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Vegetable-based Dye-Sensitized Solar Cells

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Abstract

There is currently a large effort in improving the performance of low cost renewable energy devices. Dye-sensitized solar cells (DSSCs) are emerging as one of the most promising low cost photovoltaic technologies, addressing "secure, clean and efficient solar energy conversion". Vegetable dyes, extracted from algae, flowers, fruit and leaves, can be used as sensitizers in DSSCs. Thus far, anthocyanin and betalain extracts together with selected chlorophyll derivatives, are the most successful vegetable sensitizers. This review analyses recent progress on the exploitation of vegetable dyes for solar energy conversion and compares them to the properties of synthetic dyes. In this paper, we provide an in depth discussion on the main limitation of cell performance *e.g.* dye degradation, effective electron injection from the dye into the conduction band of semiconducting nanoparticles, such as titanium dioxide and zinc oxide, outlining future developments for the use of vegetable sensitizers in DSSCs. We also discuss the cost of vegetable dyes and how their versatility can boost the advancement of new power management solutions, especially for their integration in living environments, making the practical application of such systems economically viable. Finally, we present our view on future prospectives in the development of synthetic analogues of vegetable dyes as sensitizers in DSSC.

Keywords: Renewable energy, DSSC, solar energy, vegetable dyes, solar module, scaling-up and cost.

1. Introduction

Increasing concerns about the energy crisis, climate change, decreasing availability of fossil fuels and environmental issues are motivating research of sustainable and renewable energy resources[1,2,3,4]. The key for the success of this goal lies in the development of efficient energy conversion and storage devices. Energy management, used to decouple the timing of generation and consumption of electric energy, is also fundamental for cost reduction and/or increasing income from electricity and heat generation.

Renewable energy has been estimated to be half of newly installed electric capacity worldwide in 2010 and becoming progressively more important with a total of 20.8% of the current global electricity production[5], with a prediction to reach 25% by 2018[5].

The sun can provide the ultimate solution to the challenge of a sustainable energy supply. In one hour, the earth receives 13.6TW from the sun, more than what we currently consume in a whole year (13TW). Photovoltaic (PV) cells convert sunlight into electricity[6,7]. They allow power to be produced near the end user, avoiding transmission losses and costs, and are gaining interest for applications in many sectors of daily life, from mobile devices[8] to building integrated PV[9,10,11,12].

Current PV technology is dominated by silicon (Si) solar cells[13], with energy conversion efficiency (η), see sect. 3, up to~24.7%. [14] Despite significant development over the past decades[15], high cost limits their wide-spread use. The purification to metallurgical-grade Si has high energy demand and creates significant amounts of hazardous by-products[16]. Thin film solar cells such as amorphous silicon (a-Si),[17] cadmium telluride (CdTe)[18], copper indium gallium diselenide (CIGS)[19] and thin film crystalline Si[20] are known as second generation PVs. The development of thin film solar cells has been driven by the potential of manufacturing costs reduction. However, for example, the less expensive Si alternative, a-Si modules suffer the Staebler–Wronski (SW) degradation[21]. In a typical a-Si solar cell the η is reduced by up to 30% in the first 6 months as a result of the SW degradation[22]. The effect is temperature dependent so that performance of PV cells tends to recover some in the summer months and drop again during winter time[22]. This light induced degradation is the major disadvantage of a-Si as a PV material[23].

The third generation PV cells aim to achieve similar or higher η than Si solar cells by using novel light absorbing materials[24,25]. A recent development is the meso-super-structured solar cell,[26] based on an organic halide perovskite (*e.g.* $CH_3NH_3PbX_3$ where X is bromine, iodine, chlorine, or their combination) as photosensitizer,[26,27,28,29] and an organic hole-transport material.[27] Ref. (*27*) reported an efficiency of 15.6% in a meso-super-structured (perovskite) solar cell for an un-optimized device while an efficiency of 20.1% has been recently reported on the NREL Best Research-Cell Efficiency chart and developed at KRICT (Korean Research Institute of Chemical Technology)[30]. Nevertheless, perovskites may not satisfy sustainability requirements, due to their lead content. Organic PV cells can be manufactured economically compared with Si cells, for example by a roll-to-roll process[31] or other coating techniques[32]. Another class of new PV cells, known as *dye-sensitized solar cell* (DSSC)[33], relies on the dye-sensitization of the semiconductor band gap[34], and allows reaching η~13% exploiting porphyrin sensitizers and graphene nanoplatelets (GNPs) at the counter electrode (CE)[35]. Because of their simplicity and low cost, DSSCs have great potential for large-scale applications, especially when transparency and high η under cloudy and artificial light conditions are needed.

Metal-organic dyes (mostly ruthenium[34,36] and osmium[37] polypyridil complexes) have been used as efficient sensitizers. The preparation routes for metal complexes are often based on multi step reactions involving long, tedious and expensive chromatographic purification procedures.

Contrary, natural dyes and their organic derivatives are ideal candidates for environmentally friendly solar cells, since they are non-toxic, low in cost, renewable and abundant. Thus, the possibility to achieve solar energy conversion exploiting natural pigments have been largely investigated,[38,39,40,41] suggesting a cheap and simple approach based on the chemical and physical processing of these pigments, avoiding any hazardous waste by-products. In particular, vegetable pigments can be easily extracted from fruit, leaves, flowers and algae, see Fig. 1, and used in DSSCs [38,39,40,41,42,43,44,45,46.47,48,49] since 1993, when Ref. 38 clarified the photo-electrochemical properties of chlorophylls (from the Greek "*chloros"* = green and "*phyllon"* = leaf) in DSSCs achieving η=2.6%. The same group[47] has also exploited anthocyanin (from the Greek *anthos* = flower and *kianos* = blue), a class of water-soluble, vegetable pigments extracted from flowers, *e.g.* malvaceae, anthurium, and leaves, *e.g.* Norway maple, as DSSC sensitizers. Ref. 47 extracted anthocyanins from California blackberries, achieving a η of 0.56%. Apart from the mere η value achieved, more importantly, Ref. 42 initiated an intense research activity for the exploitation of natural pigments in DSSCs. Betalain (from the Latin Beta vulgaris, the beet from which betalains were first extracted) pigments represent another class of vegetable dyes that have been exploited in DSSCs[39,40,41] achieving η up to 2.7%.[50] These pigments are present in different parts of plants, in particular in caryophyllales[51], including flower petals, fruits, leaves, stems and roots.

In this review we will present an in-depth analysis of the most significant advances made on the use of vegetable dyes in DSSCs. In section 2 we briefly highlight the device structure together with the analysis of the key component parameters and working principle of DSSCs, in section 3 we introduce the main figures of merit (FoM), section 4 is dedicated to a brief overview on inorganic and organic dyes to contextualise the use of vegetable dyes in DSSCs. In section 5 we focus on an in depth discussion of vegetable dyes, in section 6 we introduce synthetic analogues of anthocyanins, in sect. 7 we analyse the scaling up perspective and the associated costs, and finally in section 8 we outline the aspects for future development.

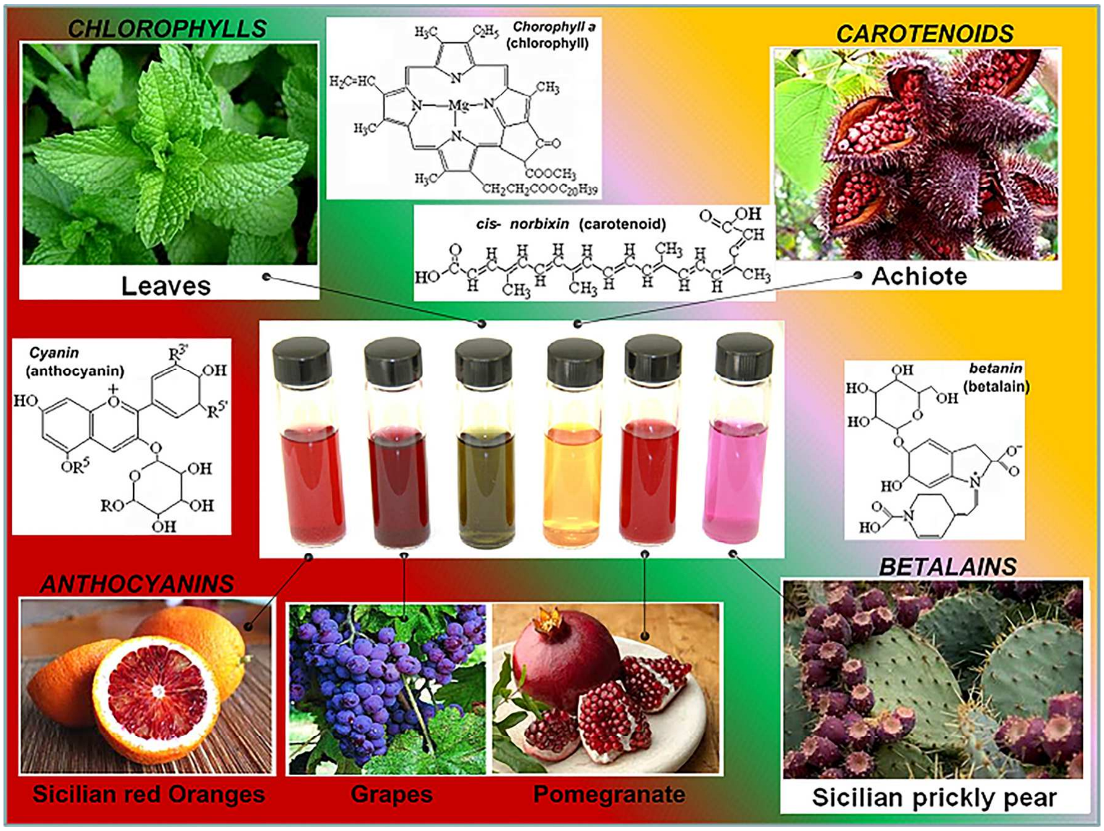


Fig. 1 *Dyes extracted from chlorophylls, anthocyanins, betalains and carotenoids exhibiting coulors covering the entire visible part of the electromagnetic spectrum. In the figure are also shown the pictures of the dyes and the molecular structures of chlorophyll a, cyanin (anthocyanin), betanin (betalain) and cis-norbixin (carotenoid).*

2. Device structure, key component parameters and working principle

Dye-sensitized solar cell is a new “type” of photo-electrochemical solar cell, which concept trace back to Becquerel’s works on PV effect almost two centuries ago[7]. A typical DSSC (see Fig. 2) is assembled with a sandwich-type approach, placing a nanocrystalline mesoporous film sensitized with a dye molecule, an electrolyte solution containing a redox system, and a catalyst coated onto a conductive substrate, usually made with a transparent conductive oxide (TCO) on glass[33]. The most widely investigated TCO for DSSC are the semiconductor-based ternary compound fluorine-doped tin oxide (FTO)[52] and indium tin oxide (ITO).[53,54] The latter is the widest used transparent conductor (TC) in many other optoelectronic applications such as touch screens and displays[55]. Unfortunately, ITO suffers severe limitations: an ever-increasing and fluctuating cost[56] due to indium scarcity, although this issue is still debated[57], processing requirements[58], difficulties in patterning[58,59] and a sensitivity to both acidic and basic environments.[55,65] Although, many other TC materials have also been proposed as window electrode for DSSCs such as doped oxide-based thin films (ZnO:Al (AZO),[60] and ZnO:Ga (GZO)[61]), metal-oxide (ZnS/Ag/ZnS[62], ZnO/Ag/ZnO,[63] and

ZnO/Cu/ZnO[64]), etc.[59], FTO is the reference TCO in DSSCs because it has the highest work function (4.9eV vs 4.8eV of ITO) [65], best thermal stability, mechanical and chemical durability, associated with the least toxicity and most of all the lowest cost with respect to all the aforementioned materials[65]. Carbon-based nanomaterials[66], *e.g.* carbon nanotubes[67] and graphene[68,69] have also been proposed as TC electrodes. However, the performances, *i.e.* sheet resistance, *Rs*, and transmittance, *Tr*, of the current carbon-based TC are below the requirement for PV application, *i.e.* Rs=10Ω/cm^2 and Tr= 90%[70]. In addition, DSSCs exploiting graphene-based TC achieved so far[71] unsatisfactory η values, thus more work is needed to improve *Rs* and *Tr* of these materials before they can be fully exploited as TC in DSSCs.

Commonly, the photoanode consists of a high porosity nanocrystalline nanoparticles (10 to 20nm diameter) *e.g.,* wide band gap semiconductor (usually the n-type semiconductor titanium dioxide - TiO_2- with a bandgap of 3.2 eV). Other nanoparticles such as Zinc Oxide (ZnO)[72] or hybrid materials *e.g.* TiO_2/ZnO[73] have been proposed as scaffold for the photoanode, but with lower performances, *i.e.* η, with respect to the ones achieved with TiO_2 nanoparticles[33]. The mesoporous photoanode is sensitized with a self-assembled layer of dye molecules (photosensitizer) anchored to the semiconductor surface.[33,74] This represents the main difference with respect to the conventional Si-solar cells, where both light absorption and the generated charge carrier transport are carried out by the same material, *i.e.* Si[13]. Contrary, in DSSCs the functional element responsible for light absorption (dye molecules) is separated from the charge carrier transport material itself[75]. The photosensitizer acts as an electrons pump, *i.e.*, absorbs the visible light, pumps an electron into the semiconductor, and accepts an electron from the charge mediator and then repeats the cycle again and again.[33] To fulfil such requirements the dye must necessary possess the following properties:

i) its absorption spectrum should cover a broad range of wavelengths ranging from the visible to the near-IR region of the solar spectrum,

ii) its molar extinction coefficient (ε, $M^{-1}\cdot cm^{-1}$) must be as high as possible to enable efficient light harvesting.

Furthermore, in order to ensure both efficient electron injection into the photoanode and efficient regeneration process it is indispensable that:

***iii*)** the lowest unoccupied molecular orbital (LUMO)[76] level of the dye should stay energetically above the CB edge of the semiconductor while,

iv) the highest occupied molecular orbital (HOMO)[76] of the dye must be below the energy level of the redox mediator to allow efficient regeneration of the oxidized dye[77,78] (see Fig. 2).

v) the electron injection pathway is optimized when the dye is strongly anchored onto the semiconductor surface.

Polypiridines complexes of transition metals such as ruthenium, [34,36,79,80,81,82,83,84,85,86] osmium,[37,79,87] cobalt,[88] iron,[89] copper,[90] rhenium,[91] as well as a large variety of metal free organic-dyes, such as coumarin,[92,93] triarylamine,[94,95] tetrahydroquinoline,[96,97] indoline,[98,99,100] squaraine,[101,102] and others such as phtalocyanins[103,104,105,106,107] and porphyrins[108,109,110,111] as well as vegetable[38,39,40,41,42,43,45,46,47,48,49] and artificial bio-inspired dyes[112] have been used as sensitizers in DSSCs.

The as-prepared photoanode is then faced to the CE with the liquid electrolyte solution containing a redox couple (*e.g.* iodide/triiodide, I^-/I_3^-) placed in between[33]. In the first nanostructured DSSC, a LiI/I_2 redox couple dissolved in acetonitrile (AcN) was used achieving a η of 7.1%[33]. The use of AcN[113] is intrinsically related to its chemical stability and[114] low viscosity (0.361mPa·S).[115] Moreover, AcN does not absorb light in ultraviolet and visible region of the electromagnetic spectrum, characteristic necessary for photochemical and photoelectrochemical experiments.[116] Furthermore, AcN is a well-known polar solvent (dielectric constant is ~36 at room temperature -RT-).[117] Moreover, solvent polarity strongly affects the electron transfer and the competing energy transfer (see sect. 6), key processes for photochemistry and photoelectrochemistry.[118]

Thus, thanks to the aforementioned properties,[118] AcN became a common solvent for DSSC applications, mostly at the laboratory scale.[222] Nevertheless, AcN has also some drawbacks such as toxicity[119] and low boiling point (78°C).[120] The latter is a practical disadvantage for long term DSSC endurance due to the leakage of the solvent due to volatility.[121]

With the aim to overcome some of the aforementioned critical factors (*e.g.* toxicity, volatilization, leakage), alternative nitrile liquids such as metoxy acetonitrile (MAcN),[118] 3-methoxypropionitrile (MePN),[118] glutarinonitrile (GN),[122] ethyl[123] and butyl[124] cianine, as well as cyclic ester (*e.g.*, ethylene[125] and propylene carbonate[126] or lactone solvents such as γ-butyrolactone (GBL)[127] have been widely investigated. Ionic liquids[128], characterized by electrochemical stability together with high viscosity[129] (*e.g.* ~30mPas for [Bmin]-[Tf2N])[32] and low vapour pressure (*e.g.* 100 pPa at RT for $[C_{4mim}][PF_6]$[130] compared with 3 kPa for H_2O[131]) have emerged as a further promising alternative for liquid solvents.

However, the high viscosity and low ionic mobility of ionic liquids negatively affect the η of the ionic liquid-based DSSCs because they limit the diffusion rate of the iodide and tri-iodide. To solve this limitation, mix ionic liquids with high boiling solvents such as sulfolane has been recently proposed.[132] DSSCs based on these new electrolyte formulations have shown excellent stability (exceeding 2320 h under full sunlight at 60 °C).[132]

In the last decade, fervent research activity has been devoted to replace the liquid electrolytes by *solid-state*[133,134,135,136] or *quasi-solid-state electrolytes*[137,138]. Commonly, a *quasi-solid-state* electrolyte is constituted by an organic polymeric matrix incorporating a liquid electrolyte to form a stable gel network structure via physical or chemical interactions[139,140,141,142]. Owing this sol-gel character quasi-solid-state electrolytes possess both the cohesive properties of solids[143] (the work of cohesion, *i.e.* the energy per unit area required to separate two flat surfaces from contact)[144] and the diffusive transport (*i.e.,* high ionic conductivity) characteristics of liquids, overcoming the disadvantage of volatility of liquid electrolites favouring the wetting of the mesoporous dye-coated nanocrystalline TiO_2 film by the electrolyte and thus favouring the regeneration of the oxidized dye molecules.[145] A η of 6.1% was achieved for a DSSC using a ruthenium dye (Z907, see sect. 4.1) and a quasi-solid-state gel electrolyte system based on 1,3:2,4-di-O-dimethylbenzylidene-D-sorbitol(DMDBS)/3-methoxypropionitrile[140].

Concerning *solid-state* electrolytes, currently, there are two main classes investigated in DSSC applications. One is based on a solid compound (*e.g.,* polyethylene oxide) containing I^-/I_3^- redox couple[146,147,148], while the other makes use of a hole transport material (HTM), such as the *spiro*-OMeTAD (2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene)[123,149,150]. Wang *et al.*,[147] reported a η=6.7% using a N-methyl-N-butylpyrrolidinium iodide ($P_{1,4}I$)-doped succinonitrile electrolyte containing I^-/I_3^- redox couple. A solid-state electrolyte containing I^-/I_3^- by introducing TiO_2 nanoparticle into poly(ethylene oxide) was used to fabricate a DSSC by Stergiopoulos *et al.,*[146] obtaining η=4.2%. More recently, Ref. 151 achieved a η of 9.48% exploiting N719 dye and a structurally interconnected block copolymer, prepared by the oligomerization of poly(oxyethylene)-segmented diamine and 4,40-oxydiphthalic anhydride, followed by a curing to generate amide-imide cross-linked gels.

Although the first attempt to use spiro-OMeTAD, reported by Bach *et al.* in 1998[149], resulted in low η (0.74%), the development in the subsequent years of this solid electrolyte permitted to achieve η up to 3.2%.[150] More recently,[152] chemical doping of *spiro*-OMeTAD-based DSSC by tris (2-(1H-pyrazol-1-yl)pyridine)Co(III), (FK102), has allowed to achieve η=7.2%.

Several other materials such as CuSCN[153], poly(3-hexylthiophene) (P3HT)[154], polyaniline[155] and poly(3,4-ethylenedioxythiophene) (PEDOT) [135], have been investigated as HTM for DSSCs with η=4.5% for P3HT and (6,6-phenyl C61-butyric acid methylester (PCBM))[156]. Recently, Kanatzidis and co-workers[157] reported an all-solid state inorganic solar cell constitutes by a p-type direct band-gap semiconductor $CsSnI_3$ (doped with SnF_2) as HTM, nanoporous TiO_2 and the dye N719 achieving η=10.2%. This result was obtained with a solvent free DSSC, thus overcoming the issue of electrolyte leakage, solvation of the dye by the electrolyte solvent and, at the same time preventing the corrosion of the catalyst by the electrolyte.[157]

The third main component of DSSCs is the CE. The role of the CE in a DSSC is twofold, first it back transfers electrons arriving from the external circuit to the redox system[33], second it catalyzes the reduction of the oxidized charge mediator.[33] The key requirements for CEs are low charge-transfer resistance –R_{ct}- (*i.e.,* the electrode-electrolyte interface resistance), high exchange current density (*i.e.,* the rate of electron transfer between electrolyte and electrode), and high specific surface area (SSA). Commonly, CEs are made of a few nanometres thick platinum (Pt) layer, acting as catalyst,[33] deposited onto TCO or, in the case where transparency is not an issue, on highly conductive and reflective substrate such as stainless steel[158]. Apart the limiting factors of ITO and FTO discussed above, Pt is costly other than having limited reserves on earth.[159] Moreover, Pt tends to degrade over time when in contact with the I_3^-/I^- liquid electrolyte, reducing the η of DSSCs[*160*]. Thus, the replacement of Pt with low-cost and/or more effective (leading to high η devices) materials is at the centre of on-going research effort. In this context, several groups have used carbon-based nanomaterials as catalyst in CE, such as amorphous carbon,[161] carbon nanotubes (CNTs),[158,162] hard carbon spherules,[163] and graphite.[163] Graphene nanoplatelets,[164] nitrogen-doped GNPs,[165] graphene oxide (GO)[166,167,168] and hybrid structures of GNPs-RGO-CNTs[169,170] with results, *i.e., η*, close to or exceeding the ones based on Pt. Indeed, the new record high of DSSCs (η=13%) has been achieved exploiting GNPs at the CE.[164]

Here below we briefly summarize the working principle of DSSCs, considering TiO_2 as semiconductor oxide and I^-/I_3^- as redox couple. Photo-excitation of the dye results in the injection of an electron in the conduction band (CB) of the TiO_2 with the consequent oxidation of the dye[33]. The cell produces voltage over and current trough an external load connected to the electrodes, see Fig. 2.

