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## *Quantum Dots versus Dyes in Sensitized Solar Cells: Synthesis, Optimization, Performance*

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## Introduction to Emerging Photovoltaic Technologies

The quality of human life is strongly dependent on the availability of energy sources. Increased energy demand (currently, the total worldwide energy consumption is about 14 terawatts) and environmental pollution require a swift transition to new, green technologies for energy generation [1, 2]. Different approaches were followed for finding and developing sustainable energy solutions. Among the alternative power sources existing today (hydroelectric, nuclear, biomass, wind, geothermal, and solar), solar energy is by far the largest exploitable resource. Enough to say that sunlight striking Earth's surface in 1 hour provides more energy than all the energy consumed by human civilization in one year [3].

Consequently, the design and manufacturing of a high - performance and low - cost photovoltaic cells, able to replace fossil fuel and related technologies, is assumed as an urgent task for multidisciplinary scientific teams worldwide [4, 5]. Considering the increasing demand for renewable energy, solar power companies are focused nowadays on manufacturing and installing solar panels [6].

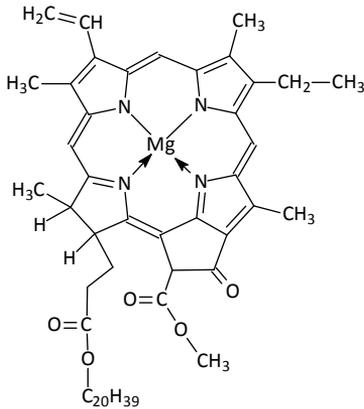
Due to the most mature technology for photovoltaic cell manufacturing, the main material used remains silicon [7]. Though Si solar panel technology exhibits many benefits (e.g. longevity, efficiency, lower installation costs [8]), it also yields several drawbacks that need to be considered:

- Cost: Traditional silicon cells use ultra-high purity silicon, which is very expensive;
- Silicon absorbs sunlight poorly: According to Prof. Michael Grätzel, from École Polytechnique Fédérale de Lausanne: "silicon solar cells use 1.000 times more light absorbing material than dye-sensitized solar cells and perovskite cells";
- Silicon is very brittle.

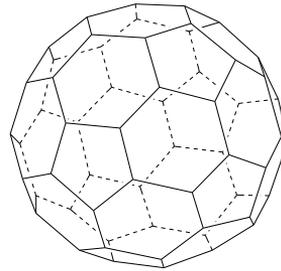
Despite the worldwide spread of the silicon-based solar modules, other emerging photovoltaic technologies have received considerable attention in the last few decades, due to their promising performance and low production costs. Among them, one can enumerate organic photovoltaics, hybrid organic-inorganic solar cells, perovskite photovoltaics, inorganic quantum dots solar cells, dye-sensitized solar cells.

An **organic photovoltaic (OPV)** cell is a type of solar cell that uses organic electronics, such as small organic molecules (chlorophyll-a, fullerene, pentacene - Figs. 6.1-3) or conductive organic polymers (MEH-PPV - Fig. 6.4, CN-PPV, PPV, polyacetylene, etc.), for performing light absorption. Typically, they are sandwiched between two electrodes [9].

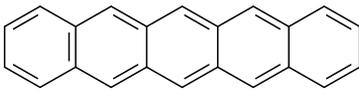
Comprising a sandwiched organic material between two electrodes with different work functions, **single layer organic photovoltaic cells** are the simplest form of OPVs, but their efficiencies are modest.



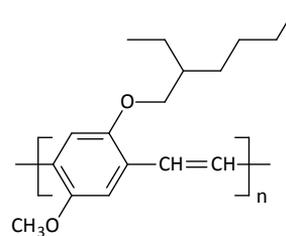
**FIGURE 6.1**  
The structure of chlorophyll A



**FIGURE 6.2**  
The structure of fullerene C60

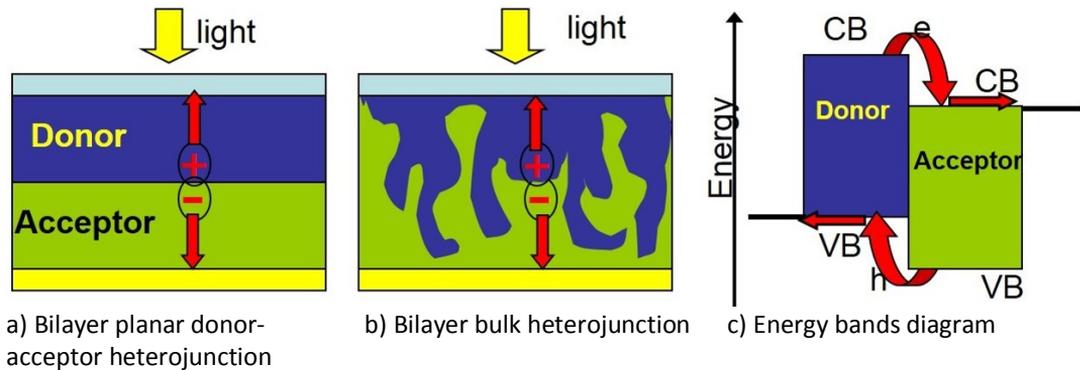


**FIGURE 6.3**  
The structure of pentacene



**FIGURE 6.4**  
The structure of MEH-PPV  
(Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene])

**Bilayer OPV cells** contain two layers placed between conductive electrodes. This type of OPVs, manufactured in different architectures (planar donor-acceptor heterojunction or bulk heterojunction – Figs. 6.5a-b), do exhibit superior performances compared to single layer OPVs. The layer with higher electron affinity and ionization potential is the electron acceptor layer (it mainly transports electrons), while the other, with lower electron affinity ionization potential, is the electron donor layer (it mainly transports holes). After capturing a photon, a bound electron-hole pair (an exciton) is generated. For obtaining free carriers (electrons and holes), this exciton needs to be dissociated. An efficient exciton dissociation occurs at the interface between two organic materials (or at the interface between an organic material and the metal electrode, in the case of single layer cells). For this reason, the area of this interface is made as large possible in the case of the bulk heterojunction structure. After the exciton dissociation, electrons move to the acceptor domains, are carried through the device and collected by one electrode, while holes move in the opposite direction and are collected at the other side (Fig. 6.5c)[10].



**FIGURE 6.5**  
Bilayer OPV cells

Among the merits of OPV solar cells, one can enumerate:

- They are thin and light, thus, they can be used in flexible solar modules;
- They are cheaper than Si-based solar cells;
- They have high optical absorption coefficient due to the organic molecule;
- Their band gap can be modified via molecular engineering (i.e., by modifying the length and type of functional groups on the polymer backbone).

On the other hand, OPV cells exhibit low efficiency (maximum certified value is 11, 5%) and low stability [11].

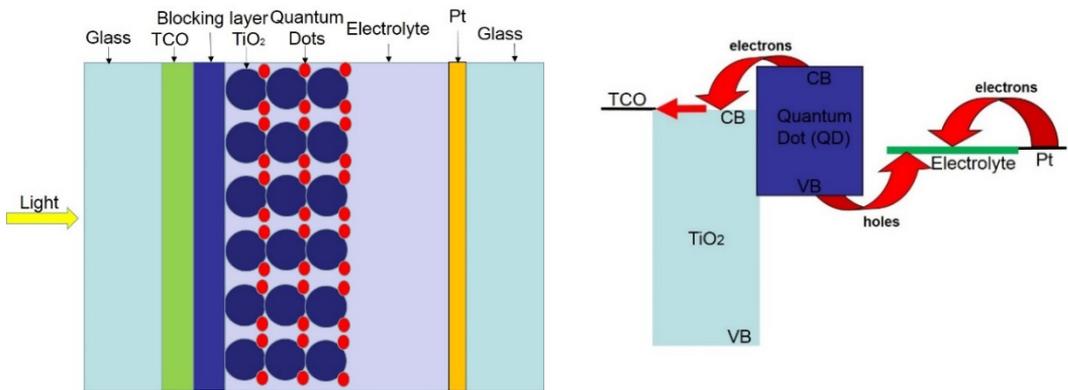
Another emergent photovoltaic technology is that of **perovskites solar cells**. These devices employ, as light absorber, compounds with perovskite crystal structure, methyl ammonium lead triiodide ( $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ ) being the most widely used [12, 13]. From the commercial perspective, perovskites solar cells are still under development, no products being yet available on the market. The maximum certified efficiency for this type of solar cell is 22.1%, demonstrated in 2013 [14 - 16]. Synthesis of materials such as methyl-ammonium lead halides is versatile and cheap. In order to emphasize the huge potential of this emergent photovoltaic technology, it is enough to note that their appearance allowed the increase of solar cells efficiency from 3.8 % in 2009 to 22.1% only one year later.

The aim of this book chapter is to discuss two emerging photovoltaic technologies, **inorganic quantum dots sensitized solar cells (QDSSCs)** and **dye-sensitized solar cells (DSSCs)**, in terms of design, manufacturing and performance. A special attention will be paid to the synthesis and molecular engineering of light absorbers (inorganic quantum dots and organic dyes). The chapter will conclude with a comparison between the two types of light absorbers in terms of cost, versatility of synthesis, stability, power conversion efficiency, manufacturing scalability, toxicity and related environmental issues.

## Quantum Dot-Sensitized Solar Cells (QDSSCs)

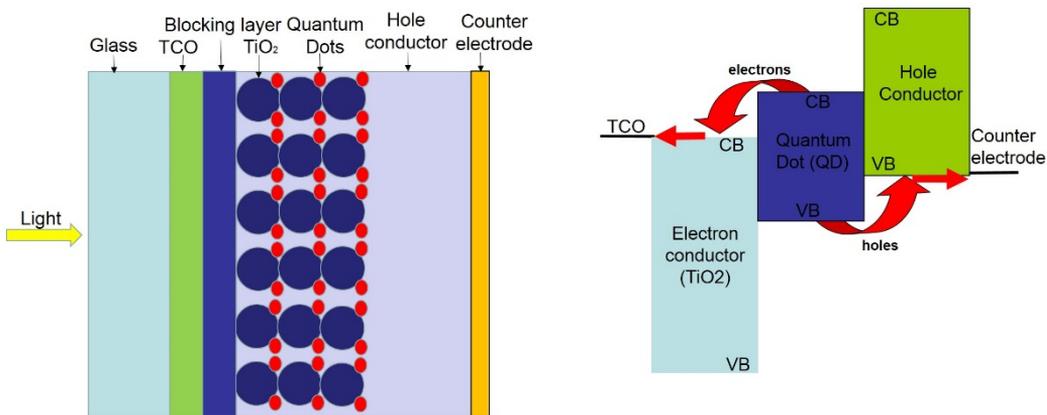
### Introduction

Among the emerging photovoltaics technology, **quantum dot – sensitized solar cells (QDSSCs)** received a great attention in the last decades due to their distinctive properties, such as theoretical conversion efficiency up to 44%, simplicity in manufacturing, capacity to realize light harvesting in a broad solar spectrum regions [17, 18]. Two possible schematic diagrams of QDSSCs are presented in Fig. 6.6 below.



