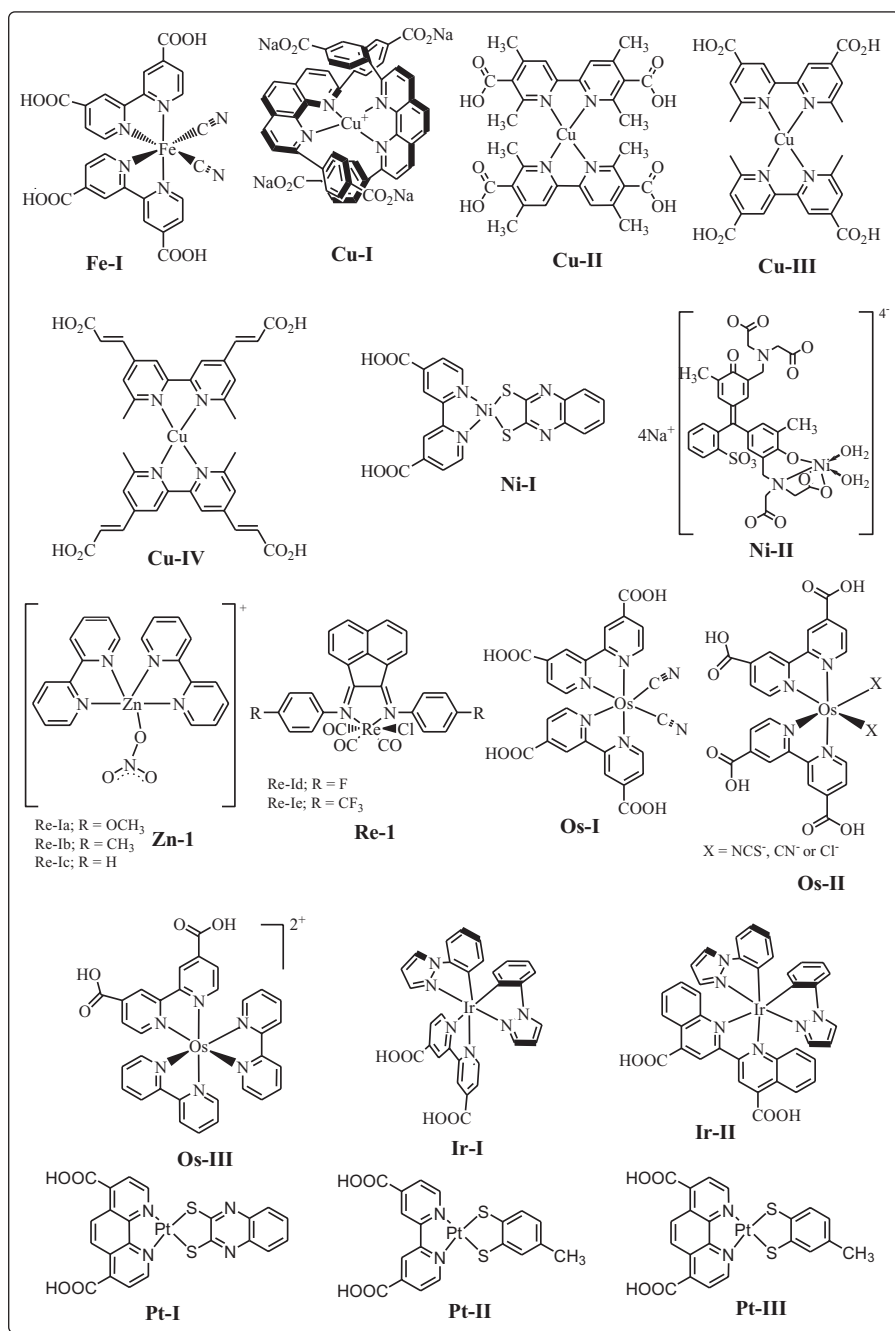


Fig. 6. Structure of other metal complexes.

IPCE spectra and current-voltage characteristics for devices fabricated with dyes **Cu-III** and **Cu-IV** were significantly different due to the different molar extinction coefficients of the two complexes. Dye **Cu-IV** with a large π -conjugated system of ligands and high molar extinction coefficients and obtained 2.3% efficiency with liquid electrolyte. Robertson et al. have explored the photosensitization of square-planar $[\text{Ni}(4,4'$ -

dicarboxy-2,2'-dipyridyl)(2,3-quinoxalinedithiol)] complex (**Ni-I**). This complex showed very poor efficiency due to a short-lived excited state.^[28] Bahadur and co-workers used hexacoordinated $\text{Ni}(\text{II})$ complex, $\text{Na}_4[\text{NiL}(\text{H}_2\text{O})_2]$, (where L is 3,3-bis[*N,N*-di(carboxymethyl)-aminomethyl]-o-cresolsulphonphthalein (**Ni-II**) with ZnO as semiconductor with an efficiency of 8.5%.^[28b] Another low-cost element next

to Ni(II) is Zn(II). Kang et al. investigated the photovoltaic properties of Zn(II)-based dye, bis(2,2'-bipyridine)nitrat zinc(II), $[\text{Zn}(\text{bipy})_2(\text{NO}_3)]^+$ (**Zn-I**), with an efficiency of 0.39%.^[29]

Re(I) complexes were employed to study the interfacial charge recombination and its driving force dependence by Hasselmann and Meyer.^[30] Chan et al. reported a series of chlorotricarbonyl bis(phenylimino)acenaphthene rhenium(I) complexes (**Re-I**) with an efficiency of 1.29%.^[30b] Osmium(II) complexes were found to be promising photosensitizers for DSSCs due to the prominent MLCT absorption band in comparison with the Ru complex. Os metal complexes have some advantages over the breakthrough Ru(II) complexes; the former one features more excited-state lifetimes than the latter. Lewis and co-workers have reported Os(II) polypyridyl complexes for DSSC applications. **Os-I** and its analogous dyes obtained by replacing the Ru metal ion with Os extended the light response region without sacrificing the good photovoltaic performances in DSSC.^[31] Electrochemical studies revealed that Os(II) polypyridyl species are more stable than the Ru(II) species in CH_3CN , so that a larger turnover number is expected for the Os system. Bignozzi and co-workers also optimized Os complexes and obtained broad photoaction spectra.^[31d] Dye **Os-II** showed an extended IPCE spectrum up to 1100 nm.^[31e] Further they demonstrated that the lower photocurrent efficiency of Os complexes was due to slower electron transfer from the iodide to the osmium ion.