The photocurrent yield of a DSSC is the outcome of competitive photo-electrochemical reactions which take place at the semiconductor/electrolyte interface and can be summarized below:

$\mathrm{Dye} + h\upsilon \rightarrow \mathrm{Dye}^*$ Light absorption (excitation) (1)

$\mathrm{Dye}^* + \mathrm{TiO_2} \rightarrow \mathrm{Dye}^+ + e^-_{\mathrm{CB}}\ (\mathrm{TiO_2})$ Electron injection ($k \sim 10^{-12}$ sec.) (2)

$2\mathrm{Dye}^+ + 3\mathrm{I}^- \rightarrow 2\,\mathrm{Dye} + \mathrm{I}_3^-$ Dye regeneration ($k \sim 10^{-6}$ sec.) (3)

$\mathrm{I}_3^- + 2\,e^-_{\mathrm{catalyst}} \rightarrow 3\mathrm{I}^-$ Electrolyte regeneration (reduction) (4)

A schematic picture of the architecture and electron transfer processes which are at the basic of the operational of a sandwich type solar cell is shown in Fig. 2. When illuminated, the dye molecules capture the incident photons ($h\upsilon$) generating electron/holes pairs.[33] The photo-excited electrons, at excited states (Dye* see Eq. 1), which lie energetically above the CB edge of the TiO_2, are quickly (typical time constant *k*, around 10^{-12} sec, under one sun illumination, *i.e.*, irradiation power =100 mW/cm^2, T=25°C, spectral intensity distribution of the light source = AM 1.5 global standard solar spectrum[171]) injected (Eq. 2) into the CB of the TiO_2.[33] Due to the photo-induced charge carriers transfer from the dye to the semiconductor oxide, the electronic density in the TiO_2 increases giving rise to an electrochemical potential difference (ΔV) between the TiO_2 and the electrolyte.[34] Regeneration of oxidized dye-molecules is accomplished by capturing electrons from the electrolyte mediator, Eq. 3, sandwiched on the cathode, that catalyses the reduction of I_3^-, (Eq. 4).[33] Thus, in this circumstance, the entire cycle is regenerative (*i.e.* regenerate the oxidized sensitizer) and the overall balance of the process will be the conversion of photons to electrons without any permanent chemical transformation.[121] Thus, in ideal conditions, a stable cell delivering photocurrent indefinitely is expected. However, several "undesirable" processes limit the electron transfer at the photoanode.[47] These loss pathways include the decay of the dye excited to ground state and the "re-capture" of injected electron in the semiconductor CB by the oxidized dye or by the electrolyte species (Eqs. 5,6,7).

$$\text{Dye}^* \rightarrow \text{Dye} \qquad \text{decay of the dye excited state} \quad (k \sim 10^{-10}\ \text{sec.}) \qquad (5)$$

$$\text{Dye}^+ + e^-_{CB}(TiO_2) \rightarrow \text{Dye} + TiO_2 \quad \text{recombination (back reaction, } k \sim 10^{-4}\ \text{sec.)} \qquad (6)$$

$$I_3^- + 2e^-_{CB}(TiO_2) \rightarrow 3I^- + TiO_2 \quad \text{electron capture from mediator (dark current, } k \sim 10^{-2}\ \text{sec.)} \qquad (7)$$

Thus, the optimization of DSSCs require that the electron injection (Eq. 2) and the dye regeneration processes by the electron donor mediator (Eq. 3), must be faster than the decay (radiative or non-radiative) of Dye* (Eq. 5) and the back reaction of the injected electron with the oxidized dye (Eq. 6), respectively.[33] In particular, the "dark current" is considered as the main loss mechanism for a DSSC.[172,173] Finally, the "efficient" regeneration of the charge mediator at the CE (Eq. 4) is fundamental; otherwise the device η could be limited.[33,172] A deep knowledge and understanding of the electron-transfer kinetics is key in identifying materials for the optimization of structure/function relationship of DSSCs.[36,174]

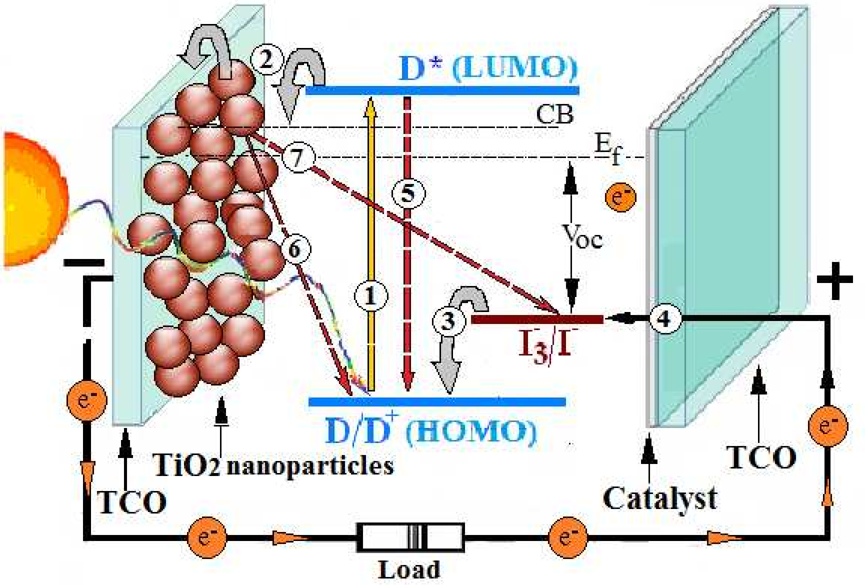


Fig. 2 *Schematic drawing showing a cross section view of a DSSC together with simplified electron transfer processes involved in the conversion of light to electric power by DSSC. Brown spheres: TiO_2 nanoparticles, red arrows: electron-loss processes.*

Extensive studies on the electron injection mechanism have been performed by numerous research groups and a plethora of experimental and theoretical data have been published.[175,176,177,178,179,180,181,182,183,184,185,186,187,188,189,190,191,192,193,194,195]

3. FIGURES OF MERIT OF DSSCs

The main FoM that characterize the performances of a DSSC are summarized below:

i)- The **short-circuit photocurrent density** (J_{SC}) generated under 1 sun represents the photocurrent per unit area ($mA\cdot cm^{-2}$) of the cell when, under irradiation, it is short-circuited. Higher is the J_{SC}, higher is both the capability of the sensitizer to absorb sunlight over a wide region of the solar spectrum, and the efficiency to inject electrons in the semiconductor CB (Eqs. 1, 2 and 3, respectively). Moreover, a high J_{SC} value is strongly linked with the reduction rate of the oxidized dye (Eq. 3). Indeed, quicker is the reduction of the oxidized dye, lower will be the dark current (see eq. 6), which reduces the Jsc.[171]

ii)- The ***open circuit voltage*** (V_{OC}) is the electrical potential difference at open circuit (no current flow) between the two terminals (photoanode and CE) of the cell under illumination conditions. The maximum V_{OC} value, of a DSSC (generally around 0.8÷0.9 V), corresponds to the difference between the quasi-Fermi level (E_F, -0.5÷ -0.4V eV vs. normal hydrogen electrode –NHE-, for TiO_2)[189] of the semiconductor and the redox potential of the charge mediator (-0.4V eV vs. NHE, for I_3^-/I^- redox couple).[189] However, actual V_{OC} is lower than the theoretical values depending on both the recombination of the injected electrons with the oxidized dye (Eq. 6) and dark current (Eq. 7). Indeed, for regenerative photo-electrochemical systems:[171]

$$V_{OC} = \left(\frac{k_B T}{e}\right) \ell n \left(\frac{I_{\text{inj.}}}{n_{cb} k_{red} [\mathrm{I}_3^-]}\right) \qquad (8)$$

where k_B is the Boltzmann's constant, T the absolute temperature, e the elementary charge, $I_{inj.}$ the charge flux resulting from sensitized injection, k_{red} the reduction rate constant of I_3^-, while n_{cb} and $[\mathrm{I}_3^-]$ are the concentration of electrons at the semiconductor surface and oxidized redox mediator (I_3^-) in the ($\mathrm{I}^-/\mathrm{I}_3^-$) solution, respectively.[196,197]

iii)- The ***fill factor*** (FF) is defined by the ratio:

$$FF = \frac{P_{\max}}{J_{SC} \cdot V_{OC}} \qquad (9)$$

where P_{max} is the maximum power output of the cell per unit area, given by the product ($J_{max}\cdot V_{max}$). In a current-voltage (J/V) curve, the FF describes how well the area under J/V curve fills-in the maximum rectangle described by the product $J_{SC}\cdot V_{OC}$ (see **Fig. 3**). The shape of this curve represents a very useful and direct tool to characterize the DSSC performance, (*i.e.,* V_{OC} , J_{SC} and η).

iv) - The ***Incident Photon Conversion Efficiency*** (IPCE) or external quantum efficiency (EQE) is a measure of the quantum efficiencies of the cell at a given excitation wavelength (λ) and, corresponds to the photocurrent density generated in the external circuit per incident monochromatic photons flux that strikes the cell[13]. Under short circuit condition, its value (as a function of λ), is calculated by the following equation[39]:

$$IPCE = 1240\,(eV\cdot nm)\frac{J_{SC}[mA\cdot cm^{-2}]}{\lambda\,[nm]\cdot\Phi_{in}(\lambda)[mW\cdot cm^{-2}]} \qquad (10)$$

where $\Phi_{in}(\lambda)$ is the photon flux of the incident monochromatic light. The IPCE can be also expressed as the product between the *light harvesting efficiency* [LHE(λ)] for photons of wavelength λ, the Φ_{inj} (quantum yield of electron injection) from the excited state of the sensitizer to the CB of the semiconductor and, the collection efficiency Φ_{coll} of the injected electron at the front electrode:

$$\mathrm{IPCE} = \mathrm{LHE}(\lambda)\cdot\Phi_{inj}\cdot\Phi_{coll} \qquad (11)$$

where the LHE(λ), is given by:

$$\mathrm{LHE}(\lambda) = 1 - 10^{-A} \qquad (12)$$

The exponent A in Eq. (12) is the dye absorbance or optical density while, the product ($\Phi_{inj}\cdot\Phi_{coll}$) which appears in Eq. (11), is the *absorbed photon to current conversion efficiency* [APCE(λ)] or *internal quantum efficiency* (IQE). Finally, Φ_{inj} is given by:[34]

$$\Phi_{inj} = \frac{k_{inj}}{k_r + k_{nr} + k_{inj}} \qquad (13)$$

where k_{inj} is the rate constant for Φ_{inj} into the semiconductor, while k_r and k_{nr} represent the radiative and non radiative rate constant, respectively.

The IPCE thus, is directly correlated both to the absorption properties and the amount of adsorbed sensitizer on the semiconductor surface (or LHE) as well as the Φ_{inj} and Φ_{coll}.

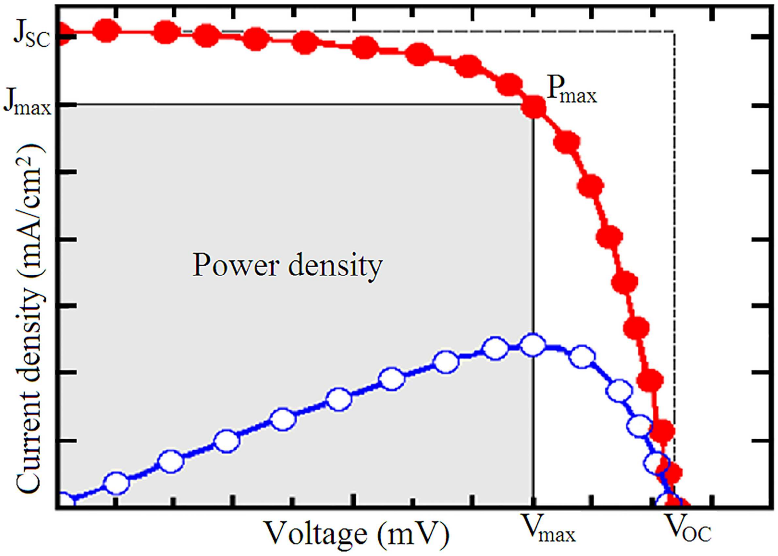


Fig. 3 *Typical Current-Voltage curve (fill circles). The FF corresponds to the shaded region, which is bounded by the V_{max} and J_{max}, divided by the area of the region which is bounded by the V_{oc} and J_{sc}. The blue curve (open circles) shows the power as a function of voltage.*

v) - the ***energy conversion efficiency*** (η) of the cell, defined as the ratio between the maximum output electrical power, P_{max}, and the energy of the incident light, P_{light}, is given by the relation :

$$\eta = \frac{P_{\max}}{P_{light}} = \frac{V_{OC} \cdot J_{SC} \cdot FF}{P_{light}} \qquad (14)$$

4. Inorganic and synthetic organic dyes

The dye plays a key role in DSSCs. Based on the requirements outlined in Sect. 2, different dyes have been studied and significant progresses in designing sensitizers for DSCCs applications have been made. Here below we briefly summarize the main properties of inorganic and organic-based dyes.

4.1 *Metal complexes*

Metal complexes consist of a central metal ion with ancillary ligands, typically bipyridines or terpyridines, bearing at least one anchoring groups[198] able to link the dye to the semiconductor surface in a dye-bridge-anchor array. This circumstance, causes a large electronic interaction (coupling) between the π*-orbital of the ligand, which is the lowest LUMO of the complex, and the d-orbital of semiconductor oxide, resulting in an electron injection from the metal complex into the semiconductor CB. Typical anchoring groups for metal oxides semiconductor are sulphonic acid ($-SO_3H$),[199,200,201] phosphonic acids $(PO)(OH)_2$[185,202,203,204] carboxylic acids (-COOH)[205,206,207] and their derivate (acid chlorides,[208] amides,[209] esters[209] or carboxylate salts[209]), carboxyl groups being largely used.[172] Carboxyl group can form bidentate-bridging-linkage (**Fig. 4**a), as well as chelating- (**Fig. 4**b) or ester-linkages (**Fig. 4**c) with the TiO_2 surface,[198] depending on the structure of the dye, the binding groups, the pH, and the metal oxide synthesis.[210]

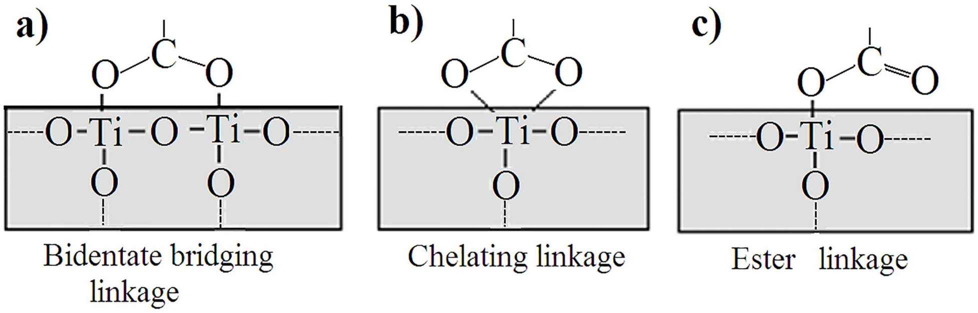


Fig. 4 *Binding modes of COOH-group by p orbital of oxygen to 3d orbital of titanium on TiO_2 surface. a) Bidentate bridging, b) chelating and c) ester linkage.*

Light absorption in the visible and near-IR regions of the solar spectrum is attributed to a metal to ligand charge transfer (MLCT)[211] transition. In this regard, polypyridine complexes of d^6 metal, such as Ru(II)[79,81,84], Os(II)[79,84] or Ru(I)[91], are typical example of compounds characterized by intense bands in the visible region due to MLCT transition .[211] The MLCT energies can be tuned by proper selection of the substituents (alkyl, aryl, heterocycle, etc.) on the ancillary ligand, as well as by changing the ligand itself.[212] Usually, electron-withdrawing substituents such as carboxylic group,[213] decrease the π*-orbital energy of polypyridine ligand.[213,214] Contrary, donating substituents such as thiocyanate (SCN)- or ammine group or alkyl chains show the opposite effect.[213,214]

Although several types of dyes have been engineered[215,216] since the publication of the O'Regan and Grätzel pioneer paper for DSSCs based on trinuclear Ru-complex dye (consisting of three ruthenium atoms hold together by polypyridine bridging ligands) in 1991,[33] the most successful metal-complexes sensitizers, in terms of both η and long thermal stability, have been based on ruthenium(II)-polypyridyl complexes with carboxylated anchoring groups.[209] These complexes are characterized by a broad absorption band extended from visible to the near infrared (NIR), excited and ground state energy levels matching the semiconductor CB energy levels and electrolyte's redox potential, IPCE over 80% in the visible region, high ε, and electrochemical stability.[217] The most efficient Ru-polypyridyl sensitizers being cis-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine)-Ru(II), coded as **N3**[34], **N719**[218](doubly deprotonated form of N3 dye) and tri-thiocyanato-4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine)-Ru(II), coded as **N749** or black dye[36,83,219]. **N3** is characterized by absorption maxima centred at 518 and 380 nm and a $\varepsilon = 1.35 \cdot 10^4\ M^{-1} \cdot cm^{-1}$ in alkaline solution at 500 nm[220]. Similar spectral features are shown by **N719** ($\varepsilon = 1.42 \cdot 10^4\ M^{-1} \cdot cm^{-1}$)[221]. N749 ($\varepsilon = 7.7 \cdot 10^3\ M^{-1} \cdot cm^{-1}$),[36,83,225] differently from many dyes (e.g. N3 and N719), thanks to its three SCN^- functional groups, absorbs from the visible to the NIR showing a dark brown-black colour. In terms of performances, N3 and N749-based DSSCs have similar V_{OC} (~720 mV), with η of 10% and 11.1 %, for N3[34,220] and N749,[83] respectively. N719 which has the same structure as N3, where two H^+ at two carboxyl groups are substitute by two tetrabutylammonium (TBA^+) groups, exhibits an η of 11.2%.[218,220,221,222]

The development of new synthesis pathways has been the main strategy to improve the PV performance achieved with the N3 and N719 dyes. A strong research effort has been done in designing many ruthenium-photosensitizers, characterized by different peripheral ligands and/or different number and type of anchoring groups.[214] Furthermore, fundamental studies to understand the parameters (spectral response of dye, ε, redox potential of sensitizer, suppression of dye aggregation, efficient electron injection, etc.) that influence the η of DSSCs have been made.[214]

Hara *et al.*[223] investigated a series of four carboxylated Ru(II)-phenanthroline complexes different for number and position of carboxyl groups on the phenanthroline ligand. Amongst the four selected dyes, cis-bis(4,7-dicarboxy-1,10-phenanthroline)-dithiocyanato-ruthenium(II), $Ru(dcphen)_2(NCS)_2$-$(TBA)_2$, has shown the best performance achieving a η of 6.6%.[223] The position and number of anchoring group (carboxyl) on the ancillary phenanthroline ligands affect significantly the electronic coupling complex/semiconductor, essential for efficient electron injection[223]. Mono-cationic bipyridyl-ruthenium complex with strongly electron donating β-acetylacetonate ligand (3-methyl-2,4-pentanedionate)[224] instead of two thioisocyanato groups, have shown, in alkaline solution, η of 6.0%. This sensitizer has an intense visible light absorption ($\varepsilon=1.35 \cdot 10^4$ $M^{-1}cm^{-1}$) with low energy MLCT maxima at 525 nm and a band tail, which allows red light absorption beyond 600 nm.[224] Islam *et al.*[225], synthesized a biquinoline (biq) complex of Ru(II), having a MLCT transition red-shifted with respect to N3. Unfortunately, the lowest excited MLCT state of this complex was not energetically favorable to effectively inject electrons into the TiO_2 CB giving rise to low IPCE (~20%) at 450 nm.[225] More recently, a sensitizer built on a tridentate bipyridine pyrazolate (bpz) ligand coupled Ru(II) complexes (coded as HY2),[226] with absorption peaks at 437 and 550 nm and ε ($=1.98 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$ at 550 nm) higher than N3 ($\varepsilon = 1.35 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$),[220] has been designed and synthesized.[226] DSSC with this emerging HY2 sensitizer reached η=8.07% and an IPCE value of 82% at 530 nm.[226] A ruthenium dimer sensitizer based on N3 structure called K20, with efficiency similar to those achieved by N3 and N719 dyes, has been reported to have a $\varepsilon = 2.2 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$ at 520 nm.[227] This ε value is higher than those of both N3 and N719 dyes. The advantage in increasing the ε of sensitizer relies in the possibility to decrease the semiconductor thickness and thus reduce cost as explained in sect.7.

In 2003, Wang *et al.*[228,229,230] developed a novel amphiphilic ruthenium complexes, named Z907 that, in combination with 1-decylphosphonic acid (DPA) as co-adsorber prevents the aggregation of dye molecules, and when integrated in DSSCs achieved and maintained stable performances (η =7.3% and IPCE=83% at 540nm) under long-term (~1000 h) thermal stress measurements.[229] The hydrophobic alkyl chains attached to one of the bipyridine ligand prevents the desorption of the dye from the TiO_2 surface because the water molecules penetrated into the electrolyte[228,229]. Small amounts of water induce dye desorption, due to hydrolysis effects or weakening of the interactions at the dye/semiconductor oxide surface[231]. Furthermore, the presence of water molecules in the electrolyte undermine the DSSC long term stability due to the oxidation of iodide to iodate (IO_3^-), instead than tri-iodide (I_3^-),[231,232] which cannot be reduced at the CE. This effect results in a I_3^- progressive depletion and subsequent decrease of the cell performance.[232] Another synthesized Ru-based dye, *i.e.* Z910,[233] an heteroleptic Ru-complexes, characterized by an extensive *π*-conjugated system of the bipyridine ligand to enhance the harvesting of solar light, has been synthesized and demonstrated as highly efficient (η =10.2%, IPCE=83% at 520 nm) and stable sensitizer for DSSCs. A better η =10,8%, was achieved by Nazeeruddin *et al.*[234] which, developed a Ru(II)-based sensitizer, named **N945**, whose absorption spectrum in AcN solution, dominated by MLCT, is characterized by two bands around 400 and 550nm, with $\varepsilon=3.4 \cdot 10^4 M^{-1} \cdot cm^{-1}$ and $1.89 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$, respectively. Driven by the need to design absorbers with high ε values (see Fig. 5), novel ion-coordinating dyes such as K51 ($\varepsilon=1.2 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$)[235], K60 ($\varepsilon= 1.85 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$)[236] and K68 ($\varepsilon=1.14 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$)[237], have been developed by extending the *π*-conjugation of the peripheral ligands with the introduction of electron donor group in the molecular structure.[235,236,237] This class of sensitizers, when incorporated in DSSCs, exhibits η of ~8%.[235,236] In particular, K51 dye has shown η of 7.8%,[235] while higher efficiency (η=8.4%) was achieved with K60.[236] Better thermal stability than other dyes such as for example the K51, was obtained with K68 thanks to an increased hydrophobicity of the dye, due to the incorporation of additional alkyl chain on the donor ligand.[237] Kuang *et al.*[237] achieved a η = 6.6% when exploited a binary ionic liquid electrolyte (*i.e.* 1-propyl-3-methyl-imidazolium iodide (PMII) and 1-ethyl-3-methyl-imidazolium tetracyanoborate ($EMIB(CN)_4$)), while higher η (7.7%) were obtained using a non-volatile MePN-based electrolyte.