**FIGURE 6.6a)**

Schematic diagram of a QDSSC with electrolyte as hole transport layer: Cell structure (left) and Energy bands diagram (right)



**FIGURE 6.6b)**

Schematic diagram of a QDSSC with p-type semiconducting polymer as hole transport layer: Cell structure (left) and Energy bands diagram (right)

The working principle of the QDSSCs is the following: after being irradiated by the incident light, quantum dots (QDs) absorb photons yielding electron – hole pairs. Electrons are injected into the conduction band of an n-type wide band gap semiconductor, like TiO<sub>2</sub> or ZnO, and transported

towards the TCO (transparent conductive oxide) electrode (typically, ITO), while holes are scavenged by hole transport material (an electrolyte or a p-type semiconducting polymer). When polymer are employed (Fig. 6.6b) as hole transport materials, glass substrate, typically used for encapsulation purposes, is no longer required. As counter electrode, metals with high work function (such as Pt, Au, Ag), suitable for obtaining ohmic contacts with p-type semiconductors, should be used.

But what are the quantum dots (QDs), why are they used as light absorbers in photovoltaic devices and how can they be synthesized? QDs are extremely small semiconductors particles or nanocrystals, consisting of elements of II-VI, III-V, or IV-VI periodic groups, with typical dimensions in the nanometer range (2-10 nm or 10-50 atoms [19, 20]). Due to their small size, QDs exhibit unique optical and electronic properties. Thus, in the last decades, QDs have attracted considerable attention and employed in various applications: optoelectronic devices (such as lasers), photovoltaic devices, transistors, photodetectors, light emitting diodes (LEDs), quantum computing [21-26]. Water-soluble and bio-conjugated QDs proved useful in biosensors and bio-imaging [27, 28].

QDs are used as light absorbers in photovoltaic devices due to the following characteristics:

- Tunable bandgap over a broad spectral range by changing their size [29];
- Larger extinction coefficient than most organic dyes [30];
- Solution processability [30];
- Multiple exciton generation with single photon absorption and large intrinsic dipole moment [31];
- Versatile and low- cost synthesis [32];
- Chemical stability towards water and oxygen [32].

### ***Synthesis of quantum dots***

There are several methods to synthesize QDs, the most common involving colloidal quantum dots (CQDs). Narrow size distribution is the key target for the majority of CQDs synthesis process. The preparation of monodisperse CQDs implies two stages:

- Rapid nucleation, process controlled by degree of supersaturation in solution, temperature and interfacial tension;
- Slow growth [33-36].

Usually, QDs are synthesized in an organic medium and employ surface passivating reagents, known as capping ligands, such as tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylphosphine (TOP), oleic acid, dodecanethiol [37, 38]. The type of capping ligand has a crucial importance because the shape, optical and electronic properties of the QDs depend on it [39]. The major drawback of using these ligands in passivation is their rapid desorption from the surface of the QDs. Moreover, the steric hindrance between the bulky organic surfactants used for passivation yields incomplete surface coverage and un-passivated dangling orbitals [40].

A more efficient passivation can be obtained through the formation of a QD semiconducting core material and of a shell from another semiconducting material. Examples of these core-shell semiconducting nanocrystals are: CdS - HgS, CdS - CdSe and ZnSe - CdSe [41]. Another method for the fabrication of QDs is plasma synthesis [42, 43]. However, colloidal synthesis remains the most versatile and cheapest method for QDs synthesis.

### Approaches for depositing QDs on TiO<sub>2</sub> surface

There are several methods to deposit QDs on the surface of TiO<sub>2</sub>:

- Successive ionic layer - by - layer adsorption and reaction (SILAR) [44];
- Chemical bath deposition [45, 46];
- Drop casting or spin-coating [47];
- Electrophoretic method [ 48];
- Bifunctional linker approach [49].

All these approaches are simple and can be successfully implemented in a large scale production.

### Bifunctional linker approach. An HSAB perspective

One of the most used method to anchor the QDs to the TiO<sub>2</sub> surface is their functionalization with bifunctional linkers (ligands) [50]. Usually, the role of the bifunctional linker is to improve the charge transfer from the QD to the n-type semiconductor (in most cases, TiO<sub>2</sub>).

Bifunctional linkers have anchors at both ends. Different carboxylic acids - such as mercaptohexadecanoic acid, mercaptopropionic acid, thiolacetic acid – can be employed to bind QDs to TiO<sub>2</sub> nanoparticles [51, 52]. Several structural features of the linkers, such as length and conjugation, are important to improve the charge transfer efficiency. Choosing the appropriate anchors is the *sine qua non* condition to ensure strong chemical bonds at the QDs – TiO<sub>2</sub> interface.

Recently, the Hard Soft acid Bases (HSAB) theory was proposed as a new tool employed in QDs functionalization [53 - 58]. Based on this theory, different type of QDs, having cations which are classified either as soft acid or as borderline acid, can be functionalized with different linkers that have anchors classified as soft base or borderline base, respectively. It is important to emphasize that according to the HSAB principle, a hard acid prefers to bond to a hard base, a soft acid prefers to bond to soft bases, while a borderline acid prefers to bond to a borderline base.

In accordance with the HSAB rule, for QDs such as CdS, CdTe, CdSe, Cu<sub>2</sub>S, Ag<sub>2</sub>S, having cations classified as soft acids, several bifunctional linkers were proposed for functionalization:

- Selenocompounds, such as selenolipoic acid (Fig. 6.7) selenopenicillamine, selenomethionine, selenohomocysteine, selenocystine, Se-methylselenocysteine, Se-propylselenocysteine, Se-ethylselenocysteine, selenogluthatione (Fig. 6.8), Se-methylselenocysteine, Se-allylselenocysteine [59];

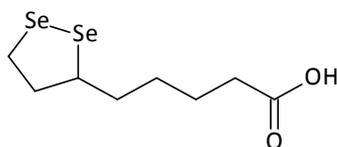


FIGURE 6.7

The structure of selenolipoic acid

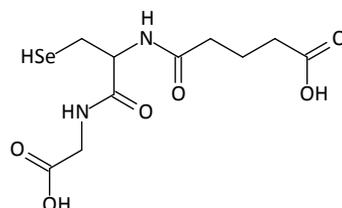
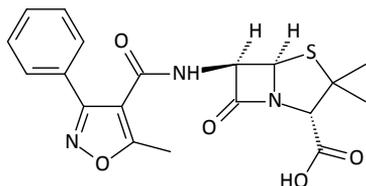


FIGURE 6.8

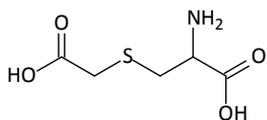
The structure of selenogluthatione

- Antibiotics that belong to the penicillin class, such as oxacillin (Fig. 6.9), penicillin G, piperacillin, cloxacillin, ticarcillin, penicillin V, ampicillin, amoxicillin [60];

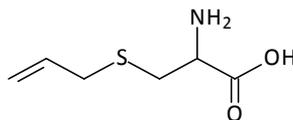
**FIGURE 6.9**

The structure of oxacillin

- Vitamins and analogues, such as biotin, norbiotin, homobiotin [60];
- Aminoacids, such as cysteine, homocysteine, isocysteine, carbocysteine (Fig. 6.10), acetylcysteine, S-allylcysteine (Fig. 6.11), S-propylcysteine, S-phenylcysteine, S-tertbutylcysteine [60, 61];

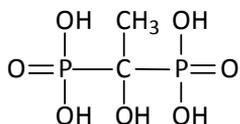
**FIGURE 6.10**

The structure of carbocysteine

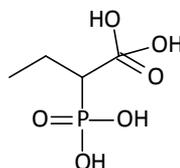
**FIGURE 6.11**

The structure of S-allylcysteine

- Phosphonic acids, such as 1-hydroxiethane-1,1 diphosphonic acid (HEDP - Fig. 6.12), propane 1,1 diphosphonic acid (Fig. 6.13), benzene 1,4 diphosphonic acid [62];

**FIGURE 6.12**

The structure of HEDP

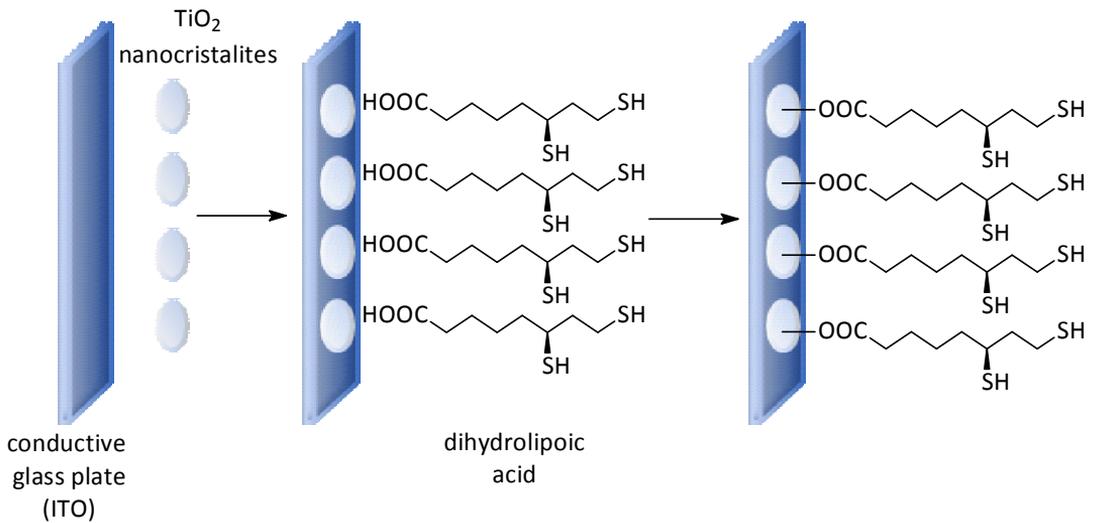
**FIGURE 6.13**

The structure of propane 1,1 diphosphonic acid

- Cephalosporins, such as cefditoren, ceftazidime, cefonicid, ceftazolidine, cefaclor, cephalotin, cefradine, cefdinir, cephalosporine C, cefcapene, cefapirin, cefacetrile, cefalexin, cefpiramide, cefaloglycin, ceforamidate, cefprozil [63];
- 2-[2-oxothiolan-3-yl] carbamoylmethylsulfanyl] acetic acid, 2-mercapto-5-benzimidazol-carboxylic acid, phytic acid, 2-mercapto-5 benzoxazole-carboxylic acid, pentetic acid, 4-mercapto hydrocinnamic acid, 2-[2-ethoxycarbonylmethylsulfanyl]ethyl]-1,3-thiazolidine-4-carboxylic acid, 3-(phenylthio)acrylic acid, lipoic acid, hexyl 3 mercaptohexanoate, hexyl 3-mercaptobutirate, hexyl 2-mercaptoacetate, asparagusic acid, 2-acetylamino-3-benzylsulfanyl propanoic acid, dimercaptoizobutiric acid and 2-mercapto histidine [64, 65].

All the bifunctional linkers listed above contain anchors (mercapto groups, sulfur atoms, phosphonic groups), able to covalently bind to the QDs (CdSe, CdTe, CdS, Ag<sub>2</sub>S) surface, and carboxylic or phosphonic moieties for anchoring to the surface of TiO<sub>2</sub>.