The photophysical and photochemical properties of Ir(III) complexes have been widely investigated in the last two decades.^[32] These investigations are aimed to understand the energy and electron transfer processes in the excited state and to apply these principles to practical applications such as in solar energy conversion. Mayo et al. have applied cyclometalated Ir complexes for DSSC with an efficiency of 1.0%.^[32c] Later, Tian and co-workers used phenylpyridine ligands and reported cyclometalated Ir complexes (**Ir-I** and **Ir-II**) with an efficiency of 2.83%.

Square-planar platinum(II) diimine dithiolate complexes (**Pt-I**, **Pt-II**, **Pt-III**) showed highly solvatochromic charge transfer (CT) absorption. Substituents on the diimine and the dithiolate could tune the electronic and photophysical properties of the LUMO and HOMO, respectively.^[33] Sugihara and co-workers have reported a series of square-planar sensitizers and investigated their photoelectrochemical behaviour.^[33a] Dye **Pt-I** has shown an IPCE of 47%, with an overall conversion efficiency of 3.0%. Although the red-shifted absorption spectra of **Pt-II** and **Pt-III** cover the entire visible spectrum of solar light, the observed overall cell efficiency as well as the photocurrent and photovoltage values were very low compared with that of **Pt-I**, which was probably due to the sluggish halide oxidation rate and the fast recombination of the injected electron with the oxidized state of sensitizers. Subsequently

Robertson et al. have reported new square-planar platinum complexes.^[33b,c] They demonstrated the influence of position of the carboxylate group on solar energy conversion. These dyes feature minimum-thickness dye coating and better photovoltaic performance.

3. Organic Dyes

The metal complex based sensitizers are not only costly but also originate from the fact that the purification of the metal complexes is generally challenging. As a result, organic dyes, amongst others (vide supra), are lately stimulating intensive research efforts.^[34] The most important advantages of using organic dyes as sensitizers in DSSCs include their easily tuneable physicochemical properties, through suitable molecular design and well-established synthetic procedures, along with their ease of purification and high molar absorption coefficients. In contrast, organic dyes also have weaknesses such as their relatively sharp absorption bands in the visible region, leading to unsatisfactory light harvesting in the entire visible spectrum, along with questionable photostability. Representative metal-free organic sensitizers are shown in Figures 7 and 8.

3.1 Triarylamines

In recent years, triarylamine or triphenylamine (TPA) based dye molecules have been found to be promising candidates for DSSC applications, primarily due to its excellent *electron-donating* ability and *aggregation resistant nonplanar molecular configuration*. The reduced aggregation of TPA based dyes facilitates the ultrafast interfacial electron injection from excited dye molecules to the conduction band. Secondly, the recombination of injected electrons with the redox couple can be suppressed due to the propeller-shaped TPA molecular structure.^[35] In addition, the oxidized TPA unit is spatially conveniently placed for the approach of the redox couple species, ensuring fast dye regeneration. Moreover, the excellent stability of TPA attracts many people for designing metal-free sensitizers. Yanagida and co-workers were the first to introduce triarylamine as electron donor and the sensitizers with various π -conjugating units (vinyl group) and acceptors were successfully investigated and sensitizer **TPA1**, bearing two vinylene units and showing a power conversion efficiency of 5.3%.^[35a] Later the same research group achieved 7.33% efficiency by incorporating a vinylene moiety and thiophene bearing ethylenedioxythiophene (EDOT) as spacer to bridge donor TPA with acceptor cyanoacrylic acid.^[35c] Since then many efforts were made on donor TPA through molecular engineering to improve the power conversion efficiency. This rapid development led to very high efficiency (9.8%) with TPA as donor and cyanoacrylic acid (**C217**) as an acceptor.^[35d] More interestingly,

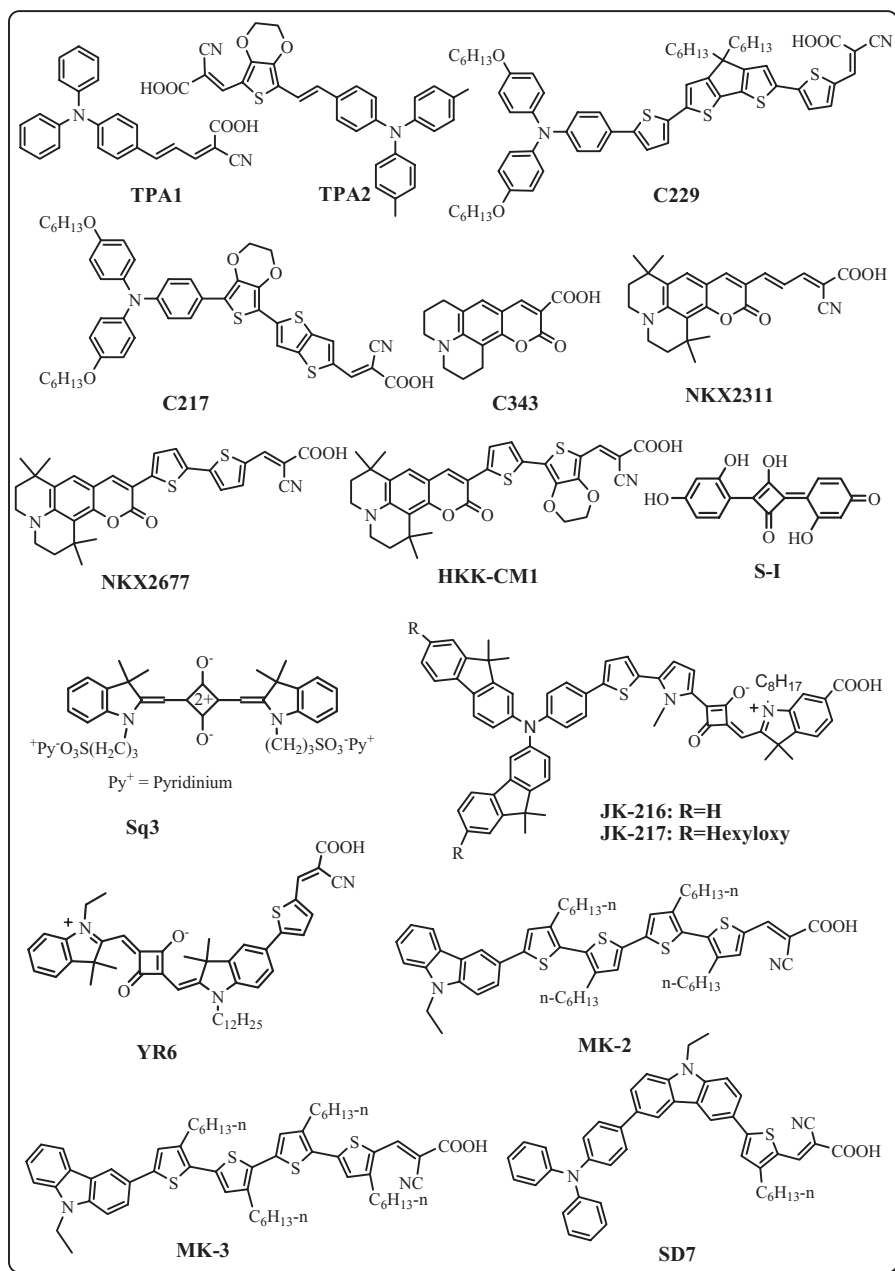


Fig. 7. Structure of metal-free based organic sensitizers.