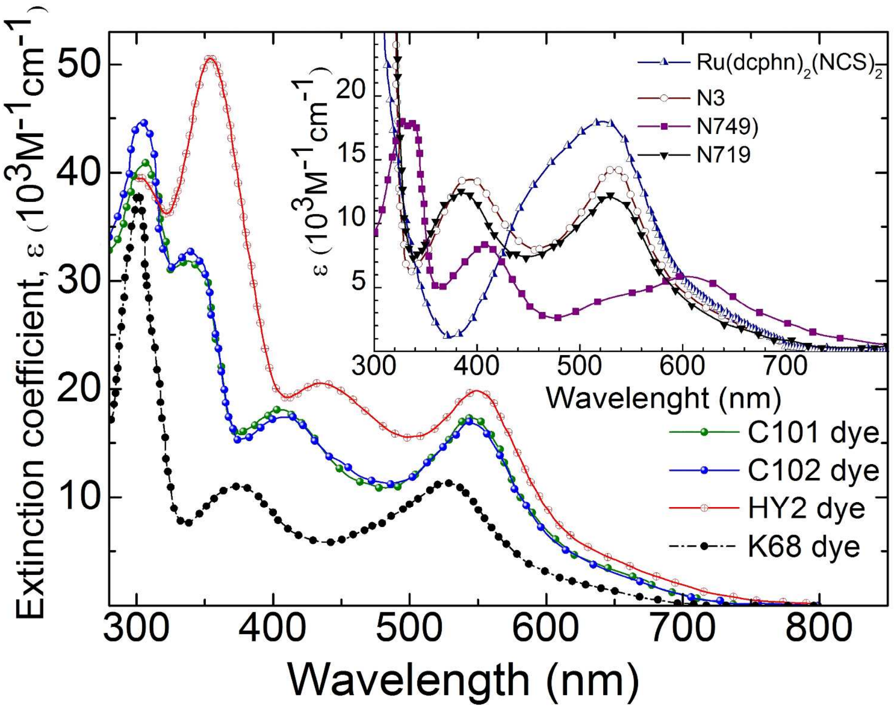


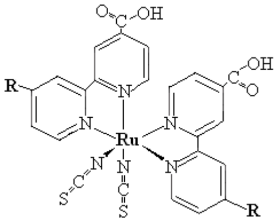
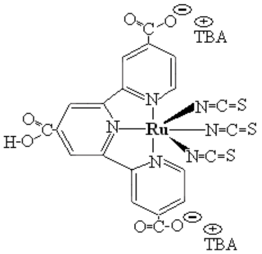
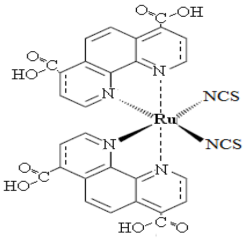
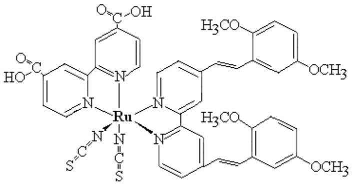
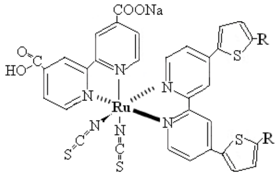
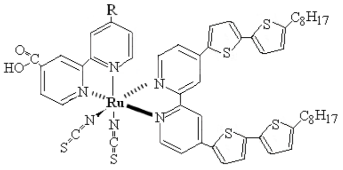
Fig. 5 *Extinction coefficient of Ru-based dyes as function of wavelength.*

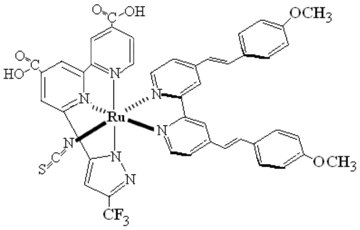
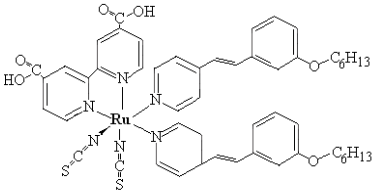
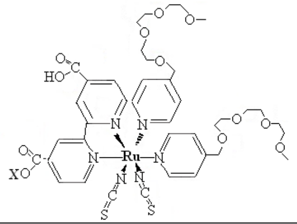
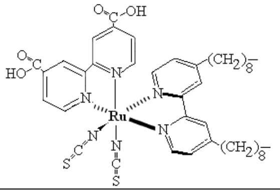
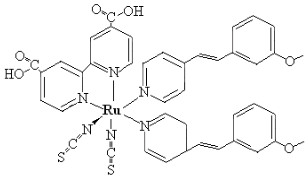
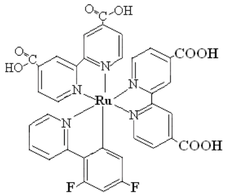
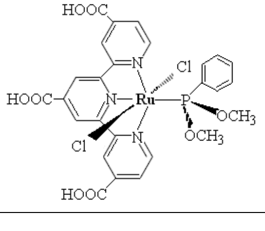
In 2008 Gao *et al.*[238] developed a very promising amphiphilic ruthenium sensitizers, coded as **C101**, **C102** having alkil-thiophene or furano moieties attached to the ancillary bipyridine (bpy) ligand. These moieties were able to enhance the light-harvesting capacity of the complexes by increasing their ε. The MLCT absorption bands appear at ~407 and ~547 nm with $\varepsilon=1.75\cdot10^{4}\ M^{-1}\cdot cm^{-1}$ and $\varepsilon=1.68\cdot10^{4}\ M^{-1}\cdot cm^{-1}$ for C101 and C102, respectively. When integrated in DSSCs, C101 dye with 4,4'-bis(5-hexylthiophenen-2-yl)-2,2'byp ligand, has shown $\eta=11.3\%$[238]. Cao *et al.*[239] synthesyzed a C101-sensitizer analogue, named **C106,** where a sulphur atom was inserted between hexyl and thiophene groups. The use of **C106** thin photoactive layers, having $\varepsilon=1.87\cdot10^{4}\ M^{-1}\cdot cm^{-1}$ at 550 nm, allowed to make DSSC with $\eta=11.29\%$.[239] The optimization of the TiO_2 film has permitted to achieve a η of 11.9%.[240] In the attempt to extend the π-conjugation length of Ru(dicarboxyl-bipyridine)(L)$(NCS)_2$ sensitizers in order to extend to the red region of the spectrum the absorption properties and thus investigate the effect on the photochemical properties, other amphiphilic heteroleptic dyes incorporating thiophenes or phenyleneviniylenes on the ancillary ligands (L), such as **K19**,[241] **K77**,[242] **CYC-B1**(Z991)[243] and **CYC-B11**[244] have been synthesized. Concerning chemical stability, the SCN^- donor ligands are believed to be the weakest part in the SCN-bpy-Ru(II) complexes and in this regard, a new-generation of SCN-free cyclometalated ruthenium sensitizer have been designed.[245,246,247,248,249,250] Although thus far, their η remains below 10% (*e.g.* $\eta=9.54\%$ with the dye TFRS2)[246], a very promising result was obtained with the **YE05** complex.[80,253,251] This dye was designed replacing the SCN^- by a cyclometalated 2,4-difluorophenyl-piridine, obtaining $\eta=10.1\%$ when integrated in DSSC.[253] Very recently, Ref. 252 developed a phosphine-coordinated Ru(II) sensitizer, called **DX1**, which when used in a DSSC achieved a $\eta=10\%$, see **Table 1** for a summary of Ru-based DSSCs.

As briefly discussed above, Ru(II)-polypiridil complexes have been considered as reference dyes for many years and used as a base for designing other Ru-dyes.

Table 1: *Photovoltaic performances (@ 1 sun irradiation) of the most popular dyes based ruthenium(II)-complex photosensitizers.*

Dye *(Structure)*	***Code***	J_{SC} (mA·cm^{-2})	V_{OC} (mV)	***FF*** (%)	***η*** (%)	***ref.***

 **N3**: **R** = COOH **N719**: **R**=$COO^{-}TBA^{+}$ TBA^{+}= tetra-butilammonium cation	**N3** **N719**	18.20 17.73	720 846	73 75	10.0 11.2	34 218
	**N749**	20.53 20.90	720 736	70 72	10.4 11.1	36 83
	**Ru(dcphn)$_2$(SCN)$_2$**	12.50	740	71	6.6	223
	**N945**	19.0	728	71	10.8	234
	**C101** R= C_6H_{13} **C106** R =-S-C_6H_{13}	17.94 18.28	778 749	79 77	11.0 11.3	238 239
	**CYC-B1** R= COOH **CYC-B11** R= $COO^{-}TBA^{+}$	23.92 20.05	650 743	55 77	8.5 11.5	243 244

	**HY2**	15.70	765	67	8.0	226
	**K19**	14.61	711	67	7.0	241
	**K51** X = Na	15.37	738	68	7.8	235
	K60 X= H	16.85	730	68	8.4	236
	**Z907**	14.60	722	69	7.3	229
	**Z910**	17.20	777	76	10.2	233
	**YE05**	17.00	800	74	10.1	253
	**DX1**	21.4	664	70	10.0	252

To develop sensitizers with better photoelectrochemical properties than Ru-based there is the need to overcome some drawbacks exhibited by these dyes: ***i)*** a limited absorption in the near-IR region of the solar spectrum, ***ii)*** a rather low ε (*e.g.* ε=$2.2 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$ for the K20)[227] requiring thick TiO_2 films (~8μm) in order to efficiently capture the incident light, avoiding both low V_{OC} (large dark current) and low FF (high electrolyte resistance) values, ***iii)*** a rather poor thermal stability, ***iv)*** the use of rare metal, such as ruthenium coupled with the complex synthesis route based on multi step procedures[25] involving tedious and expensive purification processes which burden on the total cost of the DSSC.[254,255] In this regard, performance/price ratio will play a pivotal role in future choice of various PV cells. Nevertheless, apart cost related issues, ruthenium compounds are toxic and carcinogenic.[256]

Alternative sensitizers based on platinum[257,258] and iridium[259] complexes, have been developed, but so far their η (*e.g.*, ~3% for Pt[257]) in DSSCs is lower than that achieved with Ru-complexes. Other inorganic compounds, such as Os polypyridine complexes have also been investigated as sensitizers in DSSCs.[37,79,260] These compound exhibit a broader absorption range and photo-action spectrum (the spectrum reporting the IPCE) with respect to Ru-based one.[84] However, osmium-based DSSCs suffer very low η, mainly due to slow electron transfer from the iodide electrolyte to the osmium dye cation.[84] Apart from the poor electrochemical performance achieved to date with osmium compounds, it is also important to point out that bulk metallic osmium is scarce[261] and when in the form of micro-sized particles it becomes pyrophoric[262] (*i.e.* ignites spontaneously). Moreover, all osmium compounds, such as osmium tetraoxide, OsO_4, should be considered highly toxic.[263] Indeed, OsO_4 concentrations in air as low as 10^{-7} gm^{-3} can cause lung congestion,[264] as well as skin and eye damage.[264]

4.2 *Organic synthetic dyes*

In order to replace the noble and expensive Ru(II)-complexes in DSSCs,[265] other sensitizers have been proposed as an alternative such as the organic synthetic dyes.[25,94,99,100,266,267,268,269,270,271,272,273,274,275,276,277,278,279,280,281,282] These dyes exhibit many advantages with respect to the aforementioned metal-based ones, such as: ***i)*** efficient light-harvesting capabilities (*i.e.* in the near-IR region), ***ii)*** higher ε, which depends on the fact that for this dyes the transition involved in the absorption of the light is π-π*, which generates a Ligand Centered (LC) excited state that is not distorted as MLCT state populated in the case of Ru(II) based ones,[213] ***iii)*** easiness in tailoring the molecular structure and photo-physical characteristics.

Porphyrin and phtalocyanines as well as clorin and bactero(clorin) and all the Chrorophylls (discussed in Sect. 5.3) belong to the class of macrocyclic tetrapyrrole.[283,284] The difference between these compounds depends on the level of reduction of the macrocyclic tetrapyrrole, see Fig. 6.

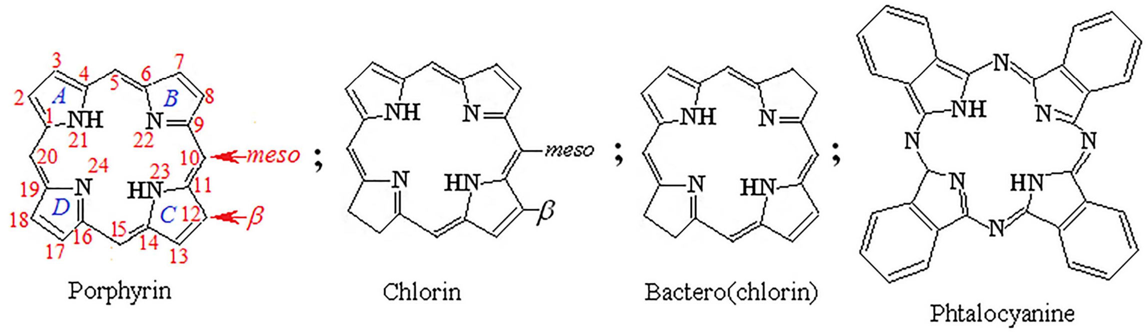


Fig. 6 *Basic structures and oxidation state of cyclic tetrapyrrole sensitizers: Porphyrins, 17,18-dihydroporphyrin=chlorins; 7,8,17,18 tetrahydroporphyrin = bactero(chlorine)*, and *phtalocyanins. The IUPAC numbering system of carbon scheleton is also reported.*

Porphyrins are composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges (=CH–).[285] The porphyrin macrocycle has 22 (18 delocalized) π-electrons (according to Huckel model) and it is a highly conjugated system.[285] Porphyrins typically have very intense absorption bands in the visible spectrum while they weakly absorb in the red region of the electromagnetic spectrum.[286]

Phtalocyanines are macrocyclic compounds consisting of four isoindole (benzo-fused pyrrole)[287] groups linked by nitrogen atoms in a large π—conjugated planar structure. This particular configuration allows phtalocyanines to also absorb light of wavelengths longer than 650 nm.[285,306] As a general rule, depending on their reduction state, tetrapyrrole macrocycles afford λ_{max} tunability.[288]

Porphyrins[109,110,111,289] and phtalocyanins[103,104,105,106,107] have a rigid molecular structure, possessing high ε (>10^5 $M^{-1}cm^{-1}$).[290] Moreover, they can be easily functionalized (*e.g.,* porphyrins at the meso and *β* position (see Fig. 6)), allowing the tuning of their optical, physical and electrochemical properties.[291]

The nature of the frontier orbitals (*i.e.,* HOMO and LUMO) in porphyrin macrocycles has been an active area of research for computational and spectroscopic investigations. The absorption spectra of porphyrin derivatives show two characteristic π–π* absorption regions, the weak Q band (transition to the first excited state (LUMO)) in the 550–700nm range and the intense Soret band (transition to the second excited state (LUMO+1)) in the 400–450nm range.[292] Ab initio methods (restricted Hartree Fock, local DFT)[293] have shown that metal-free (*e.g.,* thiophene substitute[294]) and metal (Mg(II), Cu(II), Zn(II), Ni(II)) containing porphyrins generally possess two a1u and a2u orbitals as the HOMO and HOMO-1,[294] see Fig. 7. The electron density in a1u type orbital is essentially localized on the Cα and Cβ atoms of the pyrrole rings, while in the a2u orbital is mainly confined on the pyrrole nitrogens and on the meso-carbons,[294] see Fig. 6. As for the case of the HOMO, also the LUMO levels are similar in metal free (*e.g.,* thiophene substitute) and metal containing porphyrins: there are two nearly degenerate e2g(π*) orbitals essentially centred on the porphyrin macrocycle,[294] see Fig. 7. The presence of a1u(π) and a2u(π) orbitals in many metal porphyrins can account for the formation of a π radical cation that plays an important role in the biochemical function of porphyrins. For example, the π radical cation formation is central in the photo oxidation of chlorophylls, which are essentially a Mg containing porphyrins, see Sect 5.3.

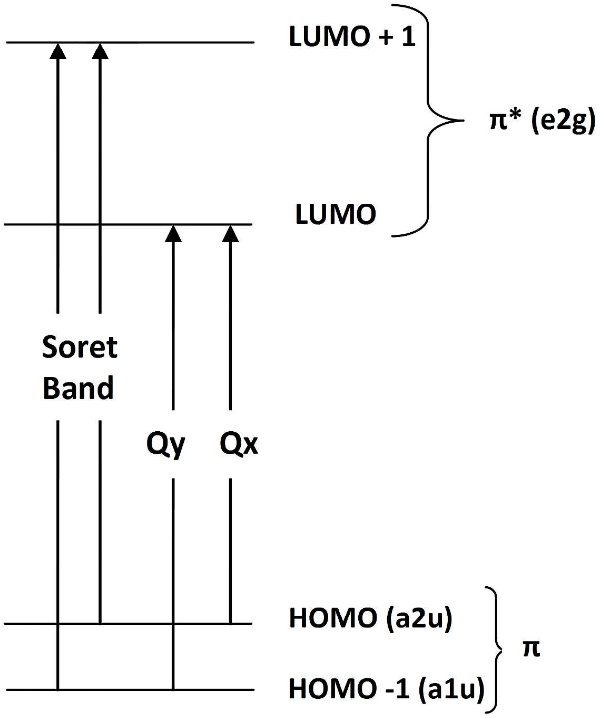
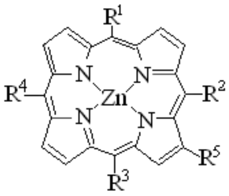
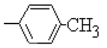
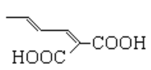
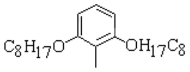
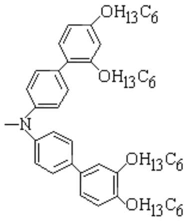
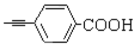
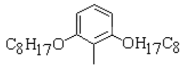
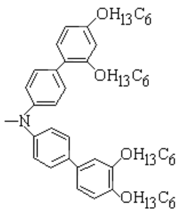
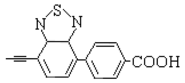


Fig. 7: *Schematic of π– π * transitions (responsible for the Soret and Q bands) for porphyrins.*

Porphyrins are used in oxygen sensor devices[295,296,297,298] and in photodynamic therapy.[299] These two applications are principally based on the changes of photoluminescence intensity of porphyrins by molecular oxygen that quenches their triplet excited states.[300] Porphyrins have also been used as catalysts in hydrocarbon oxidation reactions[301] and in energy conversion devices.[109,110,111,289]

In particular, bio-inspired by natural photosynthesis, different research groups exploited porphyrins as photosensitizers in DSSC.[109,110,111,289] After the first experimental study carried out in 1993 with a porphyrin of type copper chlorophyll (η=2.6%),[38] beta-linked zinc porphyrins (see Fig. 6 and **Table 2**) have been developed afterward with η=7.1% reported in 2007.[111] Meso-linked zinc (see Fig. 6 and **Table 2**) porphyrin sensitizers were reported in 2009.[302] These sensitizers achieved η=11%, comparably with the best η achieved by ruthenium-based ones (N719, N749 and CYC-B11, see **Table 1**), in 2010.[108] With a structural design involving long alkoxyl chains to enclose the porphyrin core (YD2-o-C8 dye) suppressing the dye aggregation suffered by zinc porphyrins,[303] the DSSC achieved a η=12.3% in 2011 with co-sensitization of an organic dye (Y123, a donor-π-bridge acceptor) and a cobalt-based electrolyte.[304] The Y123 has a complementary absorption spectrum with respect to YD2-o-C8, characterized by low absorption in the green part of the electromagnetic spectrum.[304] The co-sensitization effect has determined better PV performance (η=12.3%) with respect to DSSCs using a single dye (*e.g.,* YD2-o-C8, η=11.9%).[304]

Table 2: *Photovoltaic values (@ 1 sun irradiation) of porphyrin photosensitizers.*

Dye *(Structure)*	***Code***	***J$_{SC}$*** mA·cm^{-2})	***V$_{OC}$*** (mV)	***FF*** (%)	***η*** (%)	***ref.***
PORPHYRINS 	**ZN-TP-(COOH)$_2$** R^1=R^2=R^3=R^4=  R^5= 	14.0	680	74	7.1	111, 282
	SM371 R^1=R^2=  R^4=  R^2=  R^5= H	15.9	960	79	12.0	164
	SM315 R^1=R^2=  R^4=  R^2=  R^5= H	18.1	910	78	13.0	164

In the last year Matew *et al.*[164] reported a molecularly engineered porphyrin dye, coded SM315, which features the prototypical structure of a donor–π-bridge–acceptor, which both maximizes electrolyte compatibility and improves light-harvesting properties. The obtained η of 13% is the current record high of DSSCs.[164]

Phthalocyanines and their metallo-derivatives have been, for long time, a very well-known class of materials for their industrial applications as dyes.[305] More recently these compounds are receiving a growing interest in other areas[306,307] such as chemical sensors,[308] electrochromic displays,[309] conducting polymers,[310] photodynamic cancer therapy,[311] liquid crystal,[312] catalysts,[313] and PVs.[103,104,105,106,107]

Although phtalocyanine has some advantages with respect to porphyrins such as strong absorption in the red (Q band at ~700nm), p-type semiconducting properties and thermal stability,[107] they suffer some limitation such as very poor solubility and strong aggregation when deposited on the surface of the semiconductor.[214] Moreover, phtalocyanines are not as efficient as porphyrins[109,110,111,164] when used as sensitizers in DSSCs. Indeed, despite many efforts have been done[314,315,316,317,318,319] (see Ref. 214 for a more exhaustive list) since the pioneering works of Grätzel's group,[314,315] the η currently achieved are quite low (~3%).[103,320]

As discussed above, for macrocyclic tetrapyrrolic sensitizers, ruthenium free hybrid-organic dyes have shown potential as efficient photosensitizers.[304] Nevertheless, the search for alternatives metal free (porphyrin and phtalocyanine often contain metals, *e.g.,* zinc) and green dyes is essential for the further large scale development of DSSCs. Hara *et al.*[266] have done a remarkable advance in the use of organic dyes for DSSCs increasing the efficiency with respect state of the art organic sensitizers. Recently, the interest in organic dyes is raised considerably. Horiuchi *et al.*[268] first synthesized an indoline organic dye D102 which was the precursor of a broader indoline sensitizers family. After structural optimization, Ito and co-workers,[100] developed an indoline organic dye, D205 (see **Table 3**), achieving an IPCE in the visible over 80% and η=9.5%. Higher η were achieved exploiting the dye C217 (η=9.8 %)[94] which are promising if compared to 11.5 % obtained with DSSCs based on ruthenium complexes (*e.g.*, CYC-B11)[244].