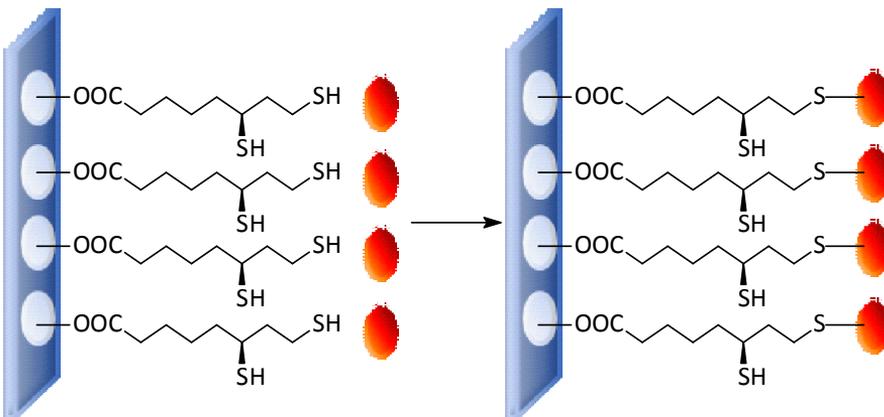
Figure 6.14 illustrates the anchoring of dihydrolipoic acid onto a nanostructured TiO<sub>2</sub> film through the carboxylic group (COOH). Functional derivatives of carboxylic acid (such as amides, ethylic esters, acid chlorides) can also be used as alternatives to the COOH groups.



**FIGURE 6.14**

Linking bifunctional linkers (dihydrolipoic acid) to TiO<sub>2</sub> surface through carboxylic groups

Fig. 6.15 depicts how QDs (CdSe, CdTe, CdS – all soft acids) can be linked to the TiO<sub>2</sub> surface through dihydrolipoic acid comprising mercapto groups (soft base) as appropriate anchors.



**FIGURE 6.15**

Linking QDs (CdSe or CdTe or CdS) to TiO<sub>2</sub> surface using dihydrolipoic acid as bifunctional linker

### **Wide band-gap semiconductors**

Titanium dioxide (TiO<sub>2</sub>) is a well-known metal oxide, stable, non-toxic and widely used in a variety of applications and products such as: sunscreens, water purification, toothpaste, food coloring (E171), photovoltaic cells, photocatalytic degradation of pollutants, biosensing, and drug delivery. It has 4 polymorph phases: rutile (tetragonal, the most stable phase), anatase (tetragonal), brookite (orthorhombic), and TiO<sub>2</sub> (B) (monoclinic) [66, 67].

TiO<sub>2</sub> is extensively used as wide band-gap semiconductors for manufacturing QDSSCs due to its excellent properties [68]:

- Good chemical stability;
- High corrosion resistance;
- Elevated hardness;
- Low - cost synthesis;
- Good charge transport properties.

It has been demonstrated that the efficiency of electron injection and light harvesting in QDSSCs depends strongly on the morphology, size and structure of TiO<sub>2</sub>. Thus, different types of TiO<sub>2</sub>, such as nanotubes [69, 70], nanorods [71], nanowires [72], mesoporous [73], porous [74, 75], spheres [76], nanoflowers [77] and nanodendrite array [78], were used as photo-anodes in order to improve the performance of QDSSCs.

Among the most commonly used methods for TiO<sub>2</sub> synthesis, one can enumerate the sol-gel method [79, 80], the hydrothermal [81] and the electrochemical one [82]. Recently, crystalline mesoporous B/N co-doped TiO<sub>2</sub> nanomaterial [83] and Ni-doped TiO<sub>2</sub> thin films [84] have been prepared in order to improve the performance of QDs-based photovoltaic devices.

ZnO is another wide band-gap semiconductor used as photo-anode in design and manufacturing of QDSSCs. As in the case of TiO<sub>2</sub>, different polymorphic ZnO semiconductors, such as nanorod arrays, nanoflowers, nanotubes, pyramids arrays, nanosheets, were synthesized and tested [17].

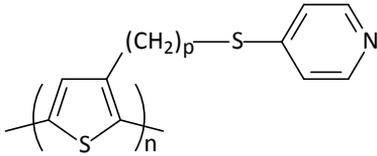
### **Hole transport layer**

Sulfide / polysulfide (S<sup>2-</sup> / S<sub>n</sub><sup>2-</sup>) is the most used aqueous electrolyte employed as hole transport layer in the design and manufacturing of QDSSCs [85, 86]. Other tested electrolytes are Co<sup>2+</sup>/Co<sup>3+</sup> [87] and Fe<sup>2+</sup>/Fe<sup>3+</sup> [88] redox system. The major drawbacks of using a liquid electrolyte is its volatilization (lowering its long-term stability, which is an important criterion when commercializing photovoltaic devices) and the permeation of oxygen and water molecules [89].

These issues can be solved by replacing the liquid, volatile electrolyte with solid state p-type semiconducting polymers. Poly (3, 4-ethylenedioxythiophene) – poly (styrenesulfonate), MEH-PPV, poly (3-dodecylthiophene), P3HT are examples of semiconducting polymers which were used as holes conductor in QDSSCs [90, 91]. The power efficiency of QDSSCs is strongly dependent on the charge transfer at the interface between the QDs and the semiconducting organic polymer. A covalent bond between the QDs and the polymer increases the charge transfer and avoids the segregation of phases.

The HSAB theory can be employed as a useful tool for the functionalization of polymers with suitable pendant anchors, in order to create a covalent bond at the QDs - holes conductor interface. Thus, for QDs like CuO, ZnO Bi<sub>2</sub>S<sub>3</sub>, PbS, Sb<sub>2</sub>S<sub>3</sub>, PbSe (all comprising cations which are classified as

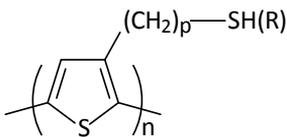
borderline acids), several polymers, such as polythiophene tailored with pyridine group (borderline base - Fig. 6.16), were proposed for the design of QDSSCs [52 - 58, 60 - 62]:



**FIGURE 6.16**

The structure of polythiophene tailored with pyridine moiety (p is 6 - 12)

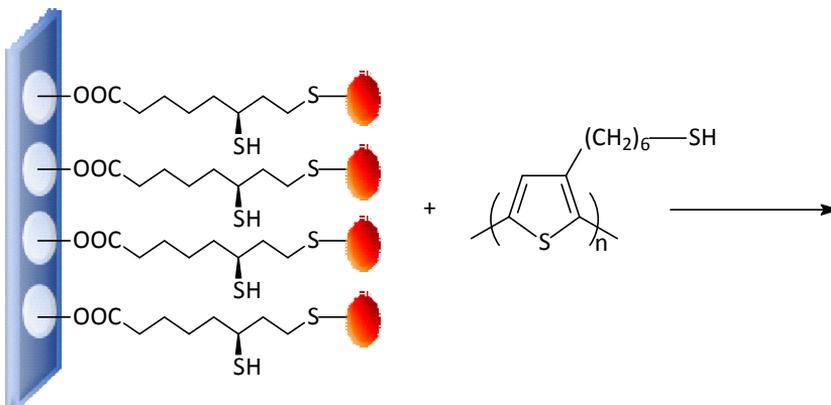
At the same time, for different types of QDs, like CdS, CdTe, CdSe, Cu<sub>2</sub>S, Ag<sub>2</sub>S (all comprising cations which are classified as soft acids), several polymers, such as polythiophene tailored with mercapto or phosphonic moieties (soft base – Fig. 6.17), were proposed for the design of QDSSCs [52 - 58, 60 - 62]:

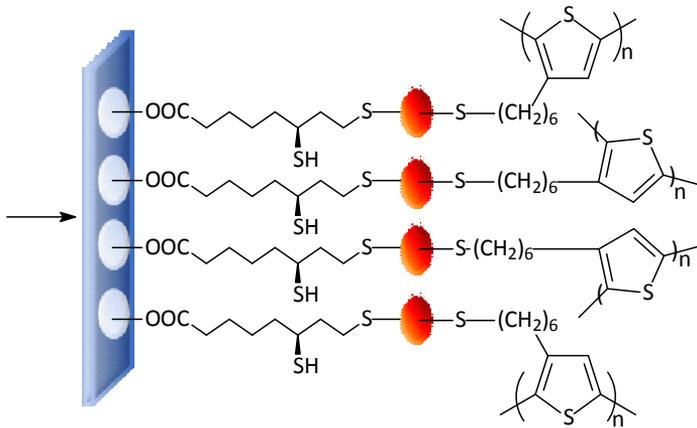


**FIGURE 6.17**

The structure of polythiophene tailored with mercapto (mercaptide group) moiety (p is 6-12)

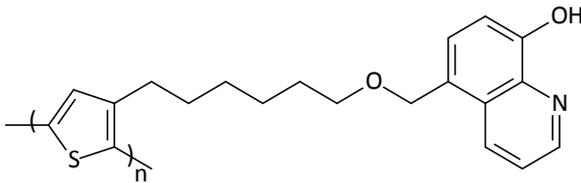
Figure 6.18 shows how a hole conductor polymer (poly[3-(ω-mercapto hexyl)]thiophene) can be linked to the QDs (CdSe, CdTe, CdS – soft acids) surface, using mercapto groups (soft base) as appropriate anchors, selected based on the HSAB theory.



**FIGURE 6.18**

Linking a hole conductor polymer (poly[3-( $\omega$ -mercapto hexyl)]thiophene) to the QDs surface (CdSe, CdTe or CdS), using HSAB theory principles

As presented in Fig. 6.19, strong QD - hole conductor polymer interface can be obtained by using polymers designed according to specific principles of coordination chemistry [64].

**FIGURE 6.19**

The structure of polythiophene with 8- hydroxi quinoline as pendant group

### Counter electrode

Counter electrodes play a vital role in the QDSSCs structure, although they generally receive less attention than the QDs and the wide band-gap semiconductors. The role of the counter electrode is to transfer electrons from an external circuit and reduce the oxidized species of the electrolyte. Different materials can be used as counter electrode in QDSSCs: noble metals (like Pt, Au, Al), Ti mesh supported mesoporous carbon (MC/Ti) [92], iron sulfide (which is prepared by simply immersing carbon steel in  $\text{Na}_2\text{S}$  solution) [93], mesocellular carbon foams (MSU-F-Cs) with high surface area ( $911 \text{ m}^2 \text{ g}^{-1}$ ) and large pores ( $\sim 25 \text{ nm}$ )[94], nanostructured metal chalcogenides (such as NiS [95] and CoS [96]), conducting polymers (like polypyrrole, polyaniline and poly(3,4-ethylenedioxythiophene)), polystyrene sulfonate (PEDOT-PSS), and combinations of these materials [97].

The morphologies and performance of counter electrodes can be investigated with different techniques, such as: scanning electron microscope (SEM), transmission electron microscope, X-ray diffraction, current density – voltage measurements, Tafel polarization measurements, electrochemical impedance spectroscopy (EIS), cyclic voltammetry [97].