the cell fabricated based on this molecule sustained for 1000 h (~96% retained of its original efficiency) after accelerated test under full sunlight soaking at 60°C. Recently, Wang and co-workers have reported an efficient donor-acceptor photosensitizer (**C229**) based on triphenylamine which showed high efficiency with the tris(1,10-phenanthroline) cobalt(II/III) redox couple.^[35e] The iodine-free dye-sensitized solar cell displayed power conversion efficiency of 9.4% measured under AM 1.5 G.

3.2. Coumarins

Grätzel and co-workers utilized coumarin 343 (**C343**) in order to estimate the electron transfer characteristics of the surface-bound dye (with the surface of TiO₂) for the first time in DSSC, and they reported an electron injection rate of 200 fs from sensitizer to the TiO₂ conduction band.^[36] Since then coumarin based dyes have become one of the promising sensitizers because of their good photoresponse in the visible

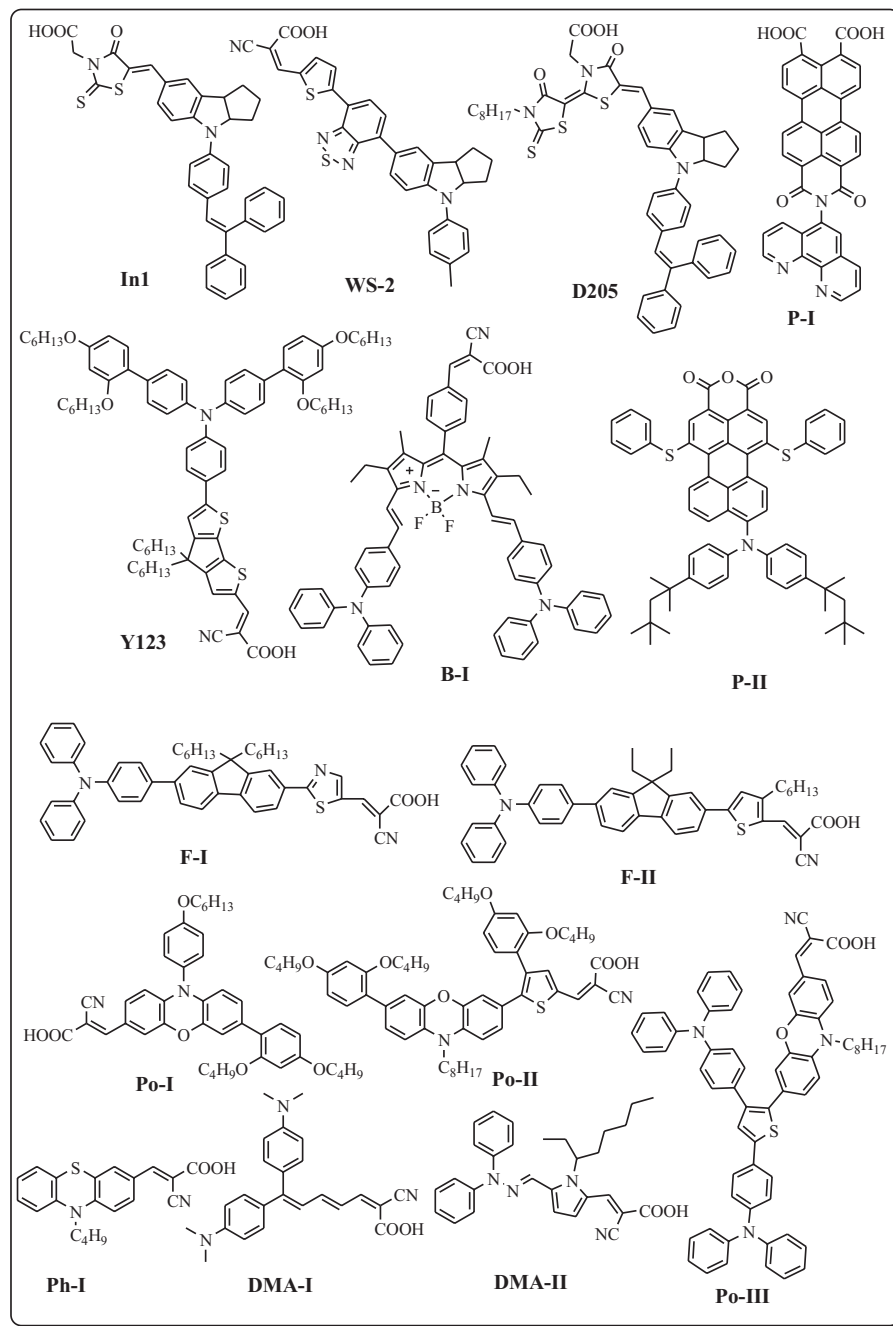


Fig. 8. Structure of metal-free organic sensitizers.

region, good long-term stability and appropriate LUMO levels matching with the conduction band of TiO_2 .

A new class of dyes based on coumarin (electron donor) and a cyanoacrylic acid (electron acceptor) has been synthesized by connecting with conjugated moieties (vinylene, isophorone, or thionyl).^[36b–d] Introduction of vinylene units in between donor and acceptor shifts the absorption spectra

towards red and has improved the efficiencies (2.6–5.2%) compared to the **C343** molecule, which showed an efficiency of 0.9%.^[36a] The sensitizer **NKX2311**, bearing two vinylene spacers, showed a promising efficiency of 5.2 % among the others. However, interestingly the increasing number of vinylene units decreased the efficiencies due to the aggregation of dye on the TiO_2 surface. Further, incorporation of thionyl

spacer instead of vinylene spacer did not affect the absorption spectra much, but dramatic changes in the photovoltaic properties were observed.^[36b] The molecule **NKX2677**, which has two thiophene units that are covalently linked between donor carbazole and acceptor cyanoacrylic acid, showed a photon conversion efficiency as high as 7.4%.^[36c] In a more recent work Kim and co-workers synthesized a series of coumarin dyes containing an electron-rich low-band-gap chromophore, ethylenedioxythiophene (EDOT), which comprises a coumarin moiety as the electron donor and a cyanoacrylic acid moiety as electron acceptor.^[36f] The sensitizer **HKK-CM1** consists of one thionyl unit and one EDOT unit, and showed better IPCE (6.07%) than relatively high conjugated molecules.