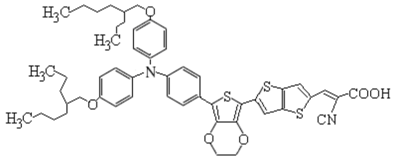
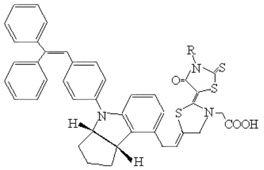
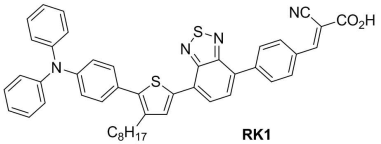
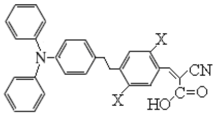
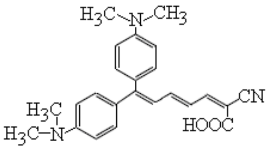
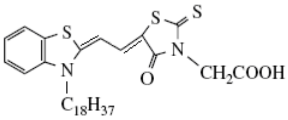
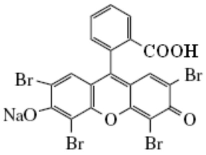
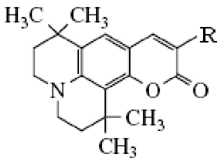
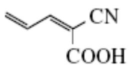
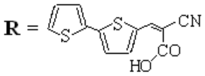
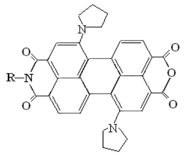
A series of dyes based on triphenylamine (TPA) donors[321,322] functionalized with p-dimethylamine (D29) and/or p,o-butoxy groups (D35, D37) have also been synthesized and investigated as sensitizers in DSSCs.[323] The D35 is a symmetric organic dye having structural benefits, with respect to *e.g.,* the asymmetric D37 dye (breaking the symmetry of the molecule gives rise to orbital re-arrangements),[324] from the large steric bulk introduced by the four butoxy groups.[323] After the first DSSCs based on D35 (η=6.0%)[323], this dye have been used in different configurations, *e.g.*, with and without co-adsorbant,[325] with different redox mediators both liquid *e.g.*, tetrathiafulvalene (η=6.5%),[326] cobalt complex (η=6.7%)[327] and solid *e.g.*, *spiro*-OMeTAD (η=4.5%),[328] and as co-sensitizer[102,329] *e.g.*, with Diketopyrrolopyrrole (DDP07-D35) (η=8.6%).[329]

Other metal-free organic dyes have also been prepared and more exhaustive details can be found in Ref. 214. For example, oligothiophene, coumarine, cyanine, etc.., have also been investigated and tested as low cost materials, see **Table 3** that reports PV performances for some representative metal-free organic dyes when integrated in DSSCs.

Despite their benefits listed above, the degradation in photo-stability (stability towards photochemical change due to light effects) of the organic dyes limits their potential applications in DSSCs. Progresses have been done in the past few years to increase the photo-stability and recently, Joly *et al.*[330] have demonstrated how the combination of RK1 dye with an ionic liquid electrolyte allows the fabrication of highly stable DSSC with no measurable degradation of initial performances (η=7.36%) after 2200 h of light soaking at 65°C under 1sun.

Table 3: *Photovoltaic values (@ 1 sun irradiation) of metal free organic photosensitizers.*

METAL FREE ORGANIC PHOTOSENSITIZERS						
Dye	***Code***	***J_{SC}***	***V_{OC}***	***FF***	***η***	***ref.***

(Structure)		$(mA\cdot cm^{-2})$	(mV)	(%)	(%)	
	**C217**:	16.10	803	76	9.8	94
	**D205**:	18.68	710	71	9.4	100
 RK1	**RK1**:	18.26	760	74	10.2	330
	**TA-St-CA**: X = H	18.10	743	67	9.1	267
	TA-DM-CA: X = OCH_3	20.85	697	66	9.7	331
	**POLYENE-DYE** **NKX-2569**	12.9	710	74	6.8	272
	**MEROCYANIN** **Mb18-N**	9.70	620	69	4.2	332
	**EOSIN-Y**	$5.15^{\#}$	$451^{\#}$	$72^{\#}$	$1.7^{\#}$	332
$^{\#}$electrolyte: 0.4 M LiI+ 0.04 M I_2 in AcN. *electrolyte: 0.4 M LiBr + 0.04 M Br_2 in AcN.		4.63*	813*	69*	2.6*	332
	**COUMARIN** **R** =  **NKX-2311**	≥ 15.20	≥ 630	62	≥ 5.2	333, 334
	R =  **NKX-2677**	14.3	730	74	7.7	266
	**PERYLENE DERIVATES**	7.8	540	63	2.6	335

5. Vegetable Dyes

Driven by the need for new "environmentally friendly" materials, vegetable pigments[336] such as betalains,[41,49,337] carotenoids,[338] anthocyanins[39,339,340,341,342,343] and chlorophylls[38,344,345,346,347] have been proposed as sensitizers in DSSCs. Vegetable dyes are available in large quantity, easily and safely extracted from fruits, flowers, leaves, low in cost and non-toxic. All these factors make the use of these natural products an intriguing challenge in the development of cheap and commercially available DSSCs.

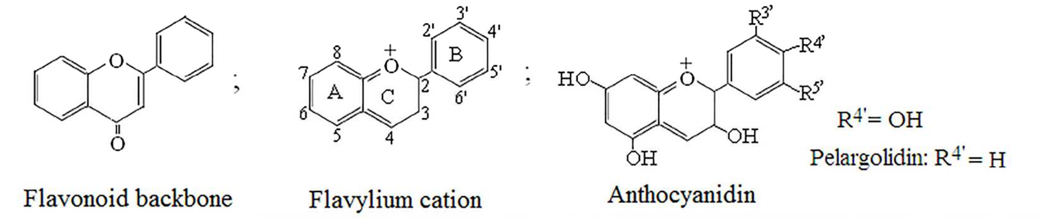
Unlike artificial sensitizers, whose desired energy levels and absorption properties can be tailored by changing the ligands and/or the central metal atom, for vegetable dyes this is a more difficult task simply because their molecular structure is designed by nature. As a consequence, the research activity is mainly devoted towards the selection of the right vegetable source to isolate the sensitizer and finding the best operating conditions (concentration, pH, extraction techniques, size of TiO_2 nanoparticles, thickness of photoanode film, soaking time, electrolyte composition, etc..).[340,348] For DSSC applications, it is possible to follow a bio-inspired strategy that through simple and clean synthesis, produces "on demand" structural modifications for a "quasi-natural biomimetic sensitizer" showing properties similar to those of the natural dyes. In this framework, optimizations in the design of suitable sensitizers have been obtained in the case of flavylium compounds.[349]

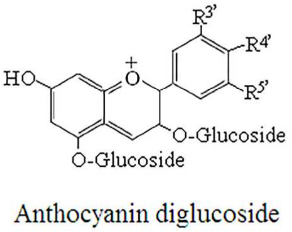
5.1 Anthocyanins

Anthocyanins belong to flavonoid group of phytochemicals (from the Greek *phyto* = plant), a family of water-soluble chemical compounds that occur naturally in plant.[350,351,352] Anthocyanins are responsible for the different colors of plants, including roots, stems, leaves, flowers and fruits.[353] Red- and blueberry, black and red raspberry, black currant, cherry, Sicilian blood orange, eggplant and red cabbage are just few examples of the multitude of vegetables that are rich in anthocyanins.[354,355,356,357,358] Amongst the large variety of vegetable compounds exhibiting the basic flavylium ion structure, the applications of anthocyanins have increased enormously in the last 20 years, not only due to their colouring and anti-oxidant properties[359,360,361,362,363] but also as pollution attractants and phytoprotective agents, protecting plant's DNA from damage caused by sunlight irradiation.[353] Currently, more attention has been devoted to anthocyanins due to their potential health benefits.[364] Moreover, in the last few years growing attention has been paid towards the exploitation of anthocyanins as multistate/multifunctional systems for information processing at the molecular level,[359,360 ,361] and for application in optoelectronics, *e.g.,* solar cells.[349]

5.1.1 Structure, photochemistry and photophysics of anthocyanins

Anthocyanins are derived by anthocyanidins or aglycones (see Fig. 8) which have, at least one pendant sugar moiety (glycoside form).[365] The core of both anthocyanidins and anthocyanins (or anthocyans), is a 2-phenyl-benzopyrylium chromophore (*i.e.,* flavilyum cation) which, consists of an aromatic ring (A) bonded to an heterocyclic ring (C) containing an oxygen atom which, in turn is linked by a C-C bond to a third aromatic ring (B) so, it may be also described as a C^6-C^3-C^6 skeleton.[365] The extended π conjugation, as well as the presence of positive charge and free -OH groups on the flavilyum cation, allow the anthocyanins to absorb light in the visible region leading to a large variety of pigments colouring.[365,366] The difference between anthocyanins of different types is mainly due to: ***i)*** the number of hydroxyl and/or methoxy groups in the molecule, ***ii)*** the nature and number of sugar moiety attached to the phenolic units, ***iii)*** the nature and number of aromatic or aliphatic acids attached to the sugar moiety.[364] The most common sugar is glucose, but galactose, arabinose, rhamnose, xylose, fructose and other may also be present in the anthocyanins structure.[367]





Basic structure of anthocyanins in flavylium cation

NAME	Substitutuent		Visible colour	Visible λ_{max} (nm) in MeOH-HCl*
	R3'	R5'		
Pelargonidin (Pg)	H	H	red	520
Cyanidin (Cy)	OH	H	magenda	535
Delphinidin (Dp)	OH	OH	purple	546
Peonidin (Pn)	OCH_3	H	magenda	532
Petunidin (Pt)	OCH_3	OH	purple	543
Malvidin (Mn)	OCH_3	OCH_3	purple	542

Fig. 8 *Basic structures of the flavonoid, flavilyum cation, anthocyanidin and anthocyanin diglucosides backbone. [(*) from Ref. 368].*

Furthermore, the sugar moiety may be acylated by aromatic acids, generally hydrocinnamic acids (coumaric, caffeic, gallic, sinapic and ferulic acids) and sometimes by aliphatic acids (acetic, oxalic, malonic, malic, and succinic acids).[369,370] Aromatic and/or aliphatic acylation may occur in the same molecule, forming a polyacylated structure.[351,352,371,372] Generally, the acylic moieties are bonded to the C^6 carbon atom in the sugar molecule. Anthocyanins occurring in nature typically have hydroxyl substituents at the position 3 (always glycosylated, *i.e.*, a hydroxyl or other functional group is attached to a carbohydrate of another molecule) and at the position 5 (occasionally glycosylated) of the flavynium cation, while the B-ring (or 2-phenyl) has one or more hydroxyl or methoxy substituents[373,374] (see Fig. 8).

Natural anthocyanins, in which the 7-hydroxyl group is glycosylated or replaced by a methoxyl group, can also occur but they are quite rare. Anthocyanins mono- and di-glycosylated at positions 3', 5' and even 4 are rare as well with respect to the anthocyanins typically having hydroxyl substituents at the position 3 and 5.[365,375] Due to this chemical complexity, there is a large variety of anthocyanins in nature[350] and more than 20 currently known anthocyanidins or aglycones. Nevertheless, only six anthocyanidins, *i.e.*, cyanidin (Cy), delphinidin (Dp), malvidin (Mv), pelargonidin (Pg), peonidin (Pn) and petunidin (Ptn) are common in higher plants.[370,376] Amongst these anthocyanidins, the three glycoside derivate non-methylated *i.e.,* Cy, Dp and Pg, are the most widespread in nature, being present in ~80% of pigmented leaves, ~70% of fruits and ~50% of flowers.[377]

The number of hydroxyl and methoxyl groups determines the intensity (*i.e.,* ε), type (*i.e.,* the absorption wavelength) and stability of anthocyanins' colour.[370] Colour stability refers to the capacity of the molecule (dye) to maintain its colour properties.[370] Generally, predominance of hydroxyl groups on the aromatic skeleton of anthocyanins give rise to an intense blue colour while, a red colour is observed when methoxyl groups prevail instead.[366,378] Glycosil substituents also influence the colour stability, probably due to a loss of co-planarity of ring B with respect to the rest of the molecule, which causes a decrease in conjugation and thus instability increase.[379] The colour stability of monoglycosides and diglycosides anthocyanidines remains higher than that of the corresponding aglycones.[379] Therefore, both hydroxylation and glycosylation influence the colour properties of the pigments.

Colour stability of cyanidin (*i.e.* cyanin without sugar moiety) is higher than that of malvidin, but lower than that of malvidin 3-glucoside.[366] Additionally, the colour stability of mono and diglycosyl anthocyanidins is dependent on the glycosyl substituent nature and its anchorage on the anthocyanin skeleton. Broennum-Hansen and Flink[380] reported that the anthocyanins containing the disaccharide sambubiose (a component of some glycoside pigments),[380] are more stable than glucose containing monosaccharidic anthocyanins. A possible explanation could be ascribed to the ability of the sugar moieties to avoid the degradation towards instable intermediates such as phenolic acid and/or aldehyde compounds.[381] For the use of anthocyanins as dye in DSSCs, the aforementioned structural variations are critical in the choice of the natural sensitizer characterized by the most favourable structural and optical properties (*e.g.,* maximum absorption-λ_{max}-, ε, colour stability). Thus, the choice is not a simple task, because anthocyanins extracts are strongly affected by pH,[382] processing and storage temperature,[383] concentration,[384] aggregation of pigments,[385] solvents,[386] light intensity and frequency,[387] presence of oxygen,[388,389] metallic ions,[390,391] enzymes and other substances.[392,393]

Due to their ionic nature, anthocyanins are involved in a series of pH-dependent equilibrium giving rise to different chemical species (red *flavylium cation* **AH$^+$,** bluish *quinonoidal base* **Q**, colorless *hemiketale* pseudobase, **H**, and colourless *chalcone* **Ch**), which are instable in neutral pH media. A change in pH modulates the anthocyanins stability.[394] Indeed, anthocyanins are more stable in acid solution (low pH) than in alkaline media (high pH)[365] (see Fig. 9). Under high acidity (pH $\leq$ 2) conditions, the reddish-coloured AH$^+$ species become predominant[395].

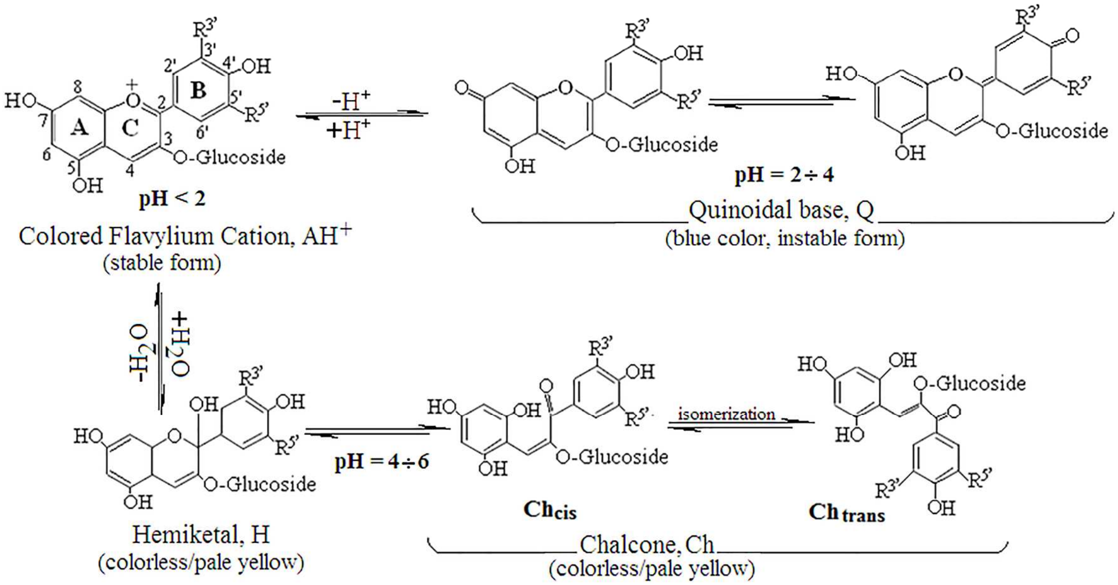


Fig. 9 *pH-dependent structural changes and colour variation of anthocyanins in aqueous solution. AH$^+$ represents the colored flavylium cation that is predominant at acid pH values. Q and H depict the unstable quinoidal basic and the colorless hemiketal specie, respectively, while Ch$_{cis}$ and Ch$_{trans}$, are the isomeric forms of the calchone Ch, species.*

With increasing pH value, the flavylium cation is involved in two parallel reactions: *i)* deprotonation to form the quinonoidal base Q, predominant at pH values between 2 and 4, and *ii)* hydration by nucleophilic attack of water,[396,397] at the charge defective C^2 and/or C^4 positions, followed by proton loss.[396,397]The latter produces a reduction of the AH$^+$ concentration and the appearance of the hemiketal pseudobase, H.[349] Due to the loss of the conjugated double bond between the A- and B-rings, the hemiketal form does not absorb visible light and appears colorless or light yellow.[396,397] With increasing pH values (pH=4-6), the hemiketal forms, due to the opening of the C-ring, the colorless *cis*-chalcone Ch$_{cis}$, which is followed by a slow isomerization to the *trans*-chalcone Ch$_{trans}$, see Fig. 9. Therefore, from the primary flavylium cation structure, secondary quinonoidal or hemichetal structures are derived. Moreover, hemichetal structures can further tautomerise (*i.e.,* migration of a proton, accompanied by a switch of a single bond and adjacent double bond) [396,397] to chalcone species. Tertiary structures, *e.g.,* isopropane that has centred carbon (defined tertiary carbon) attached to three other carbon atoms, can result from molecular associations of primary or secondary forms, either between themselves (self-association)[398] or with other molecules (inter-molecular co-pigmentation).[399,400,401,402]

At equilibrium, the system reported in Fig. 9 behaves as a single acid-base equilibrium between the flavylium cation and a conjugate base, ConBas (defined as the sum of the concentrations of the other species: [ConBas]=[Q]+[H]+[Ch_{cis}]+[Ch_{trans}]).[403] As a consequence, at diverse pH values, which are typically different for fresh and processed vegetables, each anthocyanin will be, most probably, a mixture of equilibrium forms.

Strong research effort has been done to highlight the role of pH values,[404] glucosydic or acyl patterns,[405] as well as solvent effect,[405] on the spectral and colour features (λ_{max}, ε) of anthocyanin pigments. Fossen *et al.,* [404] investigated the colour variation of cyanidin-3-glucoside (Cy 3-glc), see Fig. 10, as representative of typical anthocyanins, over a wide pH range and for a long timeframe. A spectral band shift to longer wavelengths (bathochromic or red shift effect[406]) with pH increase (*i.e.,* from 1.0 up to 8.1) and, a decreasing colour intensity (in the 1.0-5.0 pH range with a maximum intensity at pH =1.0) was observed.[404] Furthermore, at pH values from 1.0 up to 3.1, where anthocyanin occurs mainly in the flavylium cationic form, at least 90% of the colour was stable for ~60 days.[404] Above pH=3.1, the colour stability decrease with degradation at pH≈6.0-7.0,[404] due to the oxidation of the Ch_{trans}.