### The performance of QDSSCs

Despite QDSSCs theoretical conversion efficiencies up to 44%, experimental measured values of this parameter are still low. The limiting factors for efficiency enhancement are:

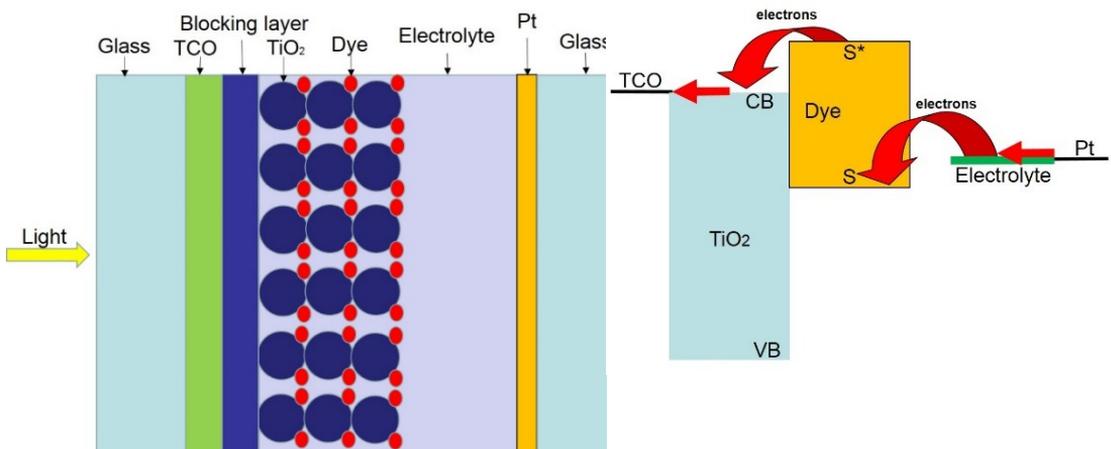
- Insufficient light absorption;
- Electrons-holes recombination in the electrolyte;
- Slow charge transfer process between the counter electrode and the electrolyte [17].

In recent years, several approaches have been pursued to improve the performance of QDSSCs. Despite of all the advantages of QDs, QDSSCs laboratory-measured were typically around 4-7%. The maximum QDSSC certified efficiency (11.6%) was obtained when using Zn-Cu-In-Se as QD [98].

## Dye-Sensitized Solar Cells (DSSCs)

### Introduction

In the early 1990s, Brian C. O' Regan and Michael Grätzel published a paper on a breakthrough work in manufacturing solar cell devices, introducing a new class of photovoltaic devices, dye – sensitized solar cell (DSSC) [99]. At the core of these devices, there is a porous network of  $\text{TiO}_2$  nanoparticles coated with light – absorber dye molecules and surrounded by a hole conductor (usually, a liquid phase electrolyte) [100]. A schematic diagram of DSSCs is presented in Fig. 6.20, below.



**FIGURE 6.20**

Schematic diagram of a DSSC: a) Cell structure; b) Energy bands diagram

The operational principle of DSSCs is pretty straight forward. Due to the irradiation with light, the dye molecules absorb photons and get into an excited state. In this excited state, the dye injects electrons into the conduction band of  $\text{TiO}_2$  (instead of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$  or  $\text{SrTiO}_3$  can also be employed). Further on, electrons are transported through the  $\text{TiO}_2$  network to the TCO

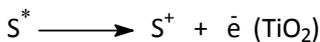
(transparent conductive oxide) electrode (typically, ITO). The initial state of the dye is restored by the electron donation from the electrolyte that is regenerated at the Pt layer, which acts as counter electrode [101]. Pt is coated on the substrate (typically, glass) for the efficient regeneration of the redox couple. In the case of solid-state DSSCs, the liquid electrolyte is replaced with a hole conducting polymer. The blocking layer is typically a layer of  $\text{TiO}_2$  (prepared by the sol-gel method, for instance). Its role is to prevent the direct contact between the TCO electrode and the redox mediator in the electrolyte [102]. Each component of this architecture can be optimized in order to improve the overall efficiency of the photovoltaic device.

The main processes occurring in a DSSC are summarized below [103]:

- The dye adsorbed on the  $\text{TiO}_2$  (or  $\text{ZnO}$ ,  $\text{SnO}_2$ , etc.) surface absorbs incident photons, being excited from the ground state (S) to the excited state ( $S^*$ ):



- The excited electrons are injected into the conduction band of the semiconductor. As a consequence, the oxidation of the dye molecule occurs:



- The electrons injected in the  $\text{TiO}_2$  conduction band are transported by the  $\text{TiO}_2$  nanoparticles towards the TCO electrode and finally reach the Pt counter electrode through the external circuit;
- The oxidized dye molecule is regenerated by accepting electrons from the reducing agent in the electrolyte;
- The oxidized redox mediator diffuses towards the counter electrode and then it is reduced.

Although its conversion efficiency is still less than the exhibited by state-of-the-art thin-film cells, the DSSC has a number of attractive features, such as [104-106]:

- Low production cost;
- Flexibility;
- Reduced weight;
- Employment of conventional roll-to-roll techniques for its manufacturing;
- Use dyes with tunable optical properties;
- Employ bifacial cells able to capture incident photons from all angles;
- Do not degrade at elevated temperature.

### ***Design, synthesis and properties of organic and inorganic chromophores for DSSCs***

Among the components of DSSC, the photosensitizer is the key constituent, playing an essential role in the DSSC efficiency. The most encountered types of chromophores, used as light absorbers in manufacturing DSSCs, are:

- Metal complexes [101];

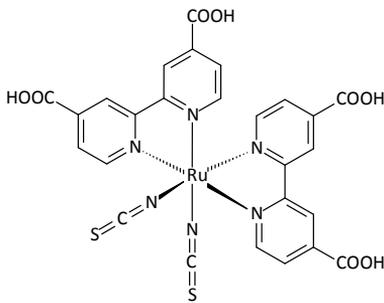
- Porphyrines and phthalocyanines [107];
- Natural dyes [108];
- Synthetic, metal-free, organic dyes [104, 109, 110].

### Metal complexes

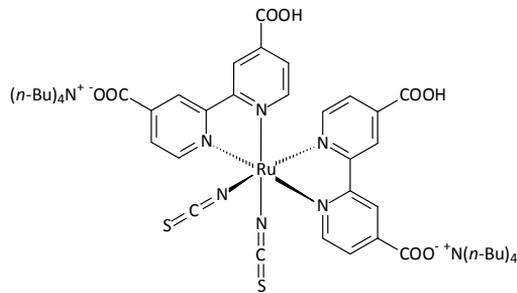
Metal complexes have received a considerable attention in the last years. Their ability to harvest energy from a broad range of light, chemical stability, favorable photovoltaic properties are of the few attractive features of this type of sensitizers. From a structural point of view, metal complex sensitizers consist of a central metallic ion and two types of ligands: ancillary and anchoring.

The metal-to-ligand charge transfer (MLCT) process is responsible for metal complexes light-absorption capability in the visible part of the spectrum. For this reason, the central metal ion has a cardinal importance in achieving superior power conversion efficiencies [111]. Anchoring ligands are required to bond the dye to the surface of the semiconducting metal oxide nanoparticles and to further facilitate the injection of excited electrons in the conduction band of  $\text{TiO}_2$  [112]. Ancillary ligands, tailored with different aliphatic chains and/or aromatic units, are important for tuning the electrochemical and photo physical properties of the sensitizer and, thus, for improving the overall photovoltaic performance of the DSSC [113].

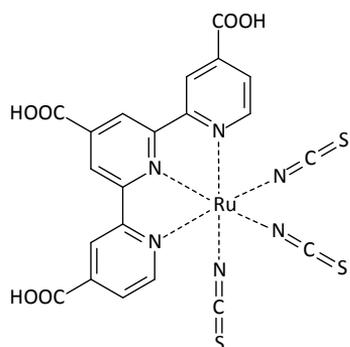
Among the metal complexes employed as cromophores, Ru complexes are the most efficient ones. DSSCs using different Ru-based sensitizers, such as N3, N719 and Black dye (Figs. 6.21-23), showed experimental efficiencies up to 11% under standard measurement conditions [114-118]. For all, the carboxylic group is the anchoring ligand.



**FIGURE 6.21**  
The structure of N3



**FIGURE 6.22**  
The structure of N719

**FIGURE 6.23**

The structure of Black dye

At the same time, different Ru-based sensitizers with other anchoring ligands, such as sulfonic acid, phosphonic acid and catechol, were also synthesized. However, their performance are inferior to those showed by sensitizers using carboxylic acid groups as anchoring ligands [119-123].

Recently, several Ru-based sensitizers were synthesized using different types of ancillary ligands, like:

- Bipyridyls containing different substituents, such as alkyl, alkoxy, triarylamine[124, 125];
- 1, 10 phenantroline [126];
- Dipyridylamine [127];
- Pyridyl-benzimidazole [128];
- Tridentate ancillary ligands, such as 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (bmipy) [129].

Generally speaking, despite exhibiting superior performance, Ru-based photosensitizers suffer from scarcity, high cost, toxicity and limited absorption in the near- infrared region of the solar spectrum. Due to these limitations, other options had to be taken into consideration [129]. Complexes of transition metals, like Os[130], Co[131], Fe [132], Cu[133], Re[134], were synthesized and tested as photosensitizers.

### *Porphyrins and phthalocyanines*

#### *Porphyrins*

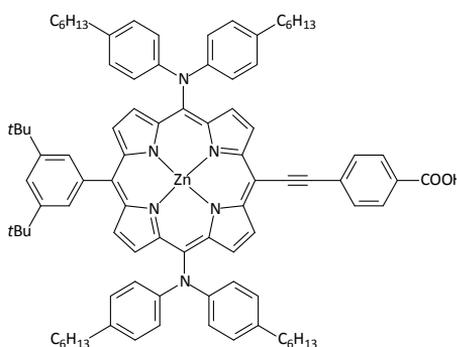
Porphyrins are one of the most frequently used sensitizers in DSSCs [135-137]. Their most attractive features are [138-141]:

- Synthesis is relatively simple and cheap;
- They exhibit good chemical, photo- and thermal stability;
- They have tunable electrochemical and optical properties (color, transparency) obtained through rational synthesis;
- They are eco-friendly;
- They have intense spectral response bands in the near IR-region.

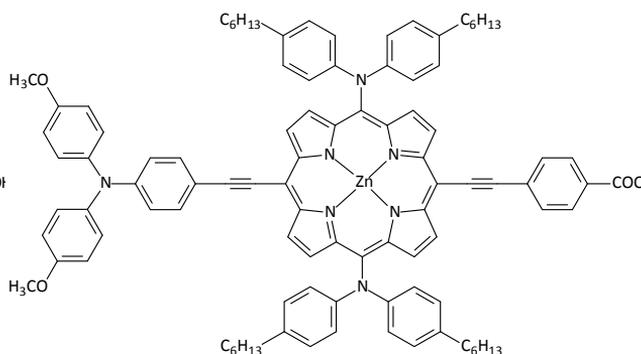
Changing the coordinating metal center, the number of porphyrin units, the anchor between the porphyrin core and the inorganic semiconductor or the type of substituents on the molecular structure are strategic alternatives in order to manipulate and optimize the properties of the porphyrins and thus to improve the overall performance of DSSCs employing them [142]. Tetrakis (4-carboxyphenyl)-porphyrinato]zinc (II) was the first porphyrin used for the sensitization of nanocrystalline  $\text{TiO}_2$  [143]. In the last years, several porphyrins - as free bases - and metalloporphyrins with different metal centers (including zinc and copper) were synthesized and tested as sensitizers for DSSCs [144]. Wang [145], Campbell and co-workers [146] developed several porphyrin sensitizers by performing the functionalization of the  $\beta$ -position of the *meso*-tetraphenylporphyrins with different functional group in order to extend the conjugated  $\pi$  system. This type of functionalization proved to be an effective tool to optimize the porphyrin photoelectric properties, and, consequently, to improve the efficiency of the DSSC.