3.3. Squaraines

Squaraine dyes exhibit sharp and intense absorption bands in the visible and NIR regions. But, squaraines also exhibit low efficiency due to aggregation and lack of directionality in the excited state. Another disadvantage of NIR dyes is the low stability under thermal stress and light-soaking test. Therefore, molecular engineering of NIR dyes with a high photovoltaic performance and an enhanced stability is strongly required. A number of squaraine dyes have been adopted for DSSCs.^[37]

Kamat and co-workers performed primary investigations on symmetrical squaraine dyes and observed very low IPCE (0.05–0.7%).^[37a,b] Later, Zhang and co-workers synthesized three squarylium cyanine dyes for DSSC application.^[37c] Among the three dye sensitizers, **Sq3** showed a relatively high conversion efficiency of 2.17%. Pandey and co-workers studied the effect of alkyl chain length and found that increasing the alkyl chain length in a symmetrical squaraine dyes reduces the aggregation of the dyes and enhances the efficiency up to 3.5%.^[37f] Das and co-workers synthesized a series of symmetrical and unsymmetrical squaraine dyes. They observed that the unsymmetrical dyes exhibit better conversion efficiencies than symmetrical dyes, due to the unidirectional flow of electrons upon excitation.^[37d] Nazeeruddin and co-workers designed and developed a novel squaraine sensitizer, which has a carboxylic acid group directly attached to the chromophore and asymmetry was created by attaching an octyl chain on one N atom.^[37e] By doing these smart modifications, they could achieve an overall conversion efficiency up to 4.5%. For extending the conjugation beyond the squaraine core and incorporating strong π -accepting carboxycyanovinyl as a surface-anchoring group, Grätzel and co-workers developed a new squaraine sensitizer (**YR6**) and reported the efficiency as high as 6.74%. Recently, a new series of stable, unsymmetrical squaraines, which consist of thiophenyl pyrrolyl (**JK-216**) and indolium groups (**JK-217**) were reported with a record efficiency of 6.29%.^[37g] In addition, the **JK-217** device showed an excellent stability under a light soaking test at 60°C for 1000 h. The

high performance of the cell is attributed to the suppressed aggregation.

3.4. Carbazoles

Koumura and co-workers reported a series of carbazole sensitizers for DSSC and systematically investigated the effect of a π -conjugate ion of *n*-hexyl-substituted oligothiophenes on DSSC performance.^[38a,b] It was found that the photovoltaic performance of these dyes strongly depended on the molecular structures of the dyes (in terms of the number and position of the *n*-hexyl chains) and the number of thiophene moieties between carbazole and acceptor cyanoacrylic acid. A DSSC based on **MK-2** consisting of four hexyl-substituted thiophenes produced a very high power conversion efficiency of 7.7%, and **MK-3** was found to show even higher IPCE, 8.3 %, by changing the alkyl chains position in the main skeleton. The high power conversion efficiency is attributed to an increased electron lifetime of the sensitizer upon binding to the semiconductor. Recently, the same research group has synthesized several molecules in order to investigate the structural modification of dyes for DSSCs with the oligo-*n*-hexylthiophene linkage to enhance the absorption wavelengths which have a different donor part such as carbazole, indole, and indoline moieties.^[38c] Tan and co-workers reported a new sensitizer, **SD7**, based on carbazole in which triphenylamine is used as an auxiliary donor and the DSSC showed an efficiency as high as 6.51%.^[38d] Yang and co-workers synthesized organic dyes consisting of multiple electron donors (carbazole) and electron acceptors (rhodanine-3-acetic acid) on TPA for DSSC application, which showed an efficiency of 4.64%.^[38e]

3.5. Indole or Indoline

Horiuchi, Uchida and co-workers first reported this type of organic dye sensitizer with simple synthetic procedures, and the **In-I** sensitizer exhibited a good power conversion efficiency of 6.1% under standard conditions.^[39a] The DSSC performance was further improved by introducing an additional rhodanine framework on the main skeleton of the dye, which very quickly reached a high efficiency of 8.0 %.^[39b] Grätzel and co-workers achieved one of the highest efficiencies among the metal-free dye sensitizers.^[39c] By employing ionic liquids as electrolyte and by optimizing the thickness of the semiconductor (TiO₂), the solar-to-electric current efficiency reached 9.03%. Later, Ito and co-workers further improved the efficiency of indoline based sensitizer, **D205**, by mimicking the molecular structure in which an *n*-octyl chain was covalently attached to the main framework and reached a very high efficiency of 9.5% under standard test conditions.^[39d]

3.6. Other Organic Dyes

In addition to the organic molecular groups which are discussed in the previous sections, many organic molecules such as perylene, BODIPY, anthracene and heteroanthracene, tetrahydroquinoline, *N,N*-dimethylaniline, pyrene, etc. have been tested for their applicability in DSSCs.^[40]

Fukuzumi, Lemmetyinen and co-workers reported boradiazaindacene (BODIPY) based photosensitizers and observed photocurrent generation although the dyes are non-fluorescent.^[40a] These dyes showed poor efficiencies when TiO₂ was employed as electrode; however, improved efficiencies (0.13–0.16%) were reported when ZnO-SnO₂ composite nanostructures film was employed in the DSSC. Later, Akkaya and co-workers reported a panchromatic BODIPY photosensitizer which gave an improved efficiency of 1.66%, and their work opens a new direction for the development of novel panchromatic dyes (**B-I**).^[40b]