Giusti and co-workers[405] compared the optical properties of glycosylate acylated and non-acylated Pg derivatives. ε of non-acylated and acylated Pg derivatives ranged from $1.56\cdot10^4$ $M^{-1}cm^{-1}$ up to $3.96\cdot10^4$ M^{-1} cm^{-1}, respectively.[405] Furthermore, depending on the structure of the acylation agent bathochromic shifts of the λ_{max} were observed.[405,406] The structure of sugar substitution was responsible of hypsochromic shifts (blue-shift of the spectral band position of a molecule).[406] The nature of the solvent is also responsible for bathochromic or hypsochromic shift in the absorption bands of anthocyanins and, more interestingly, their capability to disperse pigments depends on the pigment chemical structure itself. Non-acylated pigments have shown changes in both ε and color of the pigments (λ_{max}).[405,407] Torskangerpoll and Andersen[407] studied the influence of aromatic acyl structures on anthocyanins colour and stability at pH values ranging from 1.1 up to 10.5, for a timeframe of 98 days. Their experimental results confirmed that aromatic acyl groups influence the colour and improve stability of anthocyanins in the explored pH range (1.1-10.5).[407]

Dyrby *et al.*[408] investigated acylated anthocyanins from *red cabbage* that have shown low sensitivity to photo-degradation in the 3-7 pH range and thermal stability, with respect to other non-acylated anthocyanins obtained from red grape,[409] black currant[410] and elderberry.[411] These properties were attributed to the complex nature of red cabbage anthocyanins, most of them being di-acylate containing aromatic acids.[408] In the past years, many of the aforementioned vegetables and many others were identified as potential natural source of stable anthocyanins. DSSCs with η up to 3.1% were obtained exploiting anthocyanin-based sensitizer, extracted from roselle.[412] Acylating substituents (see **Fig. 10** c)) stabilize the anthocyanins structure as a consequence of a lower susceptibility of water nucleophile attack and subsequent formation of a pseudobase or a chalcone (intra-molecular co-pigmentation), with respect to non-acylated counterpart.[401,402,413,414]

Molecular co-pigmentation between anthocyanin and other compounds (co-pigments) is an important stabilizing mechanisms of chromophore.[400,401,402,403,415] Generally, co-pigments are rich π-electrons systems able to associate with the electron-poor flavylium ion. Polyphenols such as rutin, quercetin, chlorogenic acid, tannic acid, flavan-3-ol, lignans, stilbenes and many other unknown flavones can act as co-pigments.[415] Other molecules such as organic acids,[400,401,402,415] alkaloid,[399] acyl groups,[416] metallic ions[417] and anthocyanins themselves (self-association),[398,399] have also been identified as co-pigments. In the self-association[398,399] an aggregation between two anthocyanins, one is the chromophore while the other is the co-pigment, takes place.

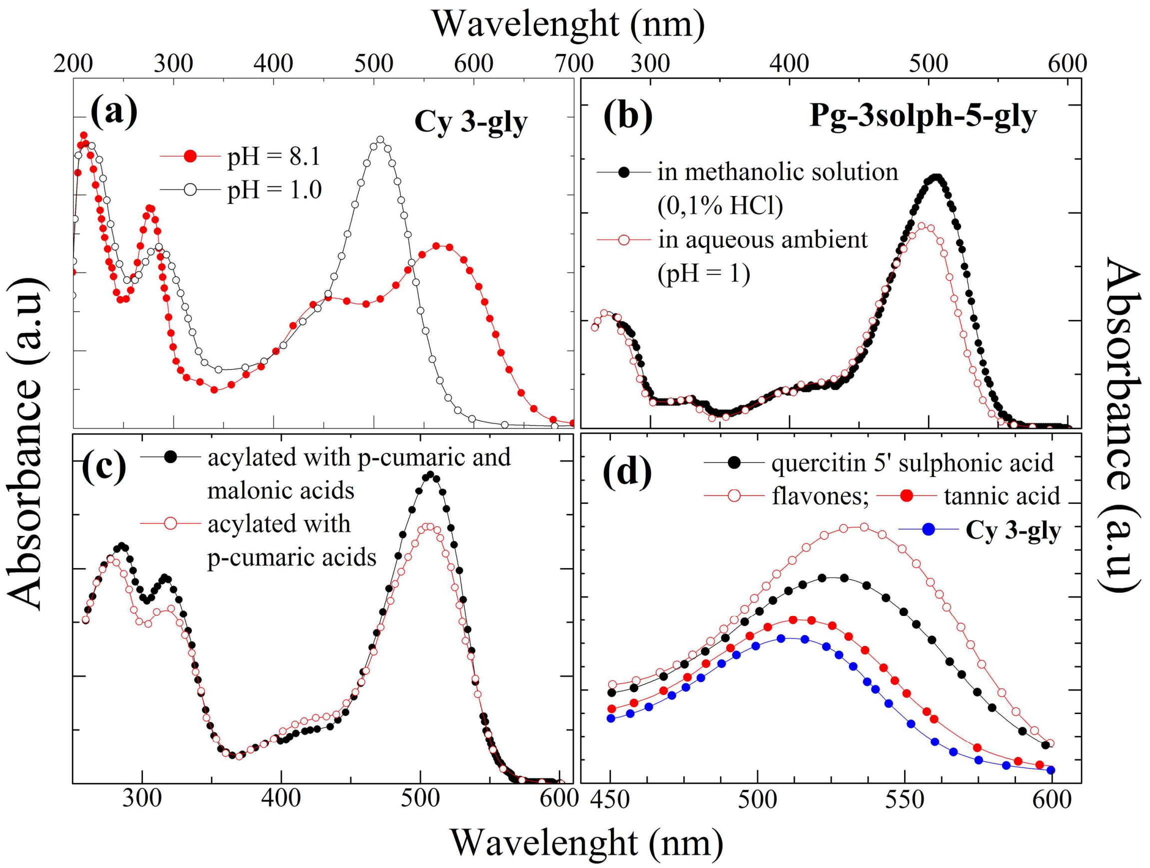


Fig. 10 *Absorption spectra of (a) cyanidin 3-glucoside as cloride salt at two different pH values and (b) spectral characteristic of pure pelargolidin-3-sophoroside-5-glucoside (pg-3soph-5gly) in methanolic (MeOH) and aqueous ambient. (c) Effect of acylating groups on the spectral characteristics of pg-3soph-5gly (as an example). (d) The influence of different copigments types on the absorption spectra (bathochromic and hyperchromic effects) of cyanidin 3-glucoside is also reported in the panel (Data taken from Refs. 404, 405 and 415).*

Co-pigmentation reaction can occurs through *inter*- and/or the *intra*-molecular interactions. In *inter-molecular* co-pigmentation, the most prominent in almost all the anthocyanin compounds,[350,351,401] a π-π interaction takes place through a vertical stacking between the planar structure of anthocyanin chromophores and the co-pigment molecules having delocalized π-electrons.[350,351,401] The result is an overlapping arrangement of molecular orbitals (see Fig. 11), which provides protection to nucleophilic attack of water at position 2 of the pyrylium nucleus, leading to colorless hemiketal and chalcone forms (Fig. 11).[350,351,401] *Intra*-molecular co-pigmentation acts in a similar way to *inter-molecular* one, with the advantage that co-pigment and anthocyanin are covalently linked by linkers or spacers, in a more effective way.[350,351,401]

At given pH values, anthocyanin-copigments have a more intense colouring (hyperchromic effect, *i.e.,* increase in absorbance) and a higher λ_{max}, in the visible spectrum with respect to free (not self-associated) anthocyanins.[418,419] In fact, due the pH sensitivity of anthocyanins, the co-pigmentation through complexes formation determines a colour change in mild acidic solutions (pH= 3-4) where, colourless hemiketal and chalcone forms (see Fig. 9) may be changed into coloured flavylium or quinonoidal species.[47] On the contrary, in strong acidic solutions, anthocyanins are already in the colored flavylium form, therefore in this condition the co-pigmentation is a simple molecular association accompanied by small hypochromic (*i.e.* decrease in absorbance) and bathochromic shifts of the absorption, which do not cause significant colour change.[420] As an example, Gris *et al.*,[421] reported that co-pigmentation with caffeic acid of anthocyanins from grape extracts determine both a bathochromic and hyperchromic shift, in the absorption spectra with respect to free anthocyanins, being the effect dependent on the co-pigment content.[370]

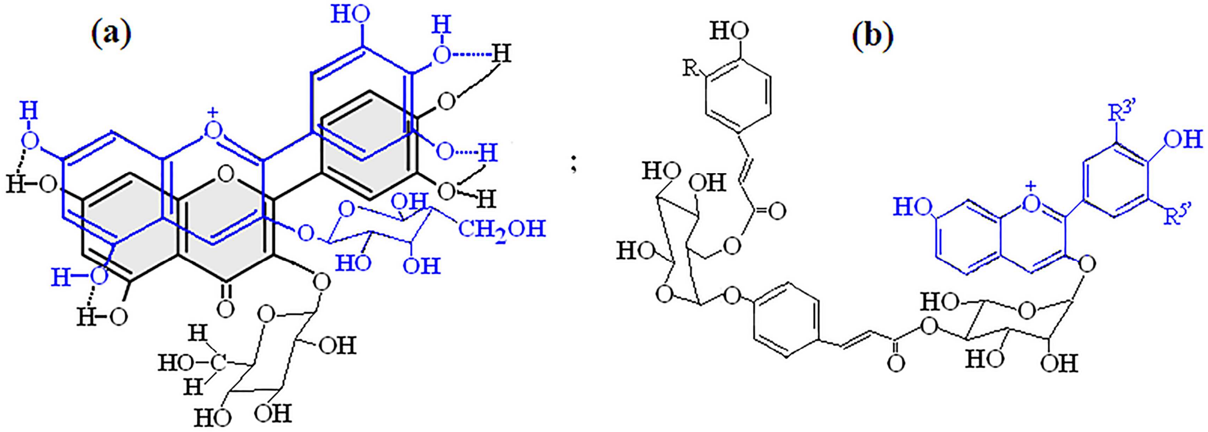
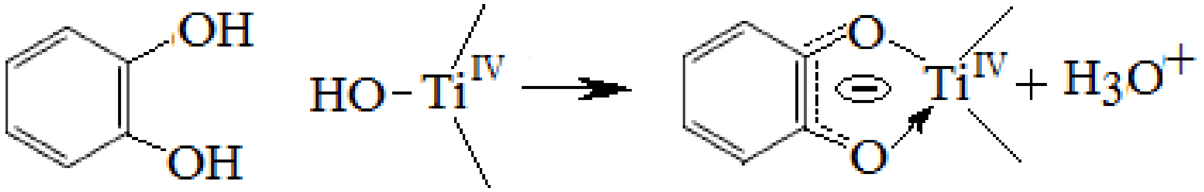


Fig. 11: *Structure of anthocyanin complexation through (**a**) inter- and (**b**) intra-molecular interactions.*

The appearance of intense blue/red colouration in anthocyanins have also been attributed to a metal-complexation reaction between anthocyanins themselves and small metal ions [422,423,424,425] with the formation of very stable compounds. This fact is crucial, for example, for the complexation of titanium ions located at the $Ti0_2$ surface. However, this complexation only occurs if anthocyanins possess a catechol group ($C_6H_{10}(OH)_2$) in their B-ring (*e.g.,* as in the case of Cy, Dp, Ptn).[47] This could be explained by the fact that catechol has a particular affinity for metal ions in high oxidation states.[426] In this context, it has been shown that the chelation (binding of molecules or ions to a metal ion) of Ti(IV) ion by catechol, involves the replacement of a surface hydroxyl group by deprotonated ligand in a mononuclear bidentate geometry which, binds strongly the cathecol to the TiO_2 surface[427,428] (see scheme I). In this configuration, an enhancement of the interfacial electron transfer rates, between cathecol and titanium(IV) ions was observed.[427] Starting from the knowledge on well-known coordination titanium complexes, the binding mode and the surface stoichiometry of the adsorbed species on TiO_2 have been established.[429]



Scheme I: *Schematic description of the complexation reaction between hydroxylated $Ti0_2$ surface and catechol ligand (Adapted from Ref. 427).*

5.1.2 Anthocyanins as photosensitizers

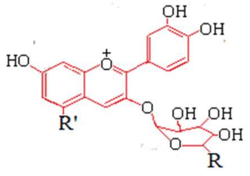
The potential of anthocyanins as sensitizers in DSSCs was firstly proposed by Tennakone *et al.* [42,430]. In these first attempts, the authors used cyanidin, extracted from *anthurium* flower, as dye in a DSSC generating a J_{sc} of ~2.9 mA/cm^2 and an V_{oc} ~435 mV, but with a sudden decay of the photocurrent owing to the degradation of the dye. Although the first results[42,430] indicated that cyanidin-type pigments were not “appropriate” sensitizers for DSSCs, these initial works were fundamental in demonstrating that cyanidin strongly adsorb on the TiO_2 as a result of a highly stable Ti^{4+}/cyanidin complex.[42,430] More importantly, cyanidin has been a model system opening the anthocyanins-based solar cells research field. Afterward, the existence of ultra-fast charge injection processes involving blackberry anthocyanins (a mixture of cyanin 3-glycoside and cyanin 3-rutinoside) has been demonstrated by the Grätzel group.[43,47] Exploiting femtosecond laser spectroscopy, Cherepy *et al.*,[47] observed a transient absorption signal with a rise-time less than 100 femtoseconds due to electrons injected from the dye (blackberry) into the semiconductor. This behaviour was attributed to a strong electronic coupling, via charge-transfer interaction, between the cathecol moiety of the blackberry cyanin and the Ti(IV) sites onto TiO_2 surface.[47] Despite cyanin injects electrons to TiO_2 very efficiently (φ_{in}=0.98),[47] the IPCE and η values achieved by the cell were quite low (19% and 0.56%, respectively).[47] These low IPCE and η values may be attributed to dye aggregation on the TiO_2 nanoparticles that hinder electrons injection by the dyes, as well as to electron recombination and recapture process by oxidized sensitizer and electrolyte mediator, respectively.[47] However, beyond the pivotal works of Tennakone *et al.,*[42] and Cherepy *et al.,*[47], it is worth to emphasize that, different natural dye extracts promote light harvesting at different wavelengths, having a distinct Φ_{inj}. These differences lead to different IPCE values obtained by the dyes therefore, the search for effective dye source has led to the discovery of many natural extracts to be used in DSSCs[43,45,46,337,431,432] (see Table 4). Dai and Rabani[43,45,46] designed a DSSC with TiO_2 sensitized by seed coats of pomegranate (a rich source of anthocyanins pigments) in acid aqueous solution, achieving high quantum yields (Φ=0.74) in combination with photovoltages of ~0.46V. Stability tests of these pigments have shown no decrement of the photocurrent after 24h illumination at 1 sun. The Φ was found to be strongly dependent on the pH condition with an increase from 0.03 up to 0.74 when pH decreases from 5.5 to 1.0.[43] Dai and Rabani also investigated the influence of counter ion (*e.g.,* Na^+) and electrolyte, as well as the presence of glucosidic moiety and the TiO_2 nanoparticles diameter (*i.e.,* 5 and 18 nm) on DSSC performances obtaining the best results (V_{OC}=0.47V, J_{SC}=2.2 mA/cm^2) using 5nm TiO_2 nanoparticles, together with high iodide concentration (2.5M), moderate amount of iodine (0.05M) and Na^+ as counter ion in aqueous ambient at pH=1.[43,45,46] The TiO_2 nanoparticles diameter was found to affect considerably the photocurrent which decreases (from 0.28 to 0.13) with increasing nanoparticles sizes (from 5nm to 18nm).[46] It is worth noting that this behaviour is opposite to that of the ruthenium complexes where the Φ appeared to increase from 0.5 to 0.75 with TiO_2 nanoparticles diameters of 5nm and 18 nm, respectively.[46] A more systematic study was carried out by Zhang *et al.*, [433] investigating the photosensitizing properties of more than 20 different natural dyes (such as, vegetables, bacteria and insects) as dyes in DSSCs. Amongst these different natural dyes, the best performances were achieved with red cabbage extract (in the presence of citric acid and glutinous starch syrup to avoid dye-aggregation) (η=1.51%) and purple sweet potatoes (η=1.1).[337] In the same work, the authors[337] determined the low injection of electrons from the vegetable dye to the semiconductor CB of ZnO with respect to TiO_2. This because the Zn(II), in contrast to TiO_2, have not free *"d"* orbitals, so the coupling between the LUMO of dye and the *"s"* orbital of the metal gives rise to a poor overlap. Hao *et al.* [434] investigated the structure and properties of different family of vegetable dye extracts (anthocyanins, chlorophylls and carotenoids). They determined that anthocyanins, thanks to their hydroxyl and/or carbonyl groups, anchor in a better way with TiO_2 nanoparticles and thus facilitating the electron transfer from the excited state of the dye to the semiconductor CB, with respect to chorophylls and carotenoids.[434] Polo and Iha[48] studied vegetable DSSCs with extracts from Jaboticaba and Calafate fruits, obtaining η of 1.15 and 0.29 for dyes extracted in ethanol and water, respectively. The difference relies on the higher solvation effect of ethanol with the dye molecules with respect to water. Kumara *et al.*[432] using a mixture containing both purified shisonin and chlorophyll components obtained a η of 1.31%. The obtained η is higher than that achieved exploiting individually shisonin and chlorophyll as sensitizer.[432] However, the synergistic effect of mixture of natural dyes is not universal and it is strongly dependent on the nature of the dyes and the charge transfer between the dye molecules of the mixture and the TiO_2 surface. Indeed, Wongcharee *et al.*[343] assembled DSSCs by using vegetable dyes extract from rosella, blue pea flowers and a mixture of them. In this case, the dye composed by the rosella and blue pea flowers mixture has shown η=0.15%, which is higher with respect to the one achieved by blue pea extract (η =0.05%), but lower if compared with rosella extract (η = 0.37%).[343] In this case the authors reported a better charge transfer between the dye and the TiO_2 when they used rosella extract alone instead of the mixture with blue pea.[343] Furthermore, by analyzing the influence of solvent, temperature and pH on the η and stability of the cell, it was also found that an improvement from η=0.37% to η=0.70% can be achieved if the aqueous rosella extract dye is treated at T=50°C and pH=1. A thermo-gravimetric and spectroscopic analysis on TiO_2 films functionalized with cyanidin from black mulberry through sol-gel method,[435] revealed that when linked to TiO_2 surface, cyanidins are stable for temperatures up to 400°C. The study revealed interactions TiO_2/dye occurring during the hydrolysis and condensation paths, rather than after the formation of TiO_2 nanoparticles.[435] Following this procedure, a material with a larger amount of adsorbed dye molecules in relation to the number of titanium atoms was obtained, leading in turn to a possible higher *η* of the cell. Fernando and Senadeera[436] sensitizing TiO_2 with different vegetable pigments containing anthocyanin, realized DSSCs whose η and FF ranged from 0.3% to 1.1% and 54% to 64%, respectively, with IPCE value of 76% for Bush sorrel (*hibiscus surattensis*). One years later, Luo and co-workers[342] utilized Cowberry (*Vaccinium vitis-idaea*), scarlet sage (*Salvia splendens)*, saka siri (*Canna indica L.*), and black nightshade (*Solanum nigrum L.*), to sensitize nanocrystalline TiO_2. The η of DSSCs based on these dyes were rather poor, ranging from η=0.13% for Cowberry to η=0.31% for *Solanum nigrum L*, respectively.[342] A possible explanation for these low η could be correlated to the use of basic components, like tert-butyl pyridine (TBP), to the pH sensitive anthocyanins, which determine consequently a change from the stable flavilyum form to the less stable quinonodial form.[342] Other effects on dye properties, due to TBP addition, are the red-shift of the absorption spectrum,[342] as well as a decrease of the ε and a partial desorption of the dyes from the TiO_2.[41] Zhou *et al.* [437], analysing the photo-electrochemical behaviour of DSSCs sensitized with twenty different vegetable extracts (containing cyanine, carotene, chlorophyll, etc.), reported the best η=1.17% for DSSC sensitized by mangosteen pericarp extract. Mangosteen pericarps are rich in anthocyanins, with cyanidin-3-sophoroside and cyanidin-3-glucoside being the most abundant.[438] η in the range 1.73-1.86% for DSSCs sensitized with Begonia dye extracted from a plant endemic from eastern Hymalayas, have been reported by Singh *et al.*[439]

Nanosecond transient absorption spectroscopy, carried out on anthocyanins sensitized-TiO_2 films in ethanol solution, revealed that the kinetic competition between electron/oxidized dye recombination and oxidized dye regeneration pathways is much more critical with respect to the one in Ru(II) sensitizers.[292] Indeed, in the case of anthocyanin, electrons accumulate in the TiO_2 nanoparticles thus favouring electron/hole recombination.[292] Thus, in order to avoid this recombination effect, the use of a kinetically fast redox couple, such as I_3^-/I^-, is an essential requirement.[292] Calogero *et al.* measured by absorption transient spectroscopy that the dye regeneration was recovered within 650ns,[292] which is longer if compared to the 200ns required for the regeneration of the ruthenium N3-dye. The sensitizing effects of red Sicilian orange, blackberry and eggplant on TiO_2 films were also recently investigated.[39] It was demonstrated that the nature and the extraction procedure of the pigments, as well as the dye aggregation inhibition and the optimization of the photo-anode (adjustment of pH value, use of co-absorber agents), are key to improve η.[39] DSSCs based on concentrated red Sicilian orange extract sensitizers have shown an increase of η from 0.78 up to 1.01% with respect to the ones based on acidified (H^+) orange juice sensitizers (pH<2).[39] DSSCs based on blackberry dye has shown η=1.07%, and a IPCE value of 46%,[39] which is close to an extrapolated theoretical value of 69% obtained by Cherepy *et al.*[47]

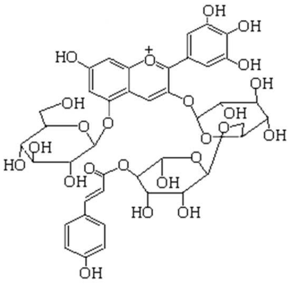
Table 4 summarizes the main results obtained so far with anthocyanin based-DSSCs. The highest η of ~2.9% was recently achieved with the red cabbage extract by Li *et al.*[440].