Different anchoring groups, like  $-\text{COOH}$  and  $-\text{PO}_3\text{H}_2$ , were employed to assemble porphyrins molecules onto a metal oxide surface. Porphyrins with a carboxylic binding group exhibited better efficiencies than those with phosphonate anchoring group. The results indicated that the number and position of the anchoring groups on the porphyrin moieties have a key role on the photovoltaic performance [144].

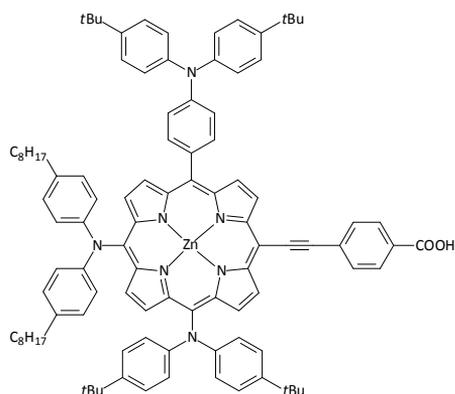
Recently, Liu and co-workers synthesized several novel porphyrins dyes with the push-pull framework. They demonstrated that different thiophene derivatives can act as conjugated bridge to broaden the absorption of the porphyrin [147]. Wu and co-workers [141] synthesized novel donor  $-\pi-$  acceptor porphyrins dyes (coded YD14-YD17, Fig. 6.24-27), containing diarylamino and/or triphenylamino moieties in different *meso*-positions. YD14 and YD17 exhibit a power conversion efficiency of 7%. New donor  $-\pi-$  acceptor porphyrins with cyanoacrylic acid moiety as electron acceptor were also synthesized [148]. Mathew and co-workers reported a new molecularly engineered porphyrin dye, coded SM315, which exhibited a remarkable power conversion efficiency of 13% [149].



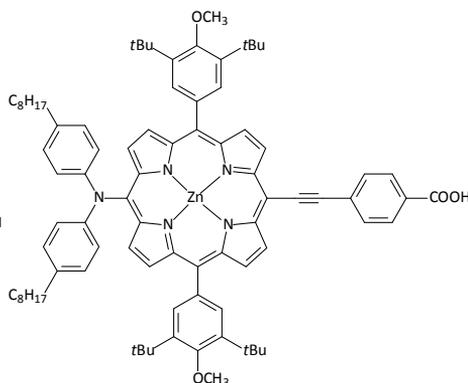
**FIGURE 6.24**  
The structure of YD14



**FIGURE 6.25**  
The structure of YD15



**FIGURE 6.26**  
The structure of YD16



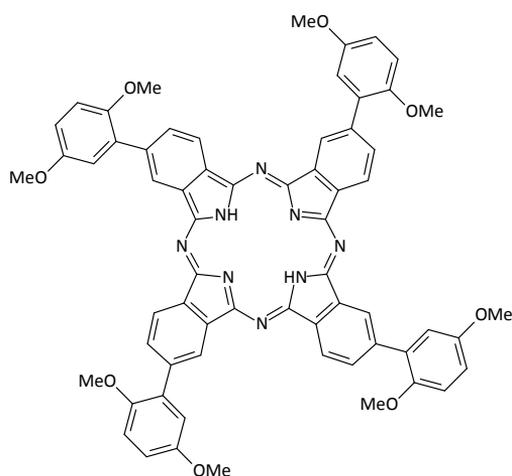
**FIGURE 6.27**  
The structure of YD17

### Phthalocyanines

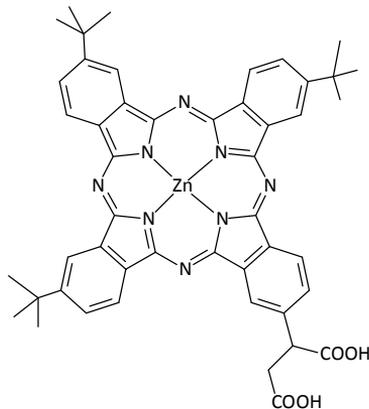
Phthalocyanine derivatives, which have a similar structure to porphyrin (Figs. 6.28 - 29) are used as sensitizers in DSSCs due to their favorable electrochemical, thermal and photochemical properties [150, 151]. However, these sensitizers have two important drawbacks:

- Very poor solubility;
- Pronounced tendency to aggregate on the TiO<sub>2</sub> surface [104].

To date, several phthalocyanines dyes have been synthesized and used as sensitizers in DSSC: Zn-free (Fig. 6.28), phthalocyanines with ester groups [150], unsymmetrical zinc phthalocyanines [152] (Fig. 6.29), metal phthalocyanines containing axial ligands with a carboxyl group [153].



**FIGURE 6.28**  
Zn-free phthalocyanine with methoxy group

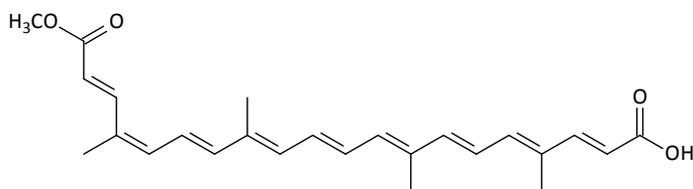


**FIGURE 6.29**  
Zn (II) – phthalocyanine with carboxyl groups

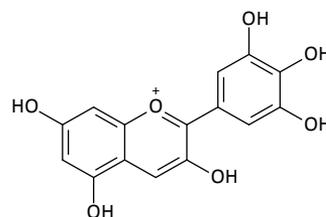
### Natural dyes

Natural dyes and their derivatives are attractive solutions as sensitizers for environmentally friendly DSSCs, since they are usually non-toxic, fully biodegradable, renewable, easily available and cost effective [154]. As a consequence, a lot of efforts have been devoted to find appropriate natural dyes yielding high energy conversion efficiency [155-158]. Natural dyes can be easily extracted from fruit, leaves, flowers and algae. The availability of their source and extraction method is reflected in their reduced price [107]. In many cases, combination of dyes work more efficiently so it is still debatable how much purification of the plant extract is needed.

Different vegetable dyes, like carotenoids [159, 160], betalains [157, 161], anthocyanins [162-165], chlorophylls [166-168], were used as sensitizers in DSSCs. Bixin, an apocarotenoid found in annatto (Fig. 6.30) [169] and delphinidin (Fig. 6.31), a primary plant pigment which belongs to the class of anthocyanidins [170], are other two well-known examples of natural dyes employed as sensitizers.



**FIGURE 6.30**  
The structure of bixin



**FIGURE 6.31**  
The structure of delphinidin

Unlike the metal complexes, porphyrins, phthalocyanines and synthetic organic dyes, for which the desired photoelectrical and absorption properties can be tuned by changing the ligands and/or the central metal atom or by functionalization, the process of tuning is more difficult for vegetable dyes. For this reason, the concentration of the dye, the pH and type of electrolyte, the type and size of the metal oxide semiconductor and the soaking time become important parameters in order to achieve superior solar power conversion [171-173]. Despite the benefits listed above, the efficiency of the DSSCs which use natural dyes as sensitizers is still by a factor of 3–4 lower than those employing synthetic dyes.

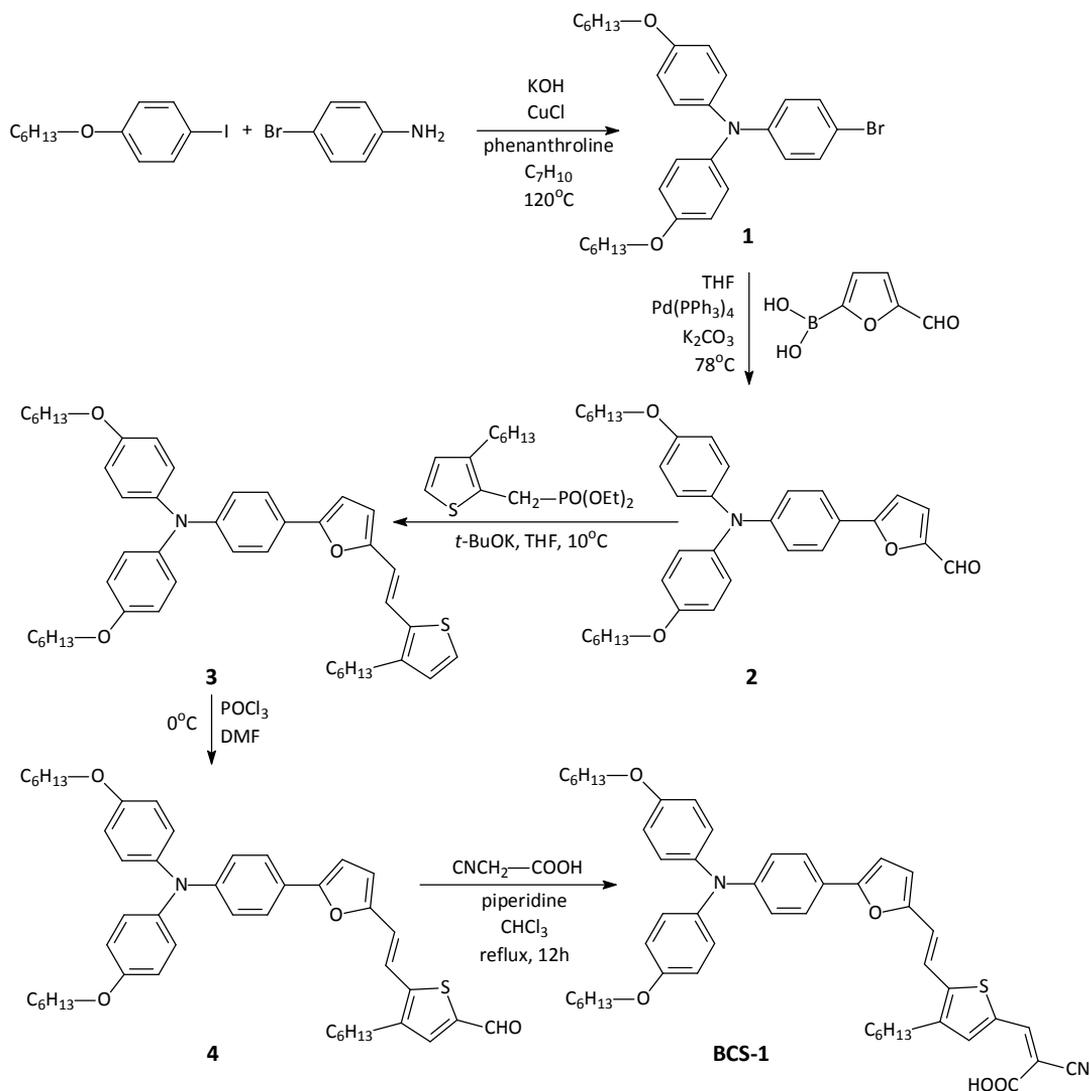
### Synthetic dyes

Organic dyes are a viable alternative to noble metal complexes sensitizers and exhibit many attractive features:

- Tunable electrochemical and optical properties through chemical synthesis and appropriate functionalization;
- The molar extinction coefficient of organic synthetic dyes are substantially higher than those of metal complexes;
- Versatile and relatively low-cost synthesis;
- Less environmental issues compared to metal complexes [174-176].