Perylene dyes are another promising class of metal-free organic sensitizers because of their high molar extinction coefficient, chemical and thermal stability. Gregg and co-workers were first to use perylene based sensitizers for the sensitization of SnO₂ semiconductor films.^[40d] The sensitizer, perylene-3,4-dicarboxylic acid-9,10-(5-phenanthroline)carboximide (**P-I**), gave an overall solar cell efficiency of 0.89% under AM 1.5 G. Since then many aspects of perylene dyes have been studied for improving the efficiency, and none of them showed an efficiency of >3.0%. However, later, Nazeeruddin and co-workers were able to synthesize a novel dye containing two thiophenol groups in the 1- and 6-positions of the perylene framework (**P-II**), which showed two absorption peaks at 462 and 620 nm and produced the highest power conversion efficiency of 6.8% and 1.8% using liquid and solid-state DSSCs under AM 1.5 G solar conditions, respectively.^[40e] The high efficiency of the dye molecules is due to the presence of thiophenol donor groups, which provides directionality of the electron flow in the excited state, thereby leading to improved device performance. In recent years the fluorene chromophore was demonstrated as a very good donor in the main core of the dye sensitizers for DSSC applications and gave promising power conversion efficiencies. Lin and co-workers reported a series of sensitizers bearing fluorene as the main core donor and a heteroaromatic ring as conjugated bridge.^[40g] The maximum efficiency was as high as 6.88% (**F-I**), and the high efficiency was attributed to the high molar extinction coefficient, the long recombination lifetime of the photoinjected electrons with the oxidized dye and low dark current. Recently, the efficiency was improved further and reached to a maximum of 7.03% in the case of a sensitizer which contains an auxiliary triphenylamine donor (**F-II**).^[40h]

Anthracene or heteroanthracene based organic dyes showed relatively low efficiency due to their narrow absorption

bands and thermal and chemical instability. Rao and co-workers reported anthracene as donor, vinylene spacer and either cyanocarboxylic acid or malonic acid as acceptor, and they studied the binding modes of sensitizers on the surface of nanocrystalline TiO₂.^[40i] Sun, Hagfeldt and co-workers reported a series of novel anthracene dyes bearing triphenylamine as auxiliary donor and observed the highest IPCE of 7.03%.^[40j] Because of the strong electron-donating ability phenothiazine and phenoxazine moieties have been extensively employed in the development of sensitizers for DSSC application. Sun, Hagfeldt and co-workers reported a simple phenothiazine dye (**Ph-I**), and it showed an efficiency of 5.5% under AM 1.5 G.^[40k] Recently, the same research group reported a series of phenoxazine dyes as sensitizers for DSSC application.^[40l] The test cells based on these sensitizers with liquid electrolyte gave overall conversion efficiencies of 6.03–7.40%, and the results are attributed to the absorption properties and electron lifetimes of the dyes (**Po-I**). In another report the same group observed an efficiency of 7.0% with **Po-II** as dye having two 2,4-dibutoxyphenyl units and using liquid redox electrolyte.^[40m] Moreover, phenoxazine dye-based solid-state DSSCs were fabricated for the first time. With the **Po-III** dye, an efficiency of 3.2% was observed.

Hara and co-workers reported an efficient and novel series of polyene dyes based on *N,N*-dimethylaniline (DMA) units as donor moiety for sensitization of nanocrystalline TiO₂ with an efficiency of 6.8% under AM 1.5 irradiation (**DMA-I**).^[41a,b] The introduction of thienothiophene and thiophene segments in the core of the molecule slightly reduced the efficiency (6.23%).^[41c] However, Giribabu and co-workers synthesized two DMA based sensitizers for DSSCs and observed a low IPCE.^[41d] Recently, Tan and co-workers synthesized two metal-free sensitizers which contain *N,N*-diphenylhydrazone as donor and cyanoacetic acid as acceptor (**DMA-II**). The DSSC of the dyes showed a very promising efficiency of 7.74%.^[41e]

4. Tetrapyrrolic Dyes

One of the drawbacks of ruthenium complexes is the limited absorption in the near-infrared region of the solar spectrum, whereas durability is the main concern for metal-free organic sensitizers. Tetra pyrrolic systems that include porphyrins, phthalocyanines and corroles are found to be the best alternative sensitizers based on their chemical, photo-, and thermal stability.^[42]

4.1. Porphyrins

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 very

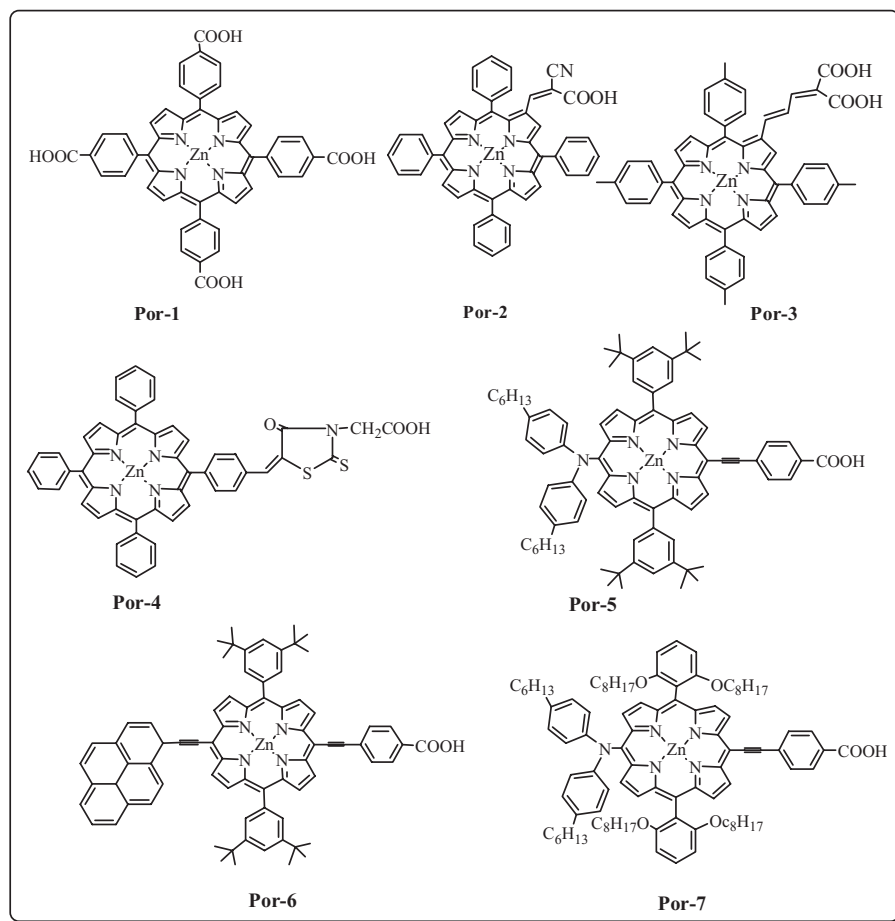


Fig. 9. Structure of porphyrin based sensitizers.