Table 4: *Molecular structure of anthocyanins and photo-electrochemical data for anthocyanins-based DSSCs under simulated AM-1.5 solar light.*

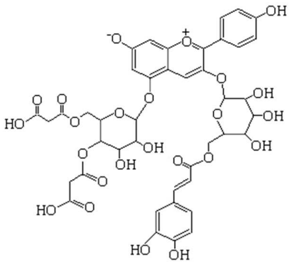
ANTHOCYANINS



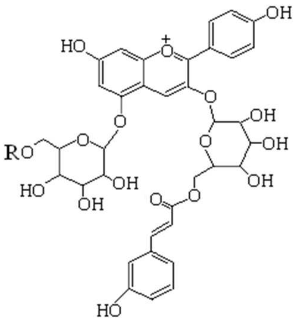
- R = H; R' = OH: Cy 3-*O*-arabinoside
- R = OH; R' = OH: Cy 3-*O*-glucoside
- R=O-CO-COO-CO-COOH; R' = OH: Cy 3-*O*-dioxalyl-glucoside
- R = O-CO-CH2-COOH; R' = OH: Cy 3-O-malonyl-glucoside



Nasium (an anthocyan in *Salvia splendens* flowers)



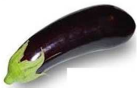
Salvianin (an anthocyanin in *Salvia splendens* flowers)















MOLECULAR STRUCTURE - FRUITS and VEGETABLES -		J_{sc}(mA/cm^2)	V_{oc} (mV)	η(%)	Year	Ref.
Berry	*Blackberry*	2.20	400	0.56	1997	47
		1.00	400	NA	1998	43
		6.53	316	1.13	2012	39
	Blueberry	4.29	360	0.52	2002	337
		3.14	520	0.64	2011	441
	Cowberry	0.40	556	0.12	2009	342
	Mulberry	1.70	444	NA	2003	431
		1.89	555	0.54	2010	441
	Red Mulberry	4.45	340	0.99	2012	39
	Strawberry	2.86	405	0.61	2002	337
	Begonia	0.63	537	0.24	2011	437
		2.33	485	1.86	2013	439
	Canna indica L.	0.82	540	0.26	2009	342
Cabbage	red *C.*	4.70	525	1.51	2002	337
		3.16	624	1.42	2013	442
				2.90	2013	440
	purple *C.*	2.08	660	0.75	2013	499
	fruit of *Calafate*	0.96	520	0.28	2006	48
	skin of *Eggplant*	3.40	350	0.48	2008	40
	Eggplant	3.48	346	0.64	2012	39
	Grape	1.81	427	0.33	2002	337
	Giacchè Grapes	3.06	333	0.57	2012	39
Hibiscus	*H.*surattensis	5.45	392	1.14	2008	436
	H. rosasinensis	4.04	400	1.02	2008	436
	H. sabdariffa	3.55	660	1.60	2012	443
	Ixora macrothyrsa	1.31	403	0.30	2008	436
	skin of *Jaboticaba*	2.60	660	1.10	2006	48
	Lily	0.51	498	0.17	2011	437
	Maple	1.00	650	0.40	2010	444
	Nerium *Oleander*	2.46	408	0.59	2008	436
Orange	red Sicilian *O.*	3.84	340	0.66	2008	40
		5.75	337	1.00	2012	39
	Red *Onion*	0.66	443	0.14	2008	445
	Perilla	1.36	522	0.50	2011	437
	Petunia	0.85	616	0.32	2011	437
	Pomegranade	2.20	440	n.d.	2001	43
	purple sweet *Potato*	5.68	393	1.13	2002	337
	sicilian *Prickly Pear*	8.80	389	2.06	2012	39
	Punica granatum peel	3.34	716	1.86	2012	443
	Radicchio	5.05	325	0.90	2012	39
	Rhododendron arboretum zeylanicum	1.15	402	0.29	2008	436

Shisonin: R =H Malonylshisonin: R = malonic acid (two anthocyanins in *Shiso* leaves)	 		black *Rice*	1.14	551	0.32	2006	434
		Rose	*Rose*	0.97	595	0.38	2011	437
			red *Rose*	4.57	485	0.81	2013	446
			Rosa xanthina	0.63	492	0.16	2006	434
			Rosella	2.72	408	0.70	2007	343
			table *Rose*	4.23	460	0.67	2013	446
			Salvia splendens	0.70	558	0.24	2009	342
			Sesbania grandiflora	4.40	406	1.02	2008	436
			Solanum nigra L.	1.01	540	0.28	2009	342
			Violet	1.02	498	0.33	2011	437

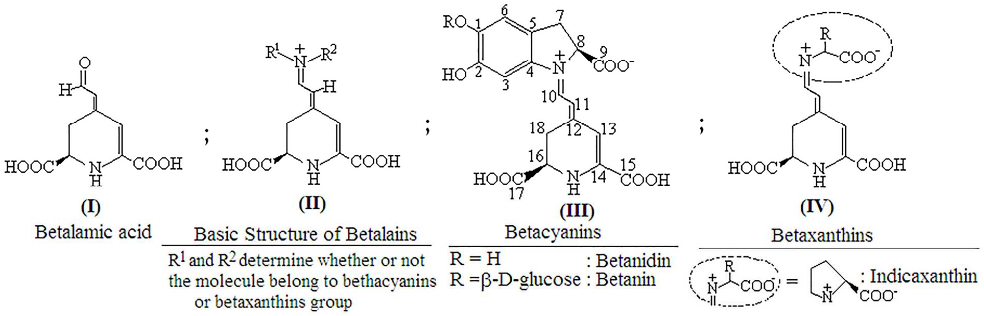
5.2 BETALAINS

Betalains represent another class of water soluble vegetable-pigments of great interest for their potentiality as light absorbers in DSSC technology.[41,447] The colour of flowering plants belonging to Caryophyllales and some Basidiomycota plants are determined by the content of betalain pigments.[448,449] Generally, these pigments have orange and red colour, mostly depending on prevailing dye content: betacyanin and betaxanthin. For example, prickly pear contains betanin and indicaxanthin and is orange, while the Bonel variety of red beet contains betanin and vulgaxanthin exhibiting an intense red coloration.

For long time betalains were erroneously categorized as flavocyanins (betaxanthins) and nitrogen anthocyanins (betacyanins). It was only in 1968 that Mabry and Dreiding[450,451] attributed to both pigments the name "*betalains*", *i.e.*, the beet from which betalains were first extracted.[450,451]

5.2.1 Structure, photochemistry and photophysics

The main betalain contained in red beets is the betanin, which is a betanidin 5-O-β-glucoside (Fig. 12) containing a phenolic and a cyclic amine group.[49]



Samples	*λ_{max} (nm)	*ε [$10^4 \cdot (M^{-1} \cdot cm^{-1})$]	***Samples***	*λ_{max} (nm)	*ε [$10^4 \cdot (M^{-1} \cdot cm^{-1})$]
Betalamic acid	424	6.50	Betanin	535	6.50
Betanidin	542	5.40	Indicaxanthin	482	4.26

Fig. 12 *Structural differences between betacyanin (betanidin and betanin) and bataxhantin pigments. The wavelengths of maximum absorption and the ε are also reported. Adapted from Ref.49.*

Structurally, betalains are immonium derivates of the main chromophore betalamic acid (**I**). In fact, all betalain molecules have a betalamic acid (**I**) moiety bearing substituent R-groups extending from the nitrogen atom (**II**). The nature of these substituent R-groups determine whether or not the molecule belongs to bethacyanins (*i.e.,* betanidin and betanin) or betaxhantins family.[394,452] The glycosidation of one of the substituent pattern at the C1- or C2-position in the benzene ring, differentiate the individual betacyanins (**III**). On the other side, betaxanthins comprise various amino acid or amino-conjugated moieties of betalamic acid. A typical example is the indicaxanthin, a proline-containing betaxanthin (**IV**), one of the first chemically identified betalains found in beet root.[453] Glucose, glucuronic acid and apiose are the most common sugar monomers for the betalain molecules, while malonic and 3-hydroxy-3-methyl-glutaric acids as well as caffeic-, p-coumaric, and ferulic acids represent typical acid substituents.[449] Therefore, betacyanins are considered the condensation product between betalamic acid and *cyclo*-3-(3,4 dihydroxyphenylalanine) (*cyclo*-DOPA) while, the condensation between betalamic acid and amines or amino acids gives rise to betaxhantins. The most common betaxhantins are vulgaxanthin I (glutamine-betaxanthin) and indicaxanthin (proline-betaxanthin), found in red beet and in yellow cactus pears, respectively.[454]

Betalains, contrary to other pigments such as anthocyanins or chlorophylls, have received much less attention for research activity, probably because the red beet has been considered the only edible betalain's source for long time. However, in the last fifteen years the research activity of betalains (*e.g.,* leaf and grain amaranth,[455] prickly pear,[456] beet root,[49] and bougainvillea[457]) have seen a rising interest both for their nutritional aspect (antioxidant[456] and radical scavenging activity[458]) and in natural food colorants.[459,460] In particular, thanks to their strong absorption in the visible part of the electromagnetic spectrum and their ability to act as electron donor, the betalains have been considered good candidates in the processes of "photon induced electron transfer". Differently from the large number of anthocyanins (up to 550),[351] betalains have a lower number (~55), including the red-purple betacyanin pigments (λ_{max} ~535nm), and the yellow-orange betaxanthins (λ_{max} ~460-480nm).[461] The bathochromic shift of the absorption spectrum of betacyanins with respect to betaxanthins is attributed to the presence of the *cyclo*-Dopa aromatic structure in the betacyanins.[462] Furthermore, in the betacyanins, the aglycone betanidin shows a slightly red-shifted absorption spectrum with respect to betanin.

Betalains have high ε (*e.g.* $\varepsilon=6.5\cdot10^4$ $M^{-1}cm^{-1}$ for betalamic acid and betanin)[49] and pH dependent redox properties.[49] Moreover, betalains exhibit a tinctorial strength (or colour strength, *i.e.* the ability of a pigment to maintain its colour upon mixing with another pigment) up to three times higher than anthocyanins.[461] In addition, betalains possess the carboxyl functional groups (–COOH) that is a key requisite to bind to the TiO_2 nanostructure via the formation of ester-type linkage.[452,463] In particular, the betalamic acid possess two –COOH groups, while its derivatives (betanidin, betanin, indicaxanthin) have a further carboxyl group attached to the heterocycle through a sp^3 atom.[464] Upon adsorption of the dye on the TiO_2 surface, the proton of the carboxyl group is transferred to the oxide (*e.g.* TiO_2).[464] Contrary, for anthocyanins the adsorption onto TiO_2 requires the presence of two ortho-hydroxyl-groups that, if from one hand leads to strong electronic coupling and a rapid electron transfer from the dye to the TiO_2, on the other hand assists also the back electron transfer (*i.e.,* recombination process). Nevertheless, a characterization and clarification of the electron injection mechanism from betalains to TiO_2, contrary to the case of anthocyanins and Chlorophylls,[283,465,466] is missing and the current explanations are mainly correlated to the analysis of the IPCE experiments.[39,41,49]

Betalains, in general, show pH stability in the 3-7 pH range[467,468] which, makes them particularly suitable for uses in low-acidity ambient as well as in pH neutral conditions.[467] Moreover, betalains are less susceptible to hydrolytic cleavage (the cleavage of chemical bonds by water addition), see Fig. 13, if compared with anthocyanins.[452] In this context, betalains can be an alternative to the less water soluble anthocyanins which under the same pH conditions lose their photochemical properties due to changes of their colours.[469] Despite their pH stability, at least in the 3-7 pH range,[467] the betalains are sensitive to temperature changes. In fact, at high temperature (50-75°C) and acidic condition (pH<6) deglycosylation, as well as hydrolytic cleavage of the aldmide bond of betalanins and decarboxylation occur,[470] see Fig. 13. A strategy to protect the aldmine bond from cleavage consists in the acylation of betalains with aromatic or aliphatic acid.[471]

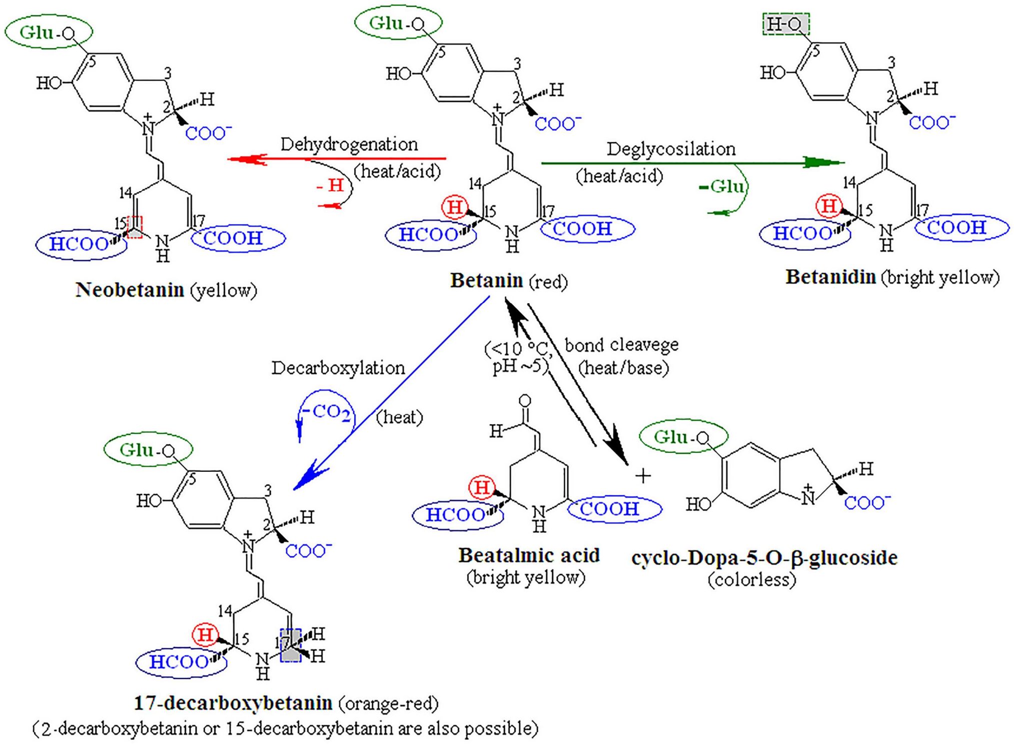


Fig. 13 *Thermal degradation pathways of betanin (as an example) and their corresponding chromatic changes. Dehydrogenation of betanin at C^{15} leads to yellow coloured neobetanin while, decarboxylation at C^{17}causes the apparence of a decarboxybetanin orange-red coulored. By thermal treatment in alkaline ambient cleavage of betanin can also occurs.* (adapted from ref.*468 and 476*).

Another critical parameter of betalains, when used as sensitizer in DSSCs, is their redox potential value and the phenomena/parameters affecting it. In fact, thermodynamically favorable electron injection from the dye to semiconductor requires that the excited state redox potential energy of the dye must be more negative with respect to the one of semiconductor (TiO_2) CB. Since 1985, the redox chemistry of betalains has been investigated,[472] with redox potential values ranging from 0.45 to 0.67 V (vs. NHE). It was found that betanidin can be oxidized more "easily" than betanin. In fact, the redox potential (at pH=6) of the betanidin is slightly lower (0.32 V) than that of the betanin (0.67 V),[49] identifying in the enediol group (alkenes with hydroxyl group on both side of the double bond) the oxidation site for the aglycone.[472] In 2002 cyclic voltammetry measurements by Butera *et al.*[456] reported for betanin three anodic waves (oxidation) at 0.62, 0.84 and 1.22V (vs. NHE). Further, by the similarity of the redox potentials of betanin and indicaxanthin (0.83 and 1.12 V), the authors assumed that the first oxidation of betanin occurs at the aromatic ring.[456]

More recently, Quin and Clark[473] published a theoretical study using the density functional theory (DFT) in order to calculate the ground- and excited-state oxidation potentials of the betalain pigments. From their results, oxidation potential values of 1.0 and -1.3 V (vs. NHE) were obtained for the ground- and excited-state, respectively.[473] This last value identifies energy level higher than the TiO_2-CB (-0.5 V vs. NHE),[190] ensuring the driving force for the photo-induced electron transfer, as well as an easy reduction of the oxidized betanin (regeneration) by the I^- mediator in the DSSC.[478] Moreover, DFT and TDFT (time-dependent density fluctuation theory) analysis have shown that during the HOMO→ LUMO transition, see Fig. 14, the benzene ring, where HOMO is mainly localized, loses electron density while the dihydropyridine (DHP) ring gains charge, indicating a partial excited state electron transfer π-π* transition.[473] Since, the DHP unit is assumed to be attached at the TiO_2 surface via carboxylic groups, the excited state has to be electronically coupled with the acceptor states of TiO_2 leading to an effective charge injection.[473]

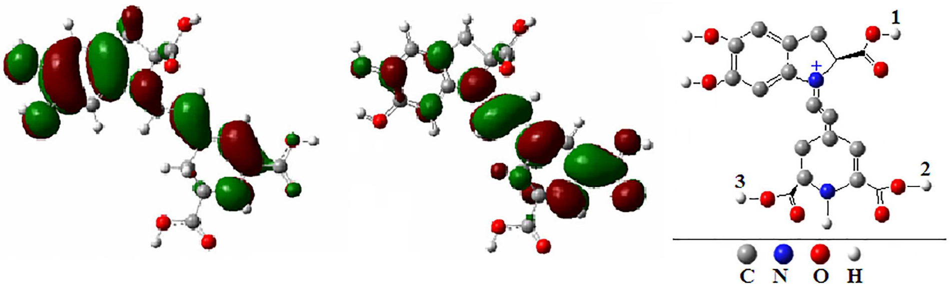


Fig. 14 *HOMO (left) and LUMO (center) for excitation of betanidin [Adapted from ref.473] and label of probable deprotonation sites (right).*

5.2.2 Betalains as photosensitizers

Concerning DSSC applications, the research, on vegetable sensitizers, has been mainly focused on anthocyanin[40,43,45,47] and chlorophyll,[38,344,345,346,347] while fewer reports have been published on betalain pigments.[41,49,50,447]

Betalains, in particular red beet extract, were first used as photosensitizer in DSSCs in 2002,[337] achieving η=0.44% and η=0.014% for TiO_2- and ZnO-based DSSC, respectively. The lower η of ZnO-based DSSC was attributed to the low Φ_{inj} from the excited dye to the CB of ZnO and/or to a higher recombination process (between the injected electron and oxidized dye) with respect to TiO_2-based DSSC.[337] By considering the strong betalains-TiO_2 surfaces linkage (through -COOH groups), the π*-orbital of the –COOH determines a faster electron injection into the CB of TiO_2, than that into ZnO due to the different symmetry.[474] In fact, the TiO_2 CB comprises mainly unfilled *d*-orbitals, while ZnO possesses predominantly *s*-orbital.[474] Thus, the overlap of the extended π*-orbital of betalains is more efficient with the titanium 3d-orbital than with the s-orbital of the ZnO.[475] In 2008, McHale and co-workers[49] published a second report on betalain-derived sensitizers extracted from red beet roots, *i.e.,* betanin, betanidin, betaxanthin and melanin. Amongst the investigated pigments, bethaxanthin-based DSSC has shown the best η (0.19%), while betanin and melanin have lower η (η=0.07% and η=0.05%, respectively). In the same work a η=0.67% was achieved for DSSCs sensitized with betanin and with MePN as solvent instead of AcN.[49] The difference in η between these different extracts from red beet roots can be explained by taking into account the different molecular structures of the aforementioned molecules.[49] Indeed, betanin molecule is larger than the bethaxantin due to the presence of both cyclo-DOPA and glucosidic group which, imply a larger steric hindrance between different betanin molecules (once they are deposited on a surface, *e.g.,* TiO_2 nanoparticles) if compared with betanin ones. As a consequence, a lower number of betanin molecules can be absorbed on the semiconductor molecules (*e.g.,* TiO_2).[460] Acid pre-treatment of photoanode permits higher dye loading (on TiO_2) which decrease the recombination effect at the TiO_2 surface.[49]

Vegetable dye extracted from red turnip (Detroit variety) and Sicilian prickly pear are other sources of betalains.[41] η ranging from 1% to 1.75% were achieved for red turnip extracts.[41] Absorption spectroscopy analysis revealed the presence of the same betanin in both red turnip and prickly pear but, different betaxhantin compounds.[41] Indeed, the red turnip extract contains *vulgaxanthin I* (which absorb at 476-478nm).[467] This determines a red shift of the absorption spectrum of the red turnip with respect to the one of the prickly pear, which contains *indicaxanthin,* absorbing at ~465nm, see Fig. 15. DSSCs fabricated with Sicilian prickly pear have shown lower η=1.26 if compared with red turnip (η=1.7%).[41] The difference in absorption properties of these two dyes, due to different betaxhantin compounds content in the extracts (higher in the red turnip),[41] could not be the key parameter determining the difference in η of these two dyes. Further investigations on Sicilian prickly pear-based DSSC were recently carried out[39] with the aim of understanding the fundamental limitations of this vegetable dye and the parameters such as (thickness of TiO_2 layer, purification procedures and amount of adsorbed dyes on TiO_2, etc.,) that can be tuned to achieve the best conditions to obtain higher η with respect to the ones achieved in the first studies.[41] In this context, Calogero *et al.*[39] attempted to increase the η of Sicilian prickly pear-based DSSC making use of an optimized TiO_2 multilayer (thickness of 13 μm) photo-anode structure in order to reduces the dark current and the recombinations process. Thanks to this photoanode architecture a η =2.06% was achieved.[39] The use of purified betanin from beet root as sensitizer in a TiO_2-based DSSC, permitted to achieve η of 2.7%,[50] which is amongst the highest reported for vegetable dye-sensitized DSSCs. The purification procedure removes the betalamic acid that, although responsible for the strong anchoring of betalains to the TiO_2, hinders electron injection from the dye to the semiconductor (*e.g.,* TiO_2).[50]

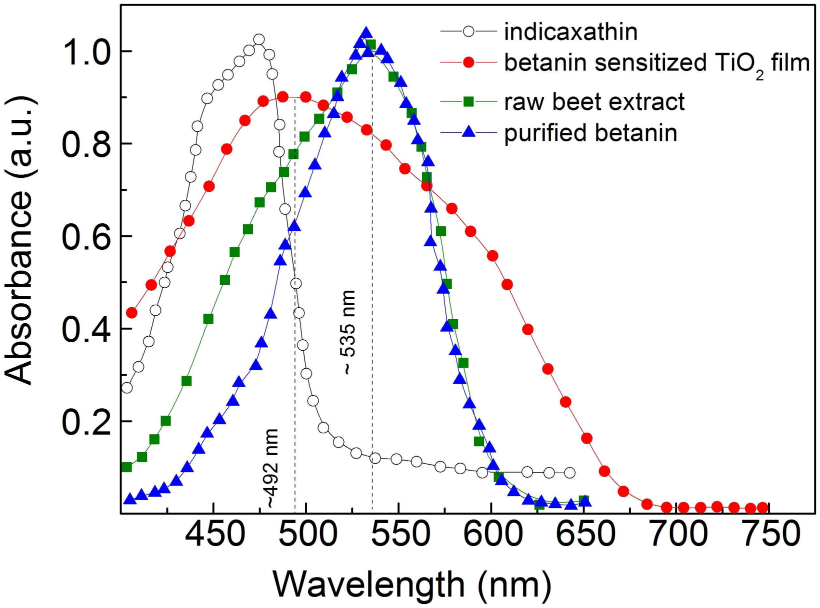


Fig. 15 *Absorption spectra of betanin sensitized TiO_2 film compared to indicaxanthin, raw beet extract and purified betanin.*

Therefore, as reported by Mc Hale and co-workers,[49] the purification of betalain pigments by removing betalamic acid and other impurities improve their sensitization activity.