Many of these sensitizers are of push–pull design featuring an electron-rich (donor-D) and an electron-poor (acceptor-A) moiety, connected through a  $\pi$ -conjugated bridge (D- $\pi$ -A). Coumarine

[177-181], triphenylamine [182 -185], indoline [186, 187], carbazole [188 -190] are widely used as donor moieties in the synthesis of dyes, while cyanoacrylic acid acts as electron acceptor unit. An example of a synthesis employing an organic dye (dihexyloxy-substituted triphenylamine-based organic dye, coded BCS-1) is depicted in Fig. 6.32, below [191]:



**FIGURE 6.32**

Synthesis route of BCS-1 organic dye

**1:** 4-bromo-N,N-bis(4-(hexyloxy)phenyl)aniline;

**2:** 5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)furan-2-carbaldehyde;

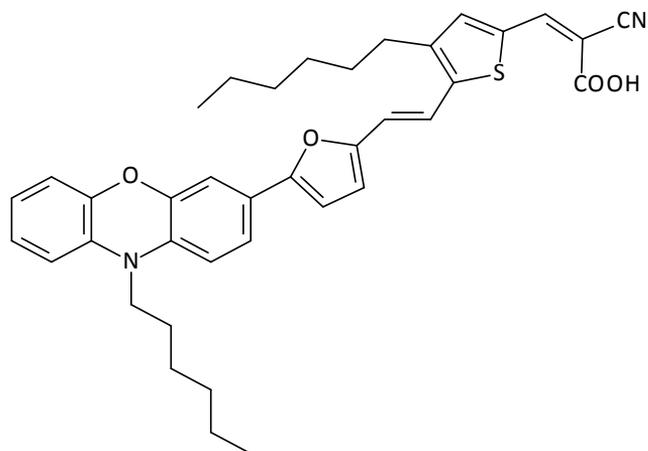
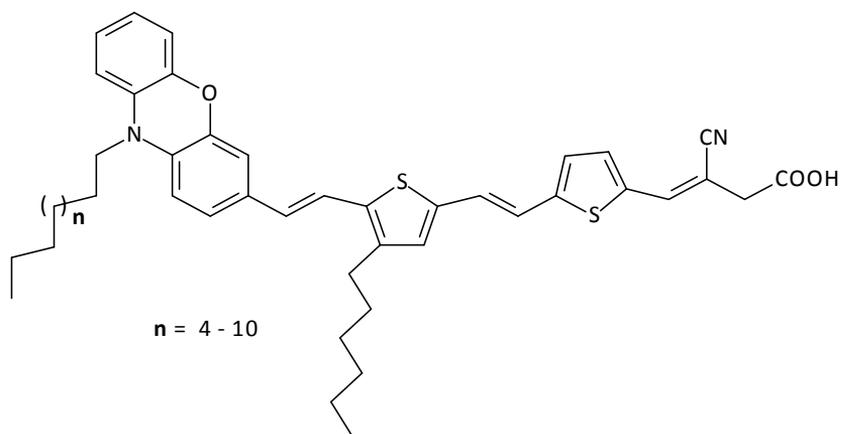
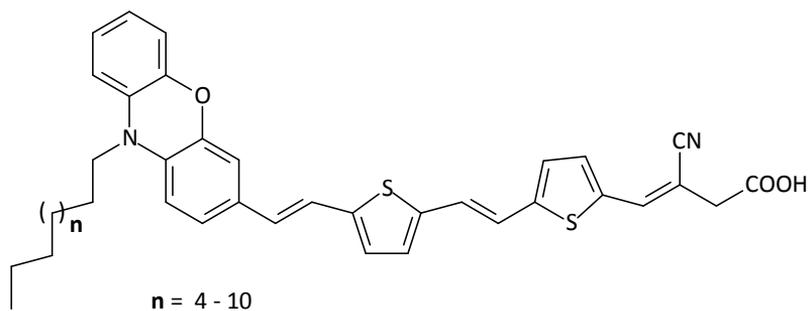
**3:** N,N-bis(4-(hexyloxy)-phenyl)-N-(4-(5-(2-(3-hexylthiophen-2-yl)vinyl)furan-2-yl)phenyl)-aniline);

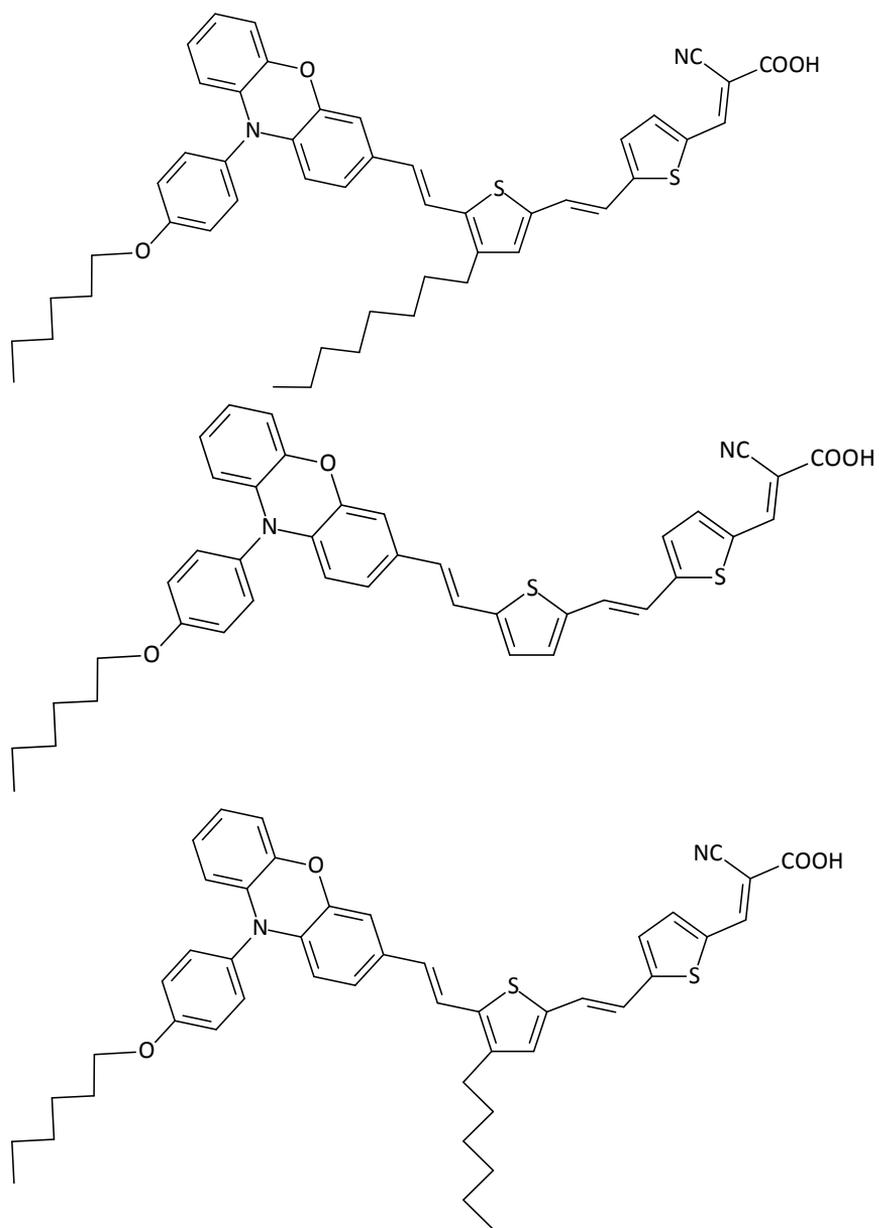
**4:** 3-[5-[2-(5-[4-[bis(4-hexyloxy-phenyl)-amino]-phenyl)-furan-2-yl)-vinyl]-3-hexyl-thiophen-2-yl]-

2-carbaldehyde; **BCS-1:** 3-[5-[2-(5-[4-[bis(4-hexyloxyphenyl)-amino]-phenyl)-furan-2-yl)-vinyl]-

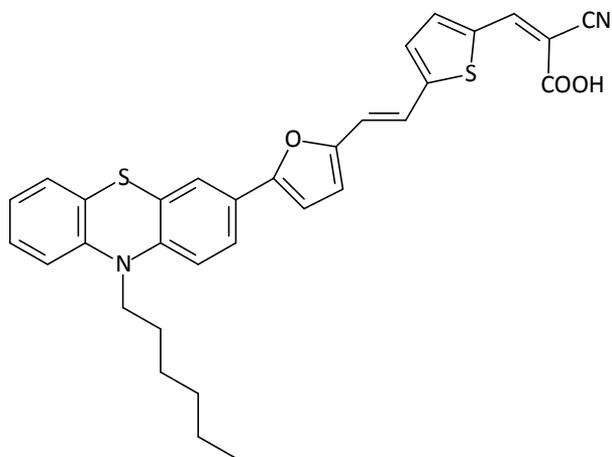
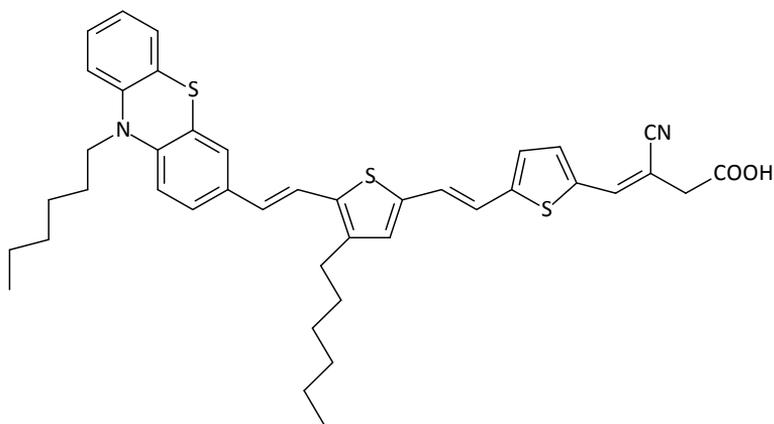
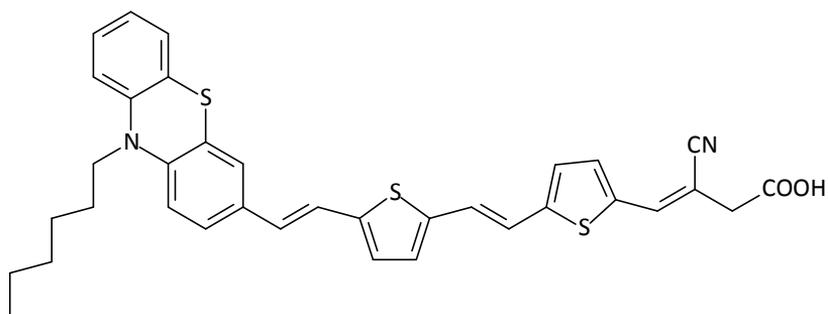
3-hexyl-thiophen-2-yl]-2-cyanoacrylic acid