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), porphyrin derivatives can be suitable as panchromatic photosensitizers for DSSCs.^[43] Several studies have demonstrated that porphyrin dyes can show efficient photoinduced electron injection into the conduction band of TiO_2 .^[44] Some representative porphyrin photosensitizers are collected in Figure 9.

The first porphyrin that was used for the sensitization of nanocrystalline TiO_2 is the tetracarboxy porphyrin without any metal.^[45] Wamser and Cherian obtained IPCE values of 55% at the Soret peak and 25–45% at the Q-band, achieving an overall energy conversion efficiency of about 3% (**Por-1**).^[46] Kay and Grätzel in pioneering work on mesoporphyrin IX (derivative of chlorophyll) dye reported high IPCE values of over 80% and an efficiency value of 2.6%.^[47] They pointed to the importance of using co-adsorbents to prevent unfavorable aggregation of this dye. Durrant and co-workers have studied in detail about the electron injection and charge recombination

dynamics of **N3** and tetracarboxyporphyrins.^[48] The poor performance of porphyrin based DSSC was due to an increased probability of excited-state decay caused by dye aggregation on the TiO_2 surface.

Ma and co-workers as well as Bignozzi and co-workers have studied the effect of different anchoring groups on the TiO_2 surface, which were found to drop following the order of $-\text{COOH} = \text{PO}_3\text{H}_2 > \text{SO}_3\text{H} > \text{H}$ while the IPCE and overall conversion efficiency decreased following the same order.^[45,49]

Nazeeruddin, Officer and co-workers developed a family of porphyrin based sensitizers having the anchoring group at the pyrrole- β position.^[50] Among these dyes, the sensitizer **Por-2** having a cyanoacetic acid group was the anchoring group on extended π -conjugation at the pyrrole- β position.^[50b] Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations show that key molecular orbitals (MOs) of porphyrin **Por-2** is stabilized and extends out onto the substituent by π -conjugation, causing enhancement and red shifts of visible transitions, thereby increasing the possibil-

ity of electron transfer from the substituent. DSSC devices based on **Por-2** porphyrin sensitizer have shown an IPCE of 85% with an efficiency of 5.60%. The same group introduced another extended π -conjugation at the pyrrole- β position and reported **Por-3**.^[50c] This sensitizer has a dicarboxylic acid group as an anchoring group. The molar absorption coefficient of both Soret and Q-bands are further increased. When using liquid redox electrolyte this sensitizer has shown an overall conversion efficiency of 7.10%. The sensitizers with high ϵ values are very compatible with solid state redox electrolytes. This sensitizer has shown an efficiency of 3.60% when spiro-MeOTAD was used as hole transport material.

Giribabu and co-workers employed the rhodanine acetic acid group as anchoring groups at different positions of free-base or zinc porphyrins for DSSC applications.^[51] In related DSSCs, the zinc porphyrins having rhodanine acetic acid group at the *meso* position gave a better performance in comparison with the corresponding free-base dyads (**Por-4**). The same group also reported a triad having two rhodanine acetic acid groups at the *meso* position, which gives better performance than the corresponding dyad.^[51b]

Grätzel and co-workers have integrated the porphyrin chromophore as π bridge into a D- π -A dye (**Por-5**) to reduce the current loss due to recombination.^[52] The sensitizer having a diarylamino donor group attached to the porphyrin ring acts as electron donor, ethylbenzoic acid moiety serves as an acceptor and the porphyrin chromophore itself constitutes the π bridge in this particular D- π -A structure. The absorption spectra shows that both Soret and Q-bands are red shifted. This sensitizer has shown an η value of 8.8% (IPCE_{Soret} = 85%, IPCE_{Q-band} \approx 80%, V_{OC} = 0.735 V, I_{SC} = 16.7 mAcm⁻²) on 11.5 μ m thick nanocrystalline TiO₂ surface using liquid redox electrolyte. Although it shows an IPCE of 85%, this sensitizer lacks absorption in the region 480–630 nm, which leads to the reduction of the J_{SC} and efficiency values of the device. Hence, co-sensitization with an organic dye, which shows complementary spectral responses in the visible spectral range, was shown to have an efficiency of 11% (V_{OC} = 0.77 V, I_{SC} = 18.6 mAcm⁻²). Wang et al. have replaced the donor diarylamino group in **Por-5** with a series of organic donor groups (phenylethynyl, naphthalenylethynyl, anthracenylethynyl, phenanthrenylethynyl or pyrenylethynyl) in a D- π -A system.^[52f] The phenanthrenylethynyl or pyrenylethynyl sensitizer **Por-6** has shown an efficiency of 10.06% (V_{OC} = 0.711 V, I_{SC} = 19.62 mAcm⁻²), which is the highest efficiency among porphyrin based sensitizers. This is due to the broad spectral response of the sensitizer between 400 to 800 nm.

In order to achieve a high efficiency of the DSSC device, the redox electrolyte, which transports positive charge carriers from the sensitizer to the back contact of the device, also plays a crucial role. The iodide/triiodide system is limited by its relatively high overpotential for dye regeneration and by com-

petitive light absorption by the triiodide.^[53] Moreover, the scale-up of DSSCs and the module stability are hindered by the corrosiveness of the iodide/triiodide redox couple toward most metals and sealing materials. One-electron outer-sphere redox couples, such as cobalt complexes, are interesting alternative redox mediators since they show weak visible light absorption and are less aggressive toward metallic conductors than iodine.^[54] Grätzel and co-workers have fabricated a DSSC device by using Co^{II/III} tris(bipyridyl) redox electrolyte and **Por-7** as sensitizer, which achieved conversion efficiencies of 11.9% under 1 sun, exceeding those obtained with today's best ruthenium sensitizers. Though **Por-7** has shown excellent performance, it lacks absorption in the 480 to 630 nm region of the spectrum, and this may reduce the J_{SC} and efficiency. To avoid this loss, co-sensitization of an organic sensitizer, **Y123**, that possesses complementary absorption spectrum to **Por-7** was carried out. The co-sensitized films using Co^{II/III} tris(bipyridyl) redox electrolyte have achieved an efficiency of 12.3% under 1 sun, with better photovoltaic performance than that of solar cells using a single dye.^[52g] The reason for the high efficiency is that the specific molecular design of **Por-7** greatly retards the rate of interfacial back electron transfer from the conduction band of the nanocrystalline titanium dioxide film to the oxidized cobalt mediator, which enables attainment of strikingly high photovoltages approaching 1 volt.