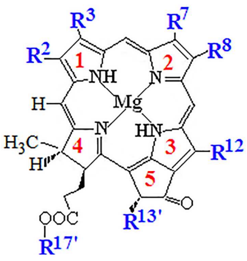
5.3 Chlorophylls

Chlorophyll is a green coloured pigment of leaves and green stems of plants, responsible for the absorption of energy from light during the photosynthesis process[476] where, the light absorbed by chlorophyll transforms carbon dioxide and water into carbohydrates and oxygen ($CO_2+H_2O \rightarrow (CH_2O)+O_2$).[477]

5.3.1 Structure, photochemistry and photophysics

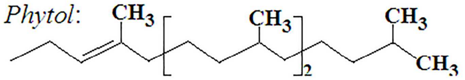
Structurally, chlorophyll refers to a class of cyclic tetrapyrrole,[283,284] similarly to porphyrin and phtalocyanines discussed in Sect. 4.2. Caventou and Pelletier[478] in 1817, identified chlorophyll as a chlorin ring having a magnesium ion at the centre. Unlike porphyrins (see sect. 4.2), chlorophylls have a reduced pyrrole ring and a phytol group, a highly hydrophobic 20-carbon atoms alcohol esterified to an acid side chain. Bacterio(chlorophylls) are similar to chlorophylls, except for the reduction of an additional pyrrole ring that determines a shift (with respect to chlorophylls) of their absorption maxima to wavelengths around 1000nm (NIR).[479]

The basic structure of the aforementioned compounds are depicted in Fig. 16. Although, after Caventou and Pelletier,[478] many new–chlorophyll structures were identified and isolated, such as *Chl-d,*[480] and *Chl-f,*[481,482] essentially *Chl-a* ($C_{55}H_{72}O_5N_4Mg$, cyan), *Chl-b* ($C_{55}H_{70}O_6N_4Mg$, chartreuse) and *Chl-c* ($C_{35}H_{28}O_5N_4Mg$, blue-green), are actually recognized as the most common chlorophyll pigments. In particular *Chl-a* and *Chl-b* are the two most diffused chlorophylls in plants. Their concentration depends on the insolation, *i.e.,* the total amount of solar energy received per unit surface area (MJ/m^2), of the plants. The main difference in the structure of *Chl-a* and *Chl-b* relies in the composition of a single side chain of the cyclic tetrapyrrole (see Fig. 16), which is a -CH_3 in *Chl-a* (blue-green) and a –CHO in *Chl-b* (yellow-green). *Chl-a* and *Chl-b* have a highly stable polycyclic network of alternating single and double bonds (polyenes) conjugated structure which, allows the orbitals delocalization, making chlorophylls ideal photosensitizers.[483]



Chlorophylls (Chls)	R^2	R^3	R^7	R^8	R^{12}	R^{13}	$R^{17'}$
Chl-a	CH_3	$CH=CH_2$	CH_3	C_2H_5	CH_3	$COOCH_3$	Phytol
Chl-b	CH_3	$CH=CH_2$	CHO	C_2H_5	CH_3	$COOCH_3$	Phytol
Chl-c₁	CH_3	$CH=CH_2$	CH_3	C_2H_5	CH_3	$COOCH_3$	-CH=CH-COOH
Chl-c₂	CH_3	$CH=CH_2$	CH_3	$CH=CH_2$	CH_3	$COOCH_3$	-CH=CH-COOH
Chl-d	CH_3	CHO	CH_3	C_2H_5	CH_3	$COOCH_3$	Phytol
Chl-f	CHO	C_2H_5	CH_3	C_2H_5	CH_3	$COOCH_3$	Phytol

Phytol:



Chl-c have a –CH=CH-COOH attached to the ring at C^{17} position

Fig. 16 *Basic structures and oxidation state of natural chlorophylls: Chl-a, Chl-b, Chl-c, Chl-c_1 and Chl-c_2, Chl-d and Chl-f.*

Chemically, chlorophylls are instable in both acid and basic ambient and have a strong tendency towards aggregation and/or interaction with their molecular environment. Differently from the other tetra-pyrrole derivates such as porphyrins[110] and phtalocyanines,[287] the production of which needs complicated and expensive synthesis and purification pathways, chlorophylls and their derivates are cheap and environmentally friendly materials. Coloured and nontoxic derivatives of chlorophylls are utilized as pigments in the cosmetic, textile, and food industries,[484,485] as well as components of luminescent materials.[486]

Beyond the natural abundance and low toxicity, as well as the capability to absorb solar energy in different region of the electromagnetic spectrum, the cyclic tetrapyrrole *Chl*-type dyes possess some fundamental advantages with respect to several inorganic and organic sensitizers. In fact, the excited states lifetime of chlorophylls can be tuned by changing the central metals (Zn, Mg, Ni, Cu, Pd, Fe, *etc.*) [for the case of Ni see as an example Ref. 487] and consequently, the LUMO orbital of the sensitizers can also be adjusted to match the energy level of the CB edges of semiconductors.

The absorption spectra of chlorophylls consist of two main bands, the Soret-band located in the blu region, deriving from the electronic transition with the strongest oscillator strength (2.88 eV) and the Q-band lying in the red region, consisting of Q_x and Q_y transitions (see Fig. 7) at 1.87 and 2.14 eV, respectively.[488] The positions and intensities of Q-bands can be appropriately adjusted by chemical modification of the macro-cycle.[488] Furthermore, chlorophylls display ε up to 10^5 M^{-1} cm^{-1}, amongst the highest observed for organic compounds. As an example, Li *et al.*[489] reported for *Chl-a* and *Chl-b* ε, as high as 7×10^4 $M^{-1}\cdot cm^{-1}$ with strong absorption bands in the blue and red regions of the visible spectrum (λ_{max}, ≈ 430 and 665 nm in *Chl-a*, and 425 and 655 nm in *Chl-b*).

The main panel of Fig. 17 compares the absorption spectra of different chlorophyll pigments based on porphyrin, bacteroclorin and clorophyll tetrapyrrol structure while, the inset shows the absorption spectra for *Chl-b*, *Chl-d* and *Chl-f*.

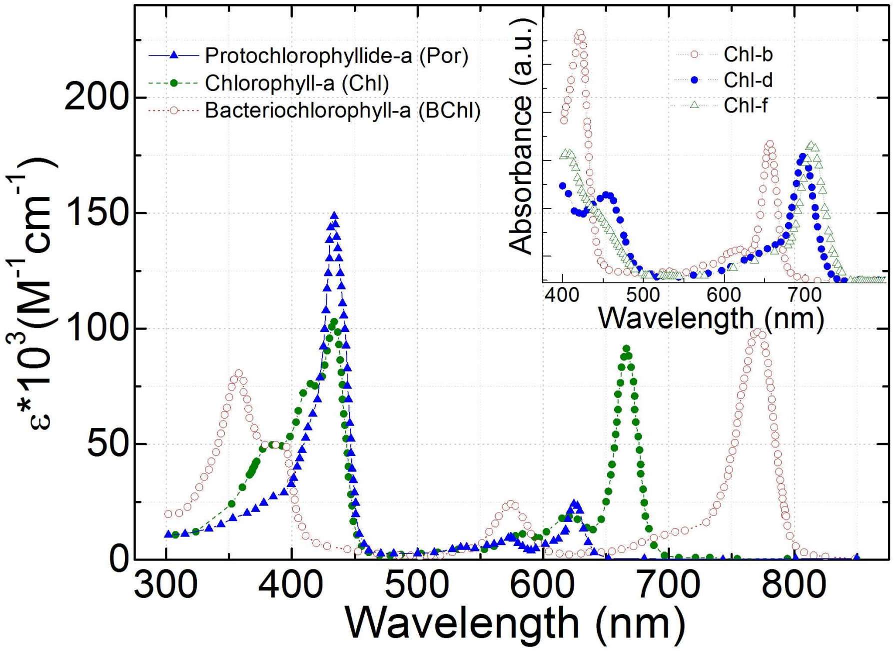


Fig. 17 *Comparison amongst the absorption spectra of naturally occurring Chls having porphyrin, bacteroclorin and chlorophyll macrocycles. Inset: Chl-b, Chl-d and Chl-f . Protochlorophyllide-a is a 17-*CH_2CH_2COOH *analog of chl-*c_1*. Data taken from refs.: 283 and, 489.*

5.3.2 Chlorophyll as photosensitizers

In the first studies on ZnO wide-bandgap semiconductor photosensitized by chlorophylls, Tributsch and Calvin[490,491] reported an extremely low EQE (up to 12.5%). In the following years, Chlorophylls as sensitizers for organic PV cells were the subject of a fervent research activity,[492,493,494,495,496] and EQE up to 30% were achieved by depositing Chl-a monolayers on SnO_2 TC electrodes.[339]

The first investigations on the photosensitization of TiO_2 using chlorophyll derivatives was carried out by Kamat and co-workers.[497,498] In 1993, Kay and Grätzel[38] published an exhaustive study on colloidal $Ti0_2$ electrodes photosensitized with chlorophylls and related derivatives, achieving EQE up to 30%. These low EQE values, may reasonable be attributed to the chlorophylls structure, where the presence of alkyl groups rather than carboxyl or hydroxyl groups make chlorophylls unable to efficiently bind with the nanoporous TiO_2 surface.[434] Kay and Grätzel[38] demonstrated that *chl-a* exhibits a poorer adsorption and sensitization on TiO_2 when compared with chlorophyll derivatives where phytyl group is replaced by carboxylic one. In addition, long alkene chains give rise to strong steric hindrances which prevent an orderly arrangement of the chlorophyll-dye molecules on the TiO_2 molecule surface.[499] Because of these effects, only chlorophyll sensitizers bearing carboxylic groups directly conjugated to π-electrons of the chromophore could exhibit an effective electron injection into the TiO_2 electrode.[283] Wang and Tamiaki[283] also remark that, the carboxyl group location on the macrocyclic structure, with respect to its x- or y-axis direction, affects the absorption characteristics and the molecular orbitals of chlorophylls. Based on these considerations, beyond the light-harvesting ability, *Chl-c* (c_1 and c_2) possessing a wide electron density at the position of -COOH group appear as the most favourable sensitizer for DSSC applications. The method of isolating *Chlc*$_1$ and *Chlc*$_2$ from *Chl a* and carotenoids is a well-known procedure, being developed by Jeffrey in 1972.[500]

Wang *et al.*[346] investigated two different types of Chl-c (c_1 and c_2) together with their oxidized forms (c_1' and c_2') isolated from the *undaria pinnatifida* seaweed. The TiO_2-based DSSCs fabricated with these sensitizers achieved η values of 3.4% and 4.6% for *Chl-c*$_1$ and *Chl-c*$_2$, respectively, and η=2.5% and η=2.6% for their oxidized forms (*Chl-c*$_{1'}$ and *Chl-c*$_{2'}$, respectively).[346] From the experimental results of NOE (Nuclear Overhauser Effect) correlations, nuclear magnetic resonance (NMR), UV-visible and mass spectroscopies, the high η of DSSC using Chl-c_2 sensitizer was attributed to several factors.[346] First, the extended conjugated system resulting in higher electron densities, then the favourable configurations of the peripheral vinyl carboxyl group with respect to other *Chl-c* and finally the absence of dye aggregation.[346] These results set a relationship between molecular structure, local electron density and photosensitizer properties of the different *Chl-c* types.[346] Moreover, the absence of dye aggregation influences the singlet-triplet transition annihilation.[213,501,502] The annihilation process limits the lifetime of singlet excitons, which consequently can reduce the η of the DSSC.[503] In Fig. 18 are reported the ε (Fig. 18 a), absorption spectra (Fig. 18 b) together with the IPCE profile (Fig. 18 c) and the I-V curve (Fig. 18 d) of Chl-c_1 and Chl-c_2.

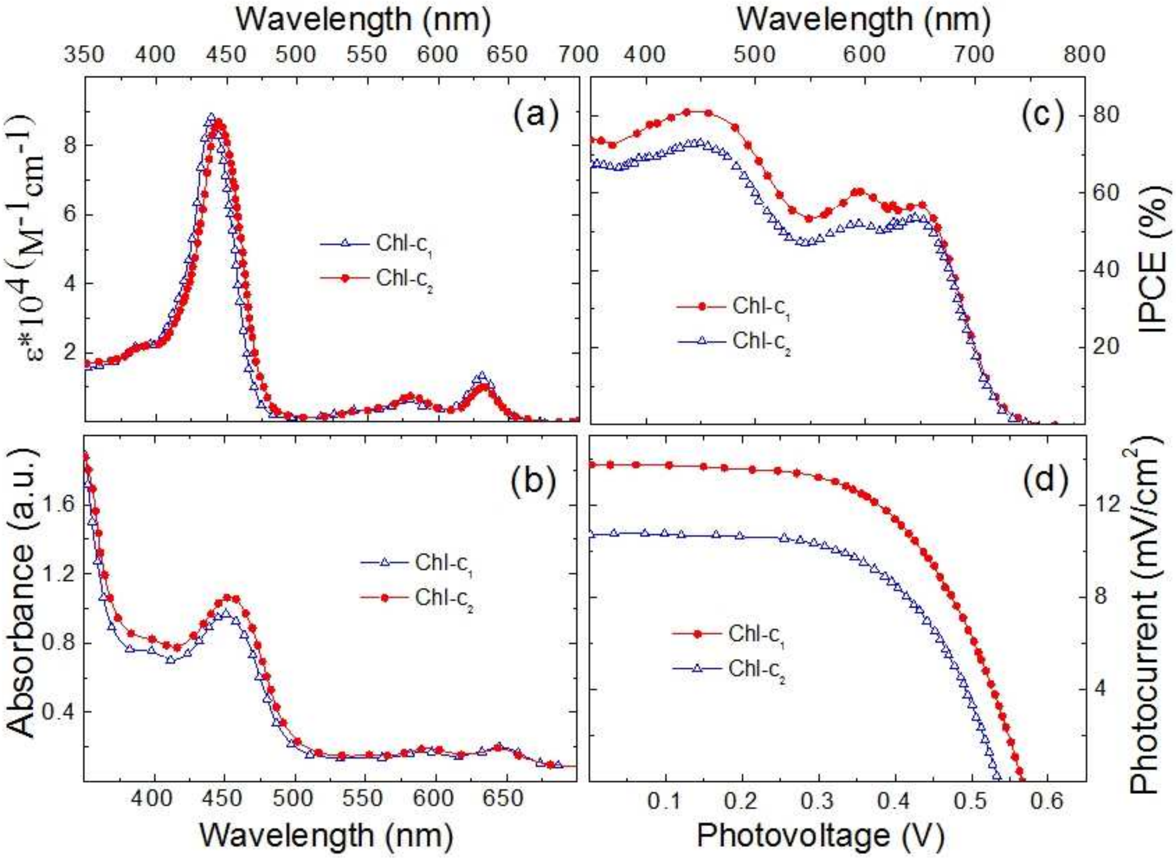
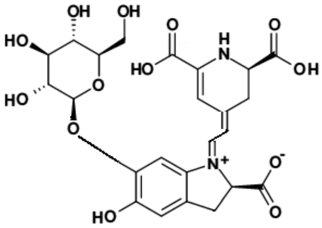
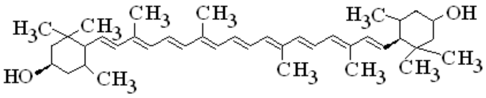
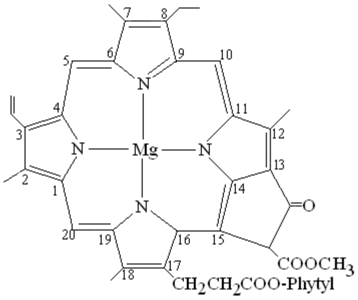


Fig. 18 *(a) Absorption spectra of Chl-c1 and Chl-c2 in solution and (b) on the* TiO_2 *layer. (c) IPCE (%) curves and (d) I/V curves of* TiO_2 *based DSSC sensitized with Chl-c1 and Chl-c2 dyes. (Data taken from: Ref. 346).*

Table 5 summarizes the main results on the photo-electrochemical properties of chlorophylls, comparing them with the ones of carotenoids and betalains.

Table 5: *Photo-electrochemical data for betalains-, carotenoids- and chlorophylls-based DSSCs @ 1 sun irradiation.*

BETALAINS / CAROTENOIDS / CHLOROPHYLLS

			J_{sc} (mA/cm^2)	V_{oc} (mV)	η (%)	Year	Ref.
   	*Betalains*	Red beet	2.90	400	0.44	2002	337
			2.42	440	0.67	2008	49
			13.91	360	2.71	2011	50
		Red Turnip	9.50	425	1.70	2010	41
		Sicilian Indian Fig	2.70	375	0.50	2010	41
		Wild Sicilian Prickly pear	9.40	350	1.26	2010	41
		Wild Sicilian Prickly pear	8.80	389	2.06	2012	39
		Bougainvillea	2.10	300	0.36	2010	41
		Red BG	2.34	260	0.45	2011	447
		Violet BG	1.86	230	0.31	2011	447
		Purified Red BG	2.33	260	0.49	2011	447
		Red BS	2.29	280	0.48	2011	447
		BS	1.88	250	0.35	2011	447
		BS	2.34	260	0.45	2012	447
	Carotenoids	Crocin	0.45	580	0.16	2007	504
		Annatto	1.10	570	0.37	2010	505
		Yellow Gardenia	0.88	580	0.34	2013	506
	Chlorophylls	Green tea	0.98	412	0.19	2002	337
		Kelp	0.43	441	0.12	2006	434
		Wakame	13.8	570	4.60	2007	346
		Spinach	0.46	550	0.25	2010	441
		Ipomoea	0.91	540	0.36	2010	441
		Bamboo	1.90	670	0.70	2010	444
		Wormwood	2.30	670	0.90	2010	444
		Pomegranade Leaves	2.05	560	0.59	2010	441
		Bougainvillea	3.23	500	0.62	2011	441
		Wormwood	1.96	585	0.54	2013	499

BG= Bougainvillea glabra; BS= Bougainvillea spectabilis

5.4 Other vegetable dyes

In addition to anthocyanins,[40,43,45,47] betalains[49] and chlorophylls[38,346] other vegetable dyes (such as carotenoid,[504,505,506] cochineal,[507] quercetin,[508] etc.) have been explored as sensitizers in DSSCs.[509,510] In this section we discuss the photo-physical (chemical) properties of such compounds, focusing on the recent efforts made towards the identification of "appropriate" additives for the improvement of cell performance (*i.e.* η) without causing dye degradation.

Similarly to anthocyanins[40,43,45] and betalains[49] the addition of carboxylic acid (*e.g.*, citric, tartaric and acetic acid) determines bathochromic or hyperchromic shifts, as well as the sensitizing activity of other vegetable dyes, such as carotenoid,[504,505] cochineal,[507] quercetin[508] adsorbed on TiO_2 surface.[39] On the contrary, basic components, such as NaOH or NH_3 and their derivatives,[34] are known to cause desorption of the dye from the TiO_2 surface resulting in the collapse of the cell performances. In this framework, Ito and co-workers[510] have demonstrated that the treatment of monascus yellow dye (extracted from red yeast rice fermentation) with CH_3COOH greatly enhance the η of the solar cell. In their report the authors observed that the absorption peak of the monascus yellow-sensitized TiO_2 electrodes shifts towards shorter wavelengths greatly increasing its intensity,[510] see Fig. 19 a). A similar increasing trend was also observed in the IPCE curve whose maximum value, almost close to zero with no acid treatment, grows up to 47% in the presence of acetic acid,[510] see Fig. 19 b). These features, justified the hypothesis of a strong interaction between the hydroxyl groups of the dye molecules and the nanocrystalline TiO_2 surface, favouring a more effective electron injection on the semiconductor surface.[510]

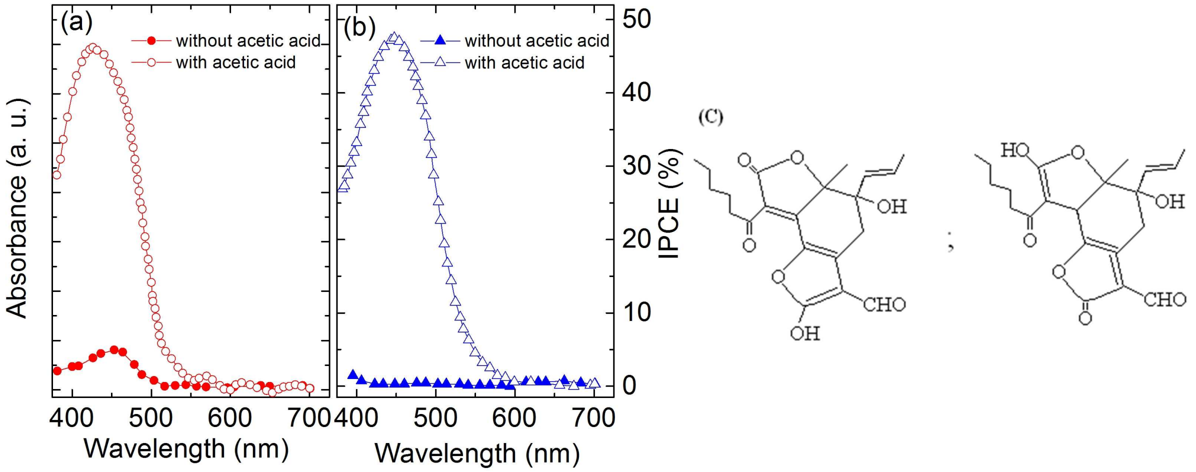


Fig. 19 (*a) UV-Vis absorption and b) IPCE spectra of Monascus yellow-sensitized TiO2 electrodes with and without the treatment of the dye solution with acetic acid. (data taken from Ref. 510). c) Molecular structures of dye molecules in Monascus yellow.*