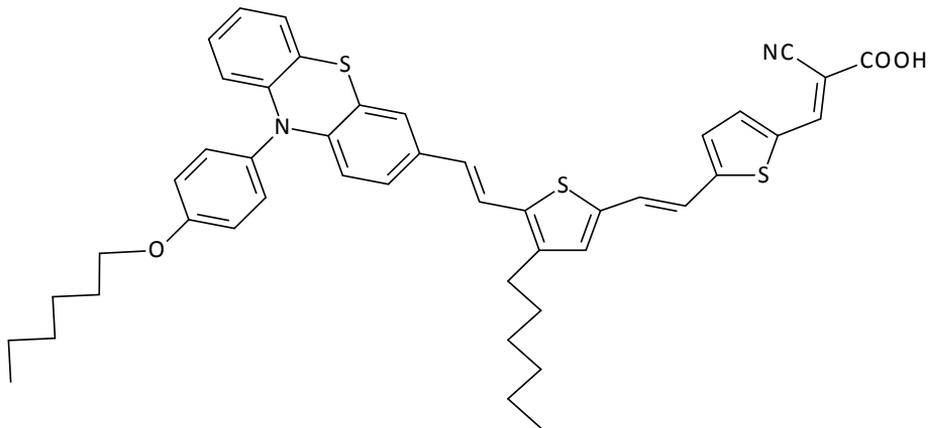
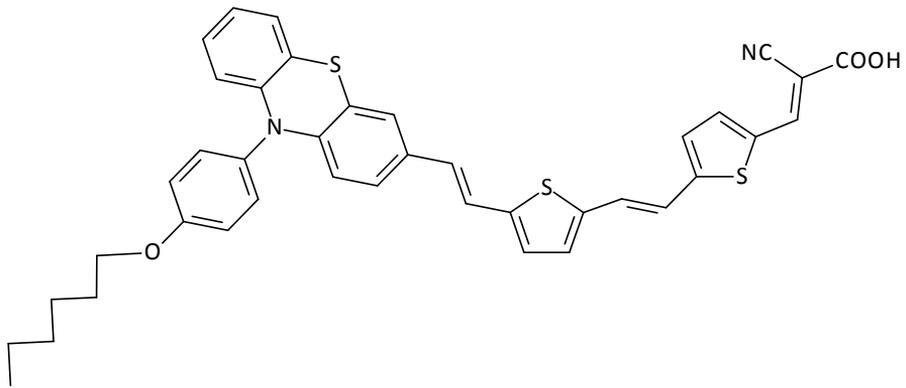
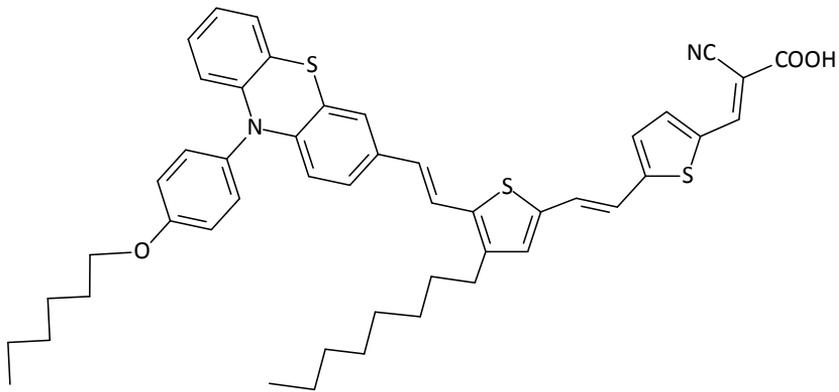
Besides the groups of organic dyes discussed above, other types of donor electron moieties, such as phenoxazines (Fig. 6.33) [192, 193] and phenothiazines [194] (Fig. 6.34), were used in the design of sensitizers.

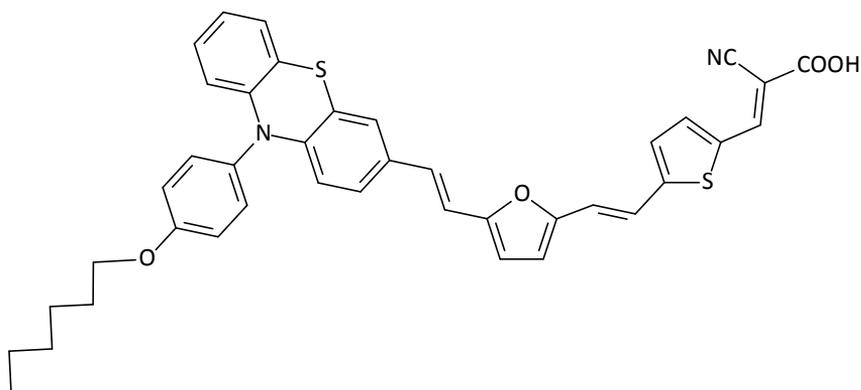


**FIGURE 6.33**

Different structures of dyes employing phenoxazine unit as electron donor moiety

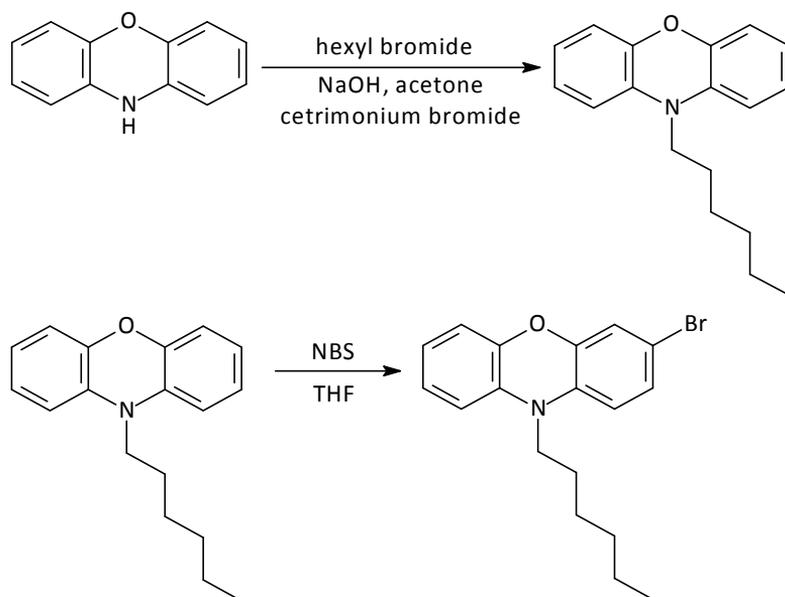


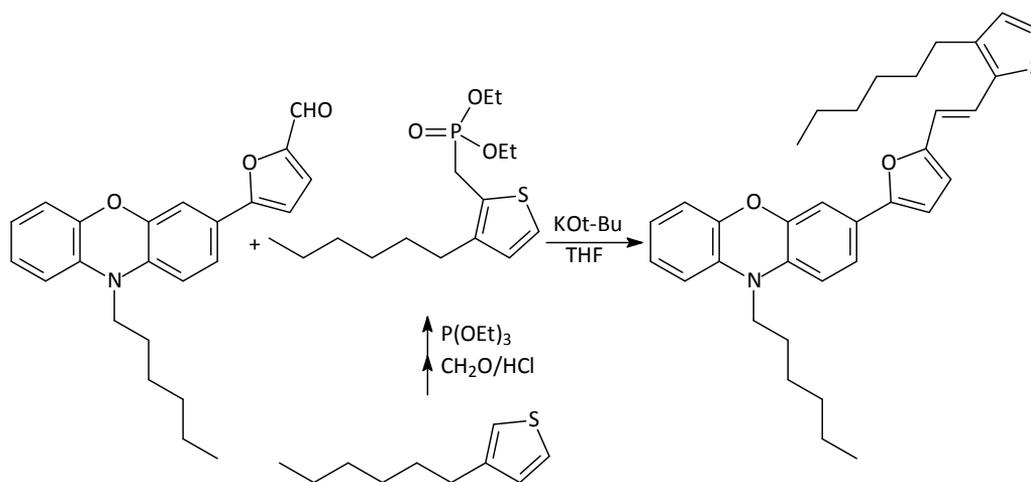
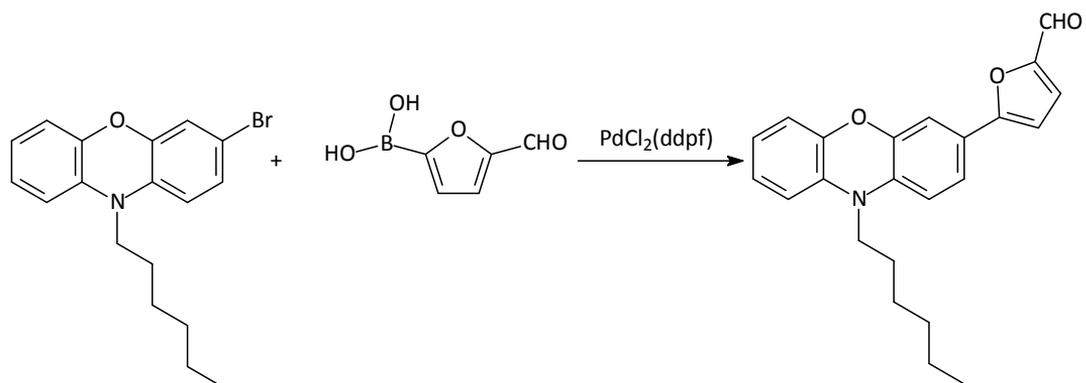