4.2. Phthalocyanines

Phthalocyanines are analogues to porphyrins and are man-made compounds. Like porphyrins, they are 18- π electron aromatic systems and possess a Soret-band at 350 nm and Q-bands in the 650–700 nm region; they also exhibit promising electrochemical, photochemical, and thermal properties, and are thus of interest to use as NIR photosensitizers for DSSCs.^[55] However, the major drawbacks of phthalocyanines are solubility and their tendency to aggregate on the surface of nanocrystalline semiconducting materials. Some representative phthalocyanine photosensitizers are collected in Figure 10.

The first phthalocyanine that was used for the sensitization of nanocrystalline TiO₂ was zinc tetracarboxy phthalocyanine (**Pc-1**) with an efficiency of 1% using 3 α ,7 α -dihydroxy-5 β -cholic acid (cheno) as co-adsorbent to minimize the aggregation.^[56] In their pioneering work, Grätzel and co-workers used Ru(II) phthalocyanine for the fabrication of a DSSC device and obtained a high IPCE value of 60%. The advantage of this sensitizer is that it has anchoring bis(3,4-dicarboxypyridine) groups at axial positions of the Ru(II) phthalocyanine, opening up a new way to improve the near-IR response of DSSCs.^[57]

Aranyos and co-workers have reported a series of phthalocyanines with aryl groups connected at the peripheral positions which show surprising sensitization of nanocrystalline TiO₂

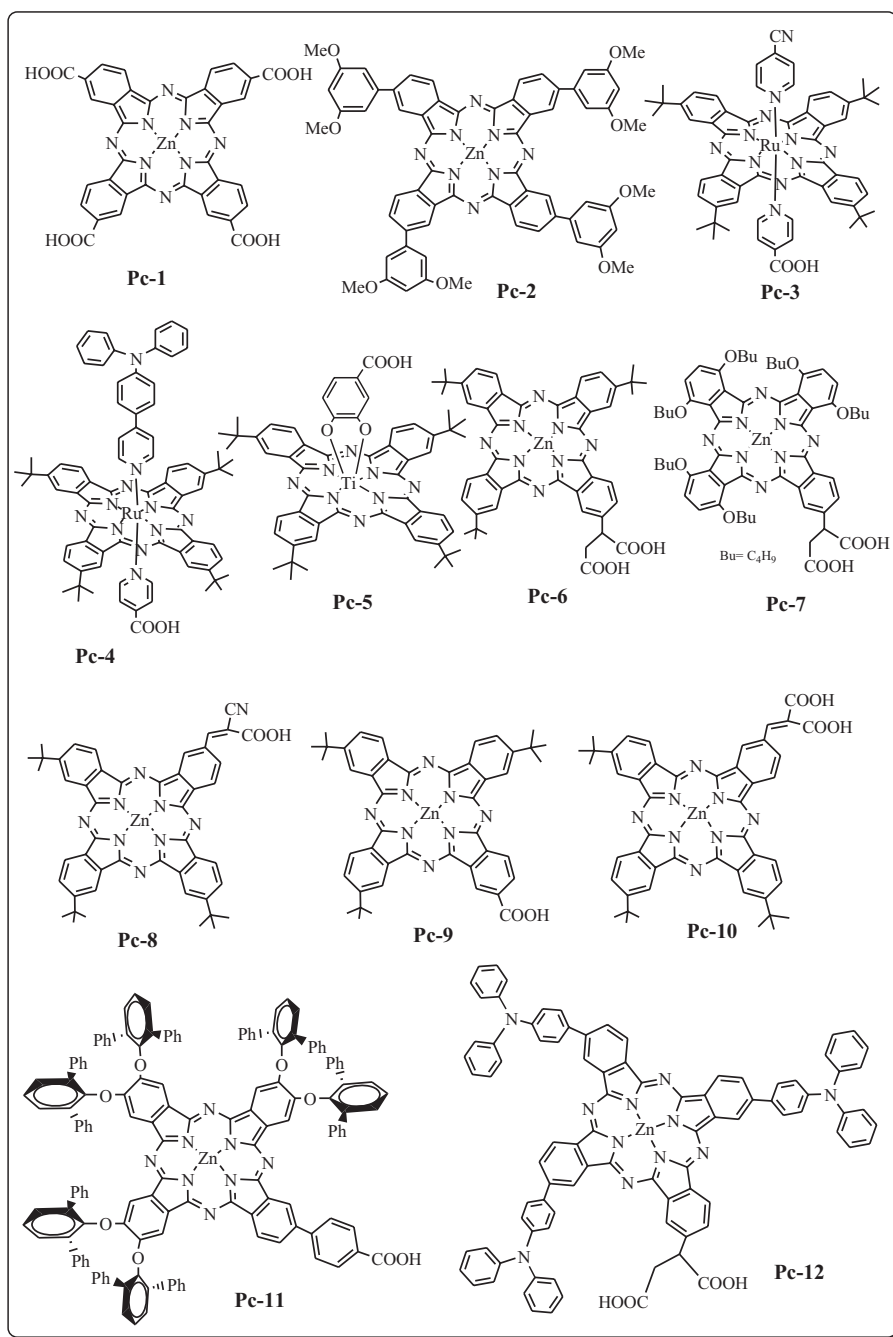


Fig. 10. Structure of phthalocyanine based sensitizers.

electrode.^[58] The aryl group connected at the peripheral positions (**Pc-2**) are designated to facilitate the adsorption of dyes at the surface of nanoparticles. These sensitizers have shown reasonable incident photon-to-current conversion efficiencies of 4 to 9%. Sundstrom and co-workers have used zinc(II) phthalocyanines substituted with amino acids for the sensitization of nanocrystalline TiO_2 .^[59] Phthalocyanine having substitution

with tyrosine showed an efficiency of 0.54%. They have also investigated the kinetics of this tyrosine substituted phthalocyanine dye on TiO_2 by femtosecond spectroscopy. They found that the electron injection from the excited state of the phthalocyanine dye to the conduction band of TiO_2 is very fast. However, the charge recombination is also fast. This might explain the reason the DSSCs based on this type of dyes have low efficiency.

In the following work, Durrant and co-workers have studied axially substituted ruthenium phthalocyanines by using transient absorption experiments.^[60] The ruthenium phthalocyanine has either 4-cyanopyridine (**Pc-3**), which is electron withdrawing, or triphenyl amine (**Pc-4**), which is electron releasing, at axial position. The other ligand 4-carboxy pyridine acts as anchoring group. The work reveals surprisingly the electron injection from the triplet state of the ruthenium phthalocyanine. The long lifetime of the triplet state leads to efficient electron injection occurring in hundreds of nanoseconds with an IPCE of 45%. Torres and co-workers have used axial positions of titanium(IV) phthalocyanines (**Pc-5**) for DSSC applications. Unlike in Ru(II) phthalocyanines, Torres et al. have connected anchoring 4-carboxy catechol at the axial position by covalent bond.^[60a] By using covalent bonding, desorption from the surface of nanocrystalline TiO₂ could be minimized. The IPCE was found to be 19 % and η was 0.2 %. The poor efficiency is due to the poor injection of electrons from the S₁ state of the phthalocyanine to the conduction band of TiO₂.

Nazeeruddin, Giribabu and co-workers developed unsymmetrical zinc phthalocyanines (**Pc-6**, **Pc-7** and **Pc-8**) based on the 'push-pull' concept.^[61] These phthalocyanines have either three bulky *tert*-butyl groups (**Pc-6** and **Pc-8**) or six alkoxy groups (**Pc-7**) in the molecular structure, which act as electron releasing groups ('push'). It has also two carboxylic acid groups which serve to graft the sensitizer onto the nanocrystalline TiO₂ and also acts as an electron withdrawing group ('pull'). The sensitizers **Pc-6**, **Pc-7** and **Pc-8** showed IPCEs of 75, 25 and 50% with overall conversion efficiencies of 3.05, 1.13 and 2.35%, respectively, using volatile liquid redox electrolyte. The high efficiency of the sensitizer, when compared to other phthalocyanine based sensitizer, is due to the directionality of excited state electrons from sensitizer to the conduction band of semiconductor TiO₂. Using the durable redox electrolyte (high boiling point solvents such as γ -butyrolactone) the unsymmetrical sensitizer, **Pc-6** has shown a conversion efficiency of close to 2% and the device was stable even after 1000 h when continuously exposed to heat and light.^[61c] The sensitizer **Pc-6** was also tested using a hole transporting material (2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) with an overall conversion efficiency of 0.87%.^[61a] In another study, Torres and co-workers have further redesigned the sensitizer having only one anchoring carboxylic acid group rather than two carboxylic acid groups (**Pc-9**). This sensitizer has shown an overall conversion efficiency of 3.52%.^[62] The high efficiency of **Pc-9** over **Pc-6** is probably due to the fact that the excited state lifetime is less in the former so that the recombination of the excited electron with oxidized phthalocyanine is less. Furthermore, the same group also determined the distance and orientation of the anchoring group to the phthalocyanine macrocycle (**Pc-**

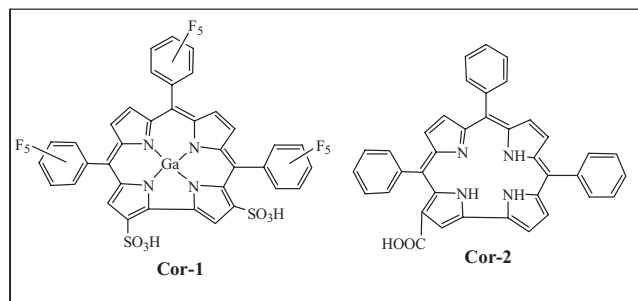


Fig. 11. Structure of corrole based sensitizers.

10).^[62b] The unsymmetrical phthalocyanine-bearing insulating spacer showed poor performance whereas those having a conductor spacer showed good performance. Recently, Taya and co-workers have introduced more bulky phenoxy groups at the peripheral positions of phthalocyanines to further reduce the aggregation of phthalocyanine macrocycle (**Pc-11**).^[63] This phthalocyanine has shown an IPCE of 78% at 700 nm with an overall conversion efficiency of 4.60%, which is the highest efficiency among phthalocyanine based sensitizers. This is due to the lower degree of aggregation of phthalocyanine on the TiO₂ surface than that of other phthalocyanine molecules.

Torres and co-workers have co-sensitized by mixing a phthalocyanine and an organic sensitizer whose absorption is around 550 nm. Such types of cocktail sensitizers have shown an overall efficiency of 7.74%.^[62b] Giribabu et al. have reported a cocktail sensitizer based on zinc phthalocyanine and bulky organic molecules, triphenylamine (**Pc-12**). It showed an IPCE of 37% with an overall conversion efficiency of 1.05%.^[64]

4.3. Corroles

Unlike the porphyrins and phthalocyanines, corroles are much less explored as sensitizers for DSSCs. Corrole is an analogue of porphyrin, and is a contracted macrocycle where one *meso* position has been eliminated, resulting in a direct pyrrole-pyrrole bond and possessing the 18- π electron aromaticity of porphyrins.^[65] Corroles also have many optoelectronic applications like porphyrins and phthalocyanines.^[66] Gross and co-workers have used Ga(III) corrole for sensitization of nanocrystalline TiO₂ (**Cor-1**; Figure 11). It has sulfonic acid as an anchoring group. This sensitizer showed an efficiency of 1.60%.^[67] Recently, Giribabu and co-workers have reported a series of corroles having a carboxylic anchoring group at the pyrrole β -position (**Cor-2**). The device fabrication studies have not yet been reported.^[68]

5. Conclusions

In conclusion, DSSCs represent a promising alternative technology to the existing solid-state p-n photovoltaic devices. The

sensitizer is one of the vital components in achieving high efficiency and durability of these devices. The widely used sensitizers in these devices are ruthenium(II) polypyridyl complexes. The major drawback of Ru(II) complexes is their low molar absorption coefficient, and moreover the absorption is limited at around 550 nm. Various Ru(II) complexes were reported by adopting a molecular engineering approach to further improve the durability of the device. This article also reviewed the other metal complexes for DSSC applications, but their efficiency is well below the Ru(II) complexes. The metal-free or organic sensitizers present no concern about the natural resources, and they are less durable. In contrast, tetrapyrrolic compounds are found to be the best alternative sensitizers to DSSC applications based on their thermal, electronic and redox properties. Porphyrins having anchoring groups at the *meso* position are shown to have an efficiency of 11.9%, which is better than Ru(II) complexes. The co-sensitization of porphyrins with an organic dye has reached an efficiency of 12.3% recently. There is hence a point to further increase the efficiency of DSSC devices based on porphyrin sensitizers. Phthalocyanines are not only low-cost but also quite efficient; however they are still poor for DSSC applications when compared to porphyrins. Nevertheless, unsymmetrical phthalocyanines based on the 'push-pull' concept have reached an efficiency of 4.6%. The highest efficiency that was observed using corroles as sensitizers is 1.6%.

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