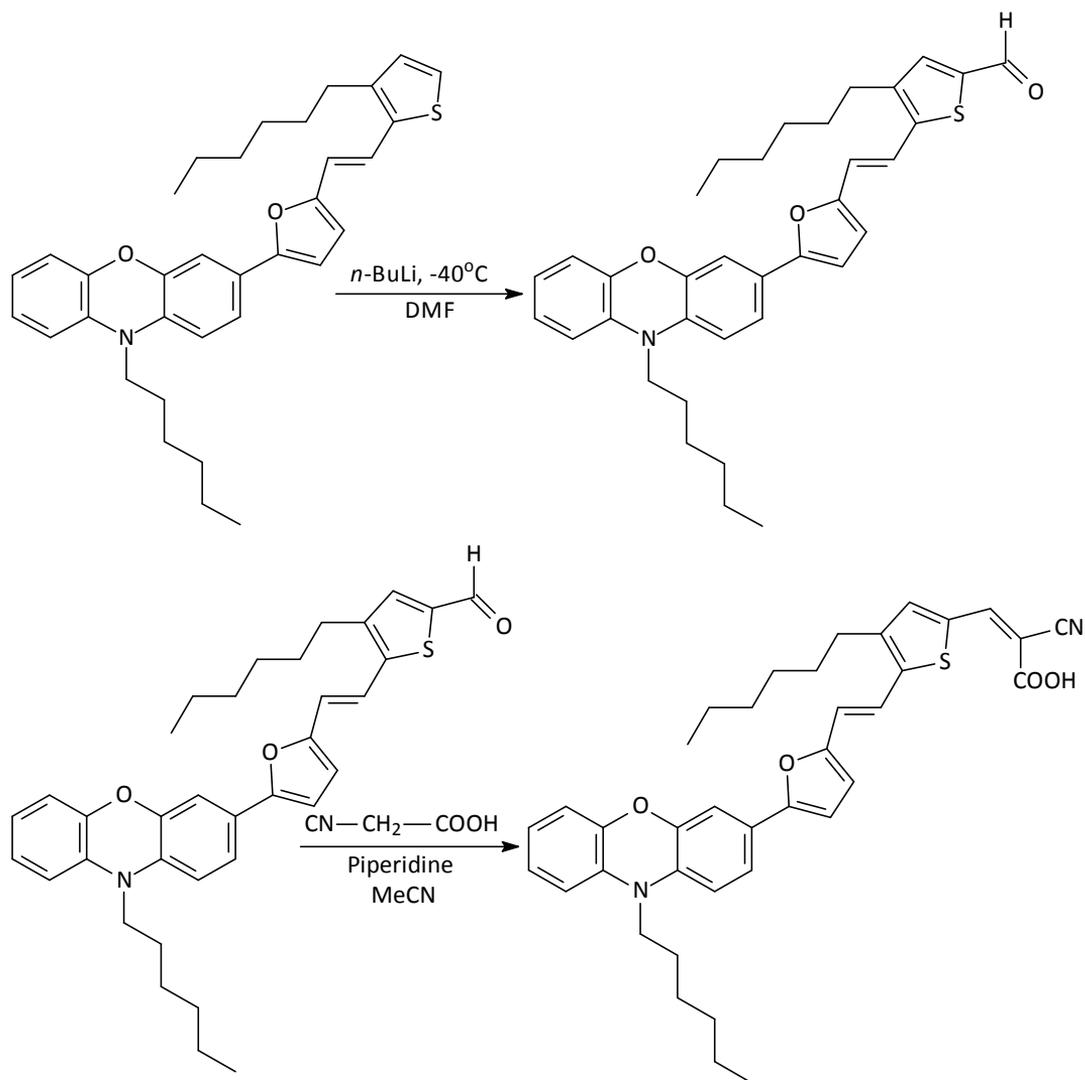
**FIGURE 6.34**

Different structures of dyes employing phenothiazine unit as electron donor moiety

An example of synthesis of a dye using phenoxazine unit as electron donor moiety is presented in Fig. 6.35, below [193].





**FIGURE 6.35**

Synthesis of a dye employing phenoxazine unit as electron donor moiety

The structure of the conjugated bridge can contain different functional units, such as phenylenevinylene, benzothiadiazole, thiophene, dithienothiophene, furane, EDOT, selenophene [174, 195]. The immobilization of the adsorbing sensitizers on the surface of the semiconducting metal oxide enables electron injection and thus has a paramount importance for building an efficient DSSC [111].

Carboxylic acid ( $-\text{COOH}$ ) is the most commonly used anchoring group for sensitizers [196]. Actually, all the dye structures depicted above contain cyanoacrylic acid, which acts as anchoring and electron acceptor unit. Functional derivatives of carboxylic acid, like acid chlorides, ester, anhydrides, amides, have also been reported as anchoring groups. Examples of other anchoring groups are phosphonic acid [197], silanol [198], hydroxamate [199], pyridine, tetracyanate,

perylene, 2-hydroxybenzonitrile, 8-hydroxyquinoline, pyridine-N-oxide, BON acid, catechol, hydroxamate, sulfonic acid, acetylacetonate, rhodanine, and salicylic acid substituents [111, 200]. The appropriate design of the sensitizers has a crucial importance for the overall efficiency of the DSSC. In the last years, a lot of effort was dedicated to understand the connection between the efficiency of the solar cell and the global hardness of the sensitizers [201-203].

### ***Wideband-gap semiconductors***

Titania is by far the metal-oxide most commonly used as n-type semiconductor in DSSCs. It has been widely accepted that the efficiency of the electron injection and light harvesting in DSSCs strongly depends on the morphology, size and structure of  $\text{TiO}_2$ . Thus, different types of  $\text{TiO}_2$ , such as nanotubes [204], nanorods, nanowires, nanoparticles, nanobowls, nanosheets [104], mesoporous [205] were used as photo anodes in order to improve the performances of DSSCs. Hydrolysis of a titanium (IV) alkoxide in acid or base catalysis, followed by hydrothermal growth and crystallization, is the most widely used synthesis method for  $\text{TiO}_2$  employed in DSSCs [206]. Recently, it has been suggested that capability of a sensitizer to inject electrons into a DSSC  $\text{TiO}_2$  anode depends on the surface crystallographic plane of the  $\text{TiO}_2$  nanoparticles. For some chromophores, at least, the short circuit current ( $I_{sc}$ ) can be maximized when the  $\text{TiO}_2$  nanoparticulate layer comprised in a DSSC has a higher percentage of {100} facets relative to {101} and {001} facets [207].

ZnO is another metal oxide semiconductor used in DSSC applications. Highly crystalline wurtzite structures, such as nanoparticles, tetrapods, nanorods, nanotubes, nanoflowers, nanosheets, nanowires, were reported as n-type semiconductor for DSSC technology [104, 208, 209]. At the same time,  $\text{SnO}_2$  [210],  $\text{SrTiO}_3$  and  $\text{Nb}_2\text{O}_5$  [211] were also shown to successfully act as semiconductors in DSSCs.

### ***Electrolytes and hole conductors***

The electrolyte is one of the most important components in DSSCs technology. It acts as a medium to transfer electrons from the counter electrode to the oxidized dye during DSSC operation [212]. The solvent used for the design of redox electrolytes must fulfill the following criteria:

- It should be a suitable solvent for redox couple components and different additives;
- It should exhibit chemical, thermal, optical and interfacial stability;
- It should have low viscosity;
- It should be compatible with the sealing material to avoid losses by evaporation [104, 213];
- It should not cause desorption and degradation of the sensitized dye;
- It should exhibit low toxicity;
- It should not exhibit absorption in the range of visible light.

Organic carbonates (such as dimethyl carbonate, diethyl carbonate, ethylene carbonate, propylene carbonate), different nitriles (like acetonitrile, valeronitrile, glutaronitrile, 3-methoxy-propionitrile), and protic solvents (such as water, ethanol, N-Methylpyrrolidone) are the most commonly employed solvents for electrolytes in DSSCs. The iodide–triiodide ( $\text{I}_3^-/\text{I}^-$ ) electrolyte has been widely used as redox system because of its favorable properties [214]. Different alternative electrolytes

have been investigated, including Co (II)/Co(III) polypyridyl complex, ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple, Cu(I)/Cu(II) complex,  $\text{Br}^-/\text{Br}_2$  [215-223].

Due to their outstanding properties (high chemical and thermal stability, low vapor pressure, non-flammability and high ionic conductivity), ionic liquids are employed in DSSCs both as solvents and sources of iodide [224-228]. Methyl-hexyl-imidazoliumiodide (MHImI) 1-propargyl-3-methylimidazolium iodide, bis (imidazolium) iodides 1-ethyl-1-methylpyrrolidinium) iodide are some examples of such ionic liquids [229-232].

Additives play an important role in enhancing the performance of DSSCs by modifying of redox couple potential. Examples of additives that have been tested in DSSC include 4-*tert*-butylpyridine, 4-ethoxy-2-methylpyridine, 1-methyl-benzimidazole, different pyrimidines, quinolines, and alkylpyridines [233-235].

An alternative to the iodide/triiodide redox system is an organic and inorganic hole conductors, such as OMeTAD, spiro-OMeTAD, polyaniline, pentacene, CUI, CuSCN, etc. [236-242].

### **Counter electrodes**

The counter electrode (CE) has the role of collecting electrons from the external circuit being used for the regeneration of the electrolyte. Platinum is one of the most popular CE materials due to its high electrocatalytic activity [243, 244]. Other noble metals, like Au and Ag, were also used as counter electrodes. Noble metals-based CE corrosion in liquid electrolyte and their elevated cost are two major concerns. For this reason, other possible replacing materials have been extensively studied:

- Carbon-based materials, such as porous carbon, carbon nanotubes (CNTs), graphene, or composites: porous carbon & CNTs [132], CNTs & graphene nano-ribbons [245-247];
- Sulfides, like  $\text{CoS}_2$ ,  $\text{CuInS}_2$ ,  $\text{Cu}_2\text{ZnSnS}_4$  [248];
- Conductive polymers, such as poly (3,4-ethylenedioxythiophene polypyrrole and polyaniline) [249].

## **Comparison between QDSSCs and DSSCs, conclusions and future prospects**

Dye sensitized solar cells and quantum dot sensitized solar cells are two emerging technologies in the field of solar cell research. A comparison performed between materials used for manufacturing these types of solar cells and performance reveals some interesting aspects. In this section, the main aspects of the technologies will be briefly summarized and compared.

### **Wide-bandgap semiconductor**

$\text{TiO}_2$  and ZnO are widely used in both QDSSCs and DSSCs. Nanotubes, nanorods, nanowires, nanoparticles, nanobowls, nanosheets, mesoporous are typical nanostructures.

### **Sensitizer**

Quantum dots act as sensitizers in QDSSCs. Many types of QDs, as CdS, CdTe or core-shell semiconducting nanocrystals ( $\text{CdS}/\text{HgS}$ ,  $\text{CdS}/\text{CdSe}$  and  $\text{ZnSe}/\text{CdSe}$ ) were employed. Their synthesis is versatile, low-cost and can adjust bandgaps over a broad spectral range. One of the most used

method to anchor the QDs to the surface of TiO<sub>2</sub> is to functionalize it with bifunctional linkers. As indicated above, the HSAB principle can be a valuable tool in order to choose the right QDs - bifunctional ligand tandems.

Metal complexes, porphyrins and phthalocyanine dyes, synthetic metal-free organic dyes act as light absorbers for DSSCs. Except natural dyes, all the dyes can be properly functionalized in order to tune the optical and electrochemical properties of sensitizers. At the same time, their synthesis versatile and relatively low-cost.

As opposed to QDs, the molecular structures of dye include the anchors for immobilization to TiO<sub>2</sub>. The advantage of QDs over traditional dyes is their very high extinction coefficients.

### Electrolyte/ hole transport

The most commonly used electrolyte in QDSSCs is sulfide/polysulfide ( $S^{2-}/S_n^{2-}$ ) aqueous solution, while for DSSCs is the redox couple iodide–triiodide ( $I_3^-/I^-$ ). For both technologies, a lot of attention is paid for finding solid materials, suitable to replace the liquid electrolyte.

### Counter electrode

Platinized layers are usually employed for both QDSSCs and DSSCs.

Low efficiency (11, 9 % is the maximum measured efficiency for DSSCs, while for QDSCs top value is 11.6%) and low stability are the most important challenges for the commercial deployment of both technologies. These parameters depend on many parameters. A trade-off between them need to be performed to enhance the performance of both QDSSCs and DSSCs.

## Acknowledgements

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