In addition, from the small absorption peak of the TiO_2 electrode without acetic acid treatment, the authors[510] hypothesized chemical and physical (van der Waals) adsorption pathways depending on the chemical treatment, *i.e.*, with or without acid, respectively. The protons coming from the acetic acid, strengthen the chemical bonding between the dye and the TiO_2 surface, resulting in the efficient injection of photo-excited electrons from the dye to TiO_2.[465,466] After optimizing photo-anode and acidity condition, the assembled DSSC has shown a η=2.3%.[510]

In 2011, Agarkar[511] *et al.* tested nontoxic and biocompatible vegetable dye-sensitizer based on isobutrin pigments extracted from *Butea monosperma* flower, see Fig. 20. Isobutrin is a yellow pigment belonging to the *chalcones*, a subclass of the flavonoids family.[511] Chalcones are aromatic ketones that form the central core of a variety of important biological compounds.[512]

Structurally, chalcones consist of open-chain flavonoids in which two aromatic rings are joined by a three-carbon α, β-unsaturated carbonyl system,[513] see Fig. 20. Compounds with chalcone-based structure are known to have anti-inflammatory,[514] anti-bacterial[515] and anti-tumor activities.[516,517] Butea monosperma flower contains several flavonoidal compounds (butein, palastrin, isobutrin, butrin, etc.) the most abundant of which is the isobutrin (tetra-hydroxy-chalcondiglucoside, $C_{27}H_{32}O_{15}$).[511]

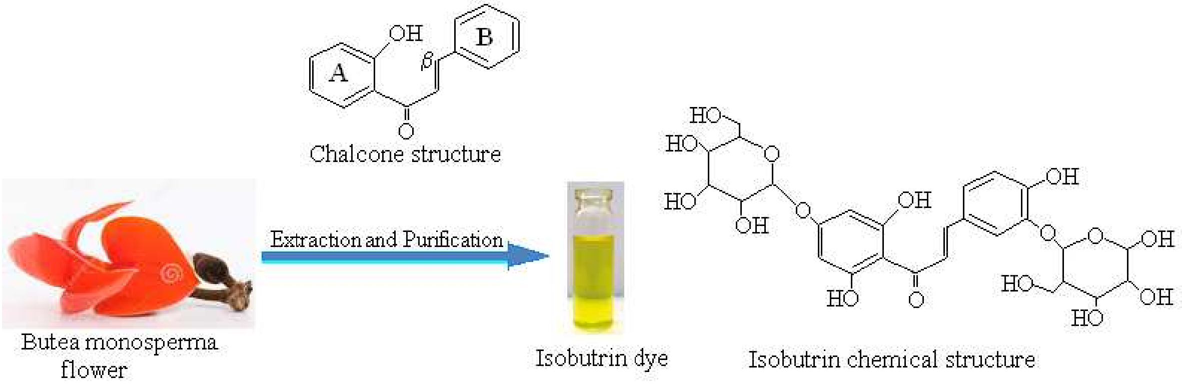


Fig. 20 *Butea monosperma flower and Isobutrin dye extracted with the corresponding molecular structure. The chemical structure of chalcone is also reported for clearness.*

Agarkar and co-workers obtained η=1.8% using purified isobutrin as dye in DSSCs.[511] Moreover, they observed that the chelation reaction (see sect. 5.1) between isobutrin dye and the Ti ions results into a strong dye-TiO_2 charge-transfer band in the visible region.[511]

Carotenoids, organic compounds which are commonly split in two sub-classes, xanthophylls and carotenes, are a further promising class of naturally occurring pigments suitable as sensitizers in DSSC.[518] The molecular structure of carotenoids determines their colouration, ranging from light yellow to red. Structurally, carotenoids are made of long polyene chains which can be terminated by rings and, may contain (*e.g.,* xanthophylls) or not (*e.g.,* carotenes) additional oxygen atoms. Carotenoids basic structure can be changed/tuned in a large variety of ways, primarily by cyclization of the terminal groups or by the introduction of oxygenated functional groups.[518] The possibility to tune the molecular structure of carotenoids resulted in a family of over 600 different compounds.[519,520]

The most striking properties of carotenoids, such as chemical reactivity and light absorption properties,[518] are due to the long central part of the molecule, constituted by alternating single and double bonds.[518] These bonds form a conjugated system in which, the π-electrons are delocalized over the entire length of the polyen chain.[518] Fig. 21a) shows the basic structure of three naturally occurring carotenoids (Lycopene, β,β-carotene and 8'-apo-β-caroten-8'-oic acid -ACOA-). Some common end groups found in natural carotenoids are shown in Fig. 21b).

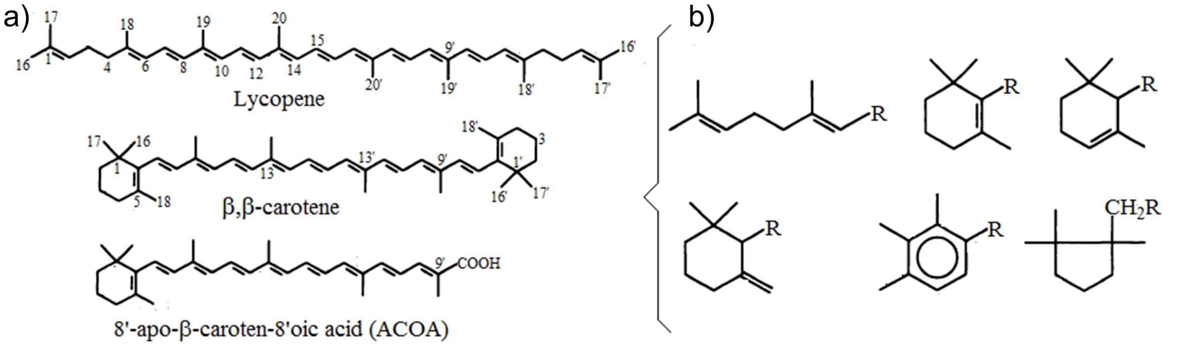


Fig. 21 *Basic structure of an acylated (Lycopene) and a dycylate (b,b-carotene) carotenoids together with the ACOA carotenoid used by Gao et. al. (ref. 302). On the right side of the figure, some of the most common end groups found in natural carotenoids are also sketched.*

The light harvesting ability of carotenoids pigments in the photosynthesis of higher plant[521] to mediate electron transfer,[522,523] as well as their characteristic light absorption in the range of 380-520nm, makes them potential sensitizer materials in PV applications and other artificial photochemical devices.[524] The photoconduction characteristics of carotenoids and the production of charge carriers by ligth excitation,[525,526,527] as well as their properties of triplet or singlet states quenching through energy transfer, [528,529 530] intramolecular charge-transfer,[531] charge separation in synthetic molecular dyads and triads[532,533,534] (covalently coupled chromophoric arrays in a single molecule of high symmetry, see sect. 6) and photo-induced electron-transfer to solvent molecules[535,536] have been extensively studied. As sensitizers in DSSCs technology, carotenoids appear capable to transfer electrons from the excited states of the sensitizer to the CB of semiconductor.[537] An early proof on the carotenoids capability to work as photosensitizers in DSSCs was given in the 2000s by Gao, Bard and Kispert.[338] They designed a cell using a nanocrystalline-TiO_2 electrode sensitized with ACOA, demonstrating the possibility to generate stable PV currents upon ligth irradiation. A J_{SC} of 4.6 mA/cm^2 (upon a 40 mW/cm^2 incident light beam at 426nm) with an IPCE=34% and a V_{OC} of 0.15 V were measured.[338] An ordered monolayer structure of the TiO_2-bound carotenoid was also hypothesized.[338]

Since then, carotenoids have been used in DSSCs[504,538] and η values up to 2.6% were achieved.[539] Wang *et al.,* using carotenoids in combination with chlorophyll derivatives, realized DSSCs with η value up to 4.2%.[540]

The influence of the carotenoid chain length, as well the effects of surfactant addition (*e.g.* with deoxycholic acid, a bile salt surfactant[541,542]) on the electrons injection efficiency from carotenoid dye to TiO_2 surface was also investigated by Wang *et al.*[543] Their fabricated TiO_2-based DSSC using 100% carotenoic acids (without surfactants), having a number of conjugated double bonds (n) ranging from 5 to 13, have shown the highest η (2.5%) at n =7 (CA7), the optimal length for carotenoids in DSSCs applications. Furthermore, based on their experimental results, Wang *et al.*[543] assumed a *η* values dependence by a singlet-triplet annihilation reaction of the dye molecules, as was further stressed in a following report.[539] In 2007, Yamazaki *et al.*[504] used crocetin (8,80-diapocarotenedioic acid) and crocin (crocetin-di-gentiobioside) carotenoid, as sensitizers in their TiO_2-based DSSCs, in order to investigate the influence about the presence or absence of carboxylic groups on the photo-electrochemical DSSC performance. The measurements revealed a higher ability of crocetin (which contains carboxylic groups) to bind the TiO_2 surface.[504] This translates in a higher η =0.56% of crocetin with respect to crocin (η =0.16).[504] The lower PV performances of crocin was attributed to both the absence of carboxylic groups and the presence of sugar moiety on the molecular skeleton.[504] The absence of carboxylic groups determines an inefficient linkage dye/semiconductor and thus a low effective charge injection process, while the presence of glucoside moieties hinders the absorption of the dye, due to steric hindrance, onto the TiO_2 nanoparticles surface.

Another carotenoid of potential interest as sensitizer for DSSCs is the extract of achiote (or annato) seeds,[505] a tropical evergreen shrub (*Bixa orellana*) native to the tropical areas of the Americas. From the achiote seeds, a dark-red extract is obtained, which is extensively used as dye for food colouring[544,545] as well as for textiles,[505] varnishes,[505] cosmetics,[505] tattoos[505] and pharmaceutical applications.[505] The major component of the pericarp extract (~80%) is the carotenoid *cis-bixin* or *α-bixin* ($C_{25}H_{30}O_4$,) with the remaining ~20% including *trans-* and *cis-norbixin* ($C_{24}H_{28}O_4$), reported in Fig. 22a) and Fig. 22b), respectively. Cis-bixin is the mono-methyl ester of the water soluble cis-norbixin di-carboxylic acid and contrarily to the latter, is water insoluble due to the presence of the methyl ester group ($-COOCH_3$) at one end of its molecular chain.

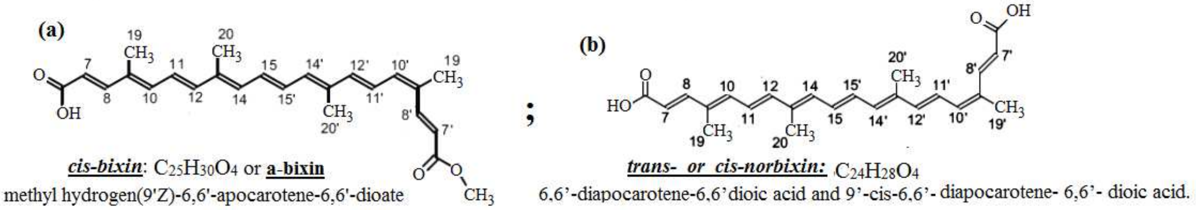


Fig. 22 *Chemical structure of the main pigments in the pericarp of the achiote seeds, a) cis-bixin and b) cis-norbixin apocarotenoids.*

Due to the vast conjugated system, the bixin chromophore exhibits strong absorption band above 400nm (see Fig. 23), due to an electronic-dipole transition oriented along the axis of the molecule. The energy and intensity of the absorption band in the 320-380nm range (so called cis-peak) depends on the position and number of the cis-bonds.[546,547] Despite the characteristic solvent dependence of the absorption spectra in polyene compounds,[548] the ε of the bixin cis-peak has been measured to be $1.24\cdot10^5$ $M^{-1}\cdot cm^{-1}$ and $1.35\cdot10^5$ $M^{-1}\cdot cm^{-1}$ in benzene and ethanol solution, respectively.[547] Moreover, the ε of the band above 400nm, see Fig. 23, is higher than that of cis-peak, and experimental measurements[506] have given $\varepsilon = 1.9\cdot10^5$ $M^{-1}\cdot cm^{-1}$. This value is higher than that of the N719 ($=1.36\cdot10^4$ $M^{-1}\cdot cm^{-1}$).[188] The norbixin, in the same spectral range, has shown $\varepsilon=1.4\cdot10^4$ $M^{-1}\cdot cm^{-1}$, thus quite similar to that of N719 one.

Taking into account that one of the major factor determining the η of the TiO_2-based cells is correlated to the maximum ε of the sensitizer, the high ε value of the bixin dye, in the blue and green region of the electromagnetic spectrum, should enable fabrication of cells with very high η. However, when bixin-sensitized was integrate in DSSCs, the achieved η was quite low, *i.e.*, η=0.53%.[505] As reported by Gomez-Ortiz *et al.*, [505] this low η, contrary to the high ε value, of bixin dye could be explained by: ***i***) relatively short life-time of the excited state due to the symmetrical molecular structure, ***ii***) weak electronic interaction between the dye (*e.g.*, in the excited state) and semiconductor CB, ***iii***) dye-multilayer deposition and possible polymerization, leading to a decrease in conjugation and, hence, a lowering of ε in the visible. Furthermore, the low absorption in the red region of the electromagnetic spectrum, see **Fig. 23**, is a further disadvantage for the use of these carotenoids in DSSC applications.

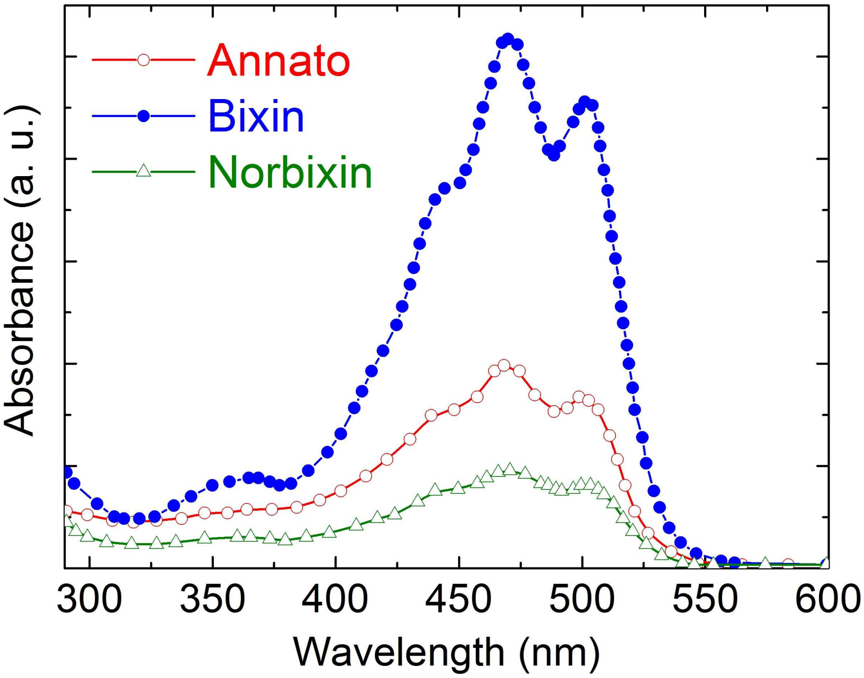


Fig. 23 *UV-Vis absorption spectra of cis-bixin, annatto extract and cis-norbixin. Adapted from Ref. 505.*

With the aim to always investigate new materials able to improve efficiencies and reduce costs, a novel and promising DSSC using a redox couple Fe^{2+}/Fe^{3+} (ferrocene) in AcN solvent as liquid electrolyte and quercetin, alizarin and luteolin pigments as natural sensitizers, has been recently, designed[509]. The Fe^{2+}/Fe^{3+} redox couple was chosen for its more favourable redox potential with respect to I_3^-/I^-,[549,550] which should result in a larger energy level difference between the Fe^{2+}/Fe^{3+} redox and TiO_2 CB [551]. Furthermore, Fe^{2+}/Fe^{3+} couple does not corrode the electrodes thank to its chemical inertness towards oxygen during manufacturing.[509] Quercetin, alizarin and luteolin dyes extracted from Hypericum perforatum, Rubia tinctorium L. and Reseda luteola plants, respectively, were chosen for their broad absorption spectra ranging from 250 to 650nm. Indeed, quercetin extract has two intense absorption bands in the UV region with maxima at 268nm and 412nm (see Fig. 24a)), while alizarin and luteolin exhibit a broad and strong absorption at around 580nm (Fig. 24 b)) and 354nm (Fig. 24c)), respectively.[552,553] The absorption bands around 300nm and 450nm can be attributed to the π–π* transition and, intramolecular charge transfer (ICT) between the donor and the acceptor, respectively.[554,555]

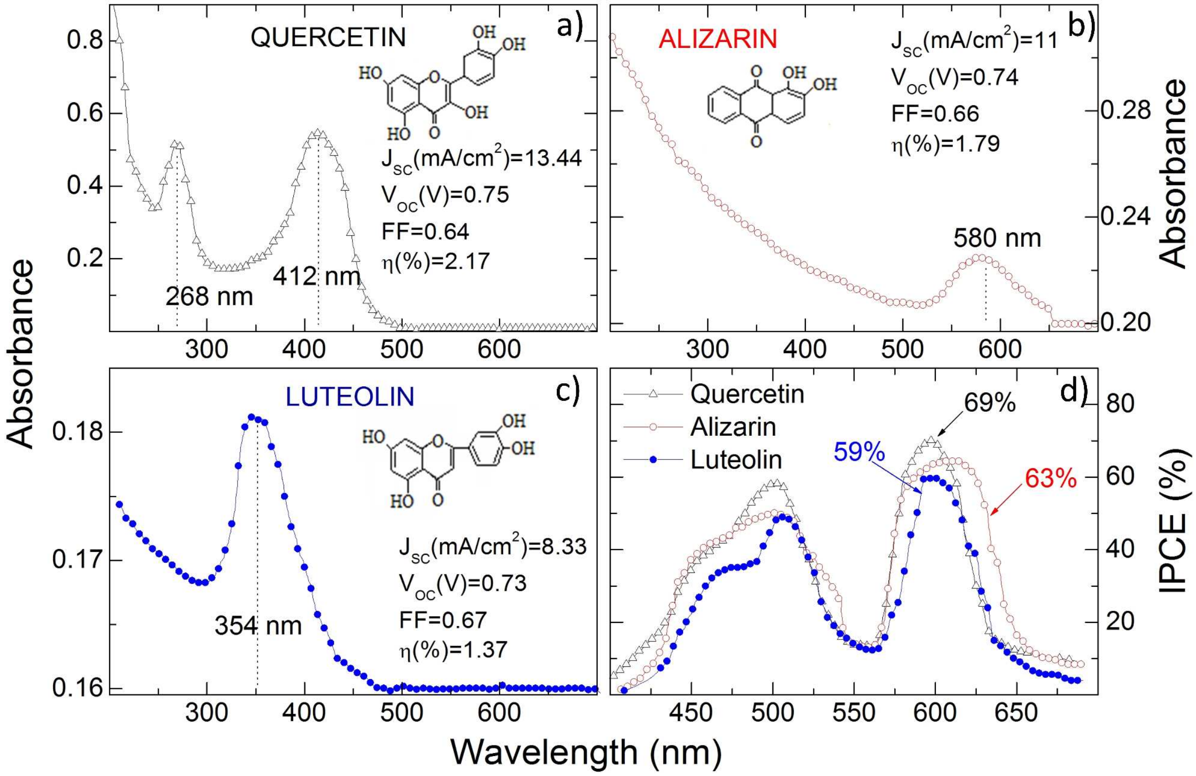


Fig. 24 *Absorption spectra and molecular structures of (a) quercetin, (b) alizarin and (c) luteolin. (d) IPCE spectra for DSSCs fabricated exploiting the aforementioned molecules as sensitizers and ferrocene as electrolyte. (Adapted from ref. 509)*

Quercetin, alizarin and luteolin dyes, when assembled in DSSCs, have shown IPCE values in the wavelength range 580–600nm of 69%, 63% and 59% (see Fig. 24 (d)), respectively. The quercetin dye has also shown the best PV performance with η=2.17%, higher compared to those of alizarin (η = 1.79%) an luteolin (η =1.37). The best performances of quercetin-based DSSC are due to a higher intensity and broader range of light absorption of the dye molecules onto TiO_2. Moreover, the hydroxyl group on the C3 atom of the quercetin molecule C-ring affects the distribution of the electron density and the molecular dipole moment enhancing the sensitizing dye performance.[112] The donor ability of the hydroxyl group increases the dye dipole moment and increases both its ground (HOMO) and excited state (LUMO) energies, favouring the charge separation. Pina *et al.* [349] also argued that the C3 position has a prominent role regarding the dye colour and absorption properties in the flavinum compounds. The authors have investigated pelargonidin and luteolinidin, having similar structures with the difference of a single –OH group in C3 position of pelargonidin.[349] Pelargonidin has shown a more broad red shift absorption compared to luteolinidin.[349]

6 Synthetic analogues of vegetable dyes

As herein reviewed, vegetable dyes are promising for their use as-sensitizers in DSSC technology.[38,39,40,42,43,44] A plethora of literature exists about the ability of vegetable dyes to tune their optical properties (*e.g.*, colours[469] and ε[41,405,407]) depending on external factors (pH,[382,404] temperature,[383,470] peripheral groups,[307,556,557] etc.). In this framework, a bio-inspired strategy has been followed in order to produce, with adequate structural modifications, quasi-natural biomimetic sensitizers having optical properties comparable to those of natural extracts.[351,558,559,560,561,562] In Ref. 112 quasi-natural biomimetic compounds based on flavylium structure have been proposed, see Fig. 25. The introduction of different electron donor/acceptor groups in the flavylium molecular structure has been analyzed both theoretically and experimentally.[112] Diethylamine unit in position 7 of the flavylium core expands the dye π-conjugation increasing the effective electron injection from the dye to the TiO_2 CB.[112] The diethylamine donor group acts as an electron donor,[112] while the catechol and the benzopyran systems constitute the acceptor and the π bridge, respectively, defining a donor–π–acceptor structure (D-π-A).[563]

Dye-sensitized solar cells based on these novel structures have shown η ranging from 0.63%[112] up to 2.15%.[112] The best PV performance was obtained by a DSSC based on a 7-(N,N-diethylamino)-3',4'-dihydroxyflavylium (see Fig. 25), achieving η=2.15% and IPCE = 51%, a value which is (18%) lower with respect to the theoretical limit (IPCE =69%) predicted by Grätzel and co-worker for natural anthocyanins.[47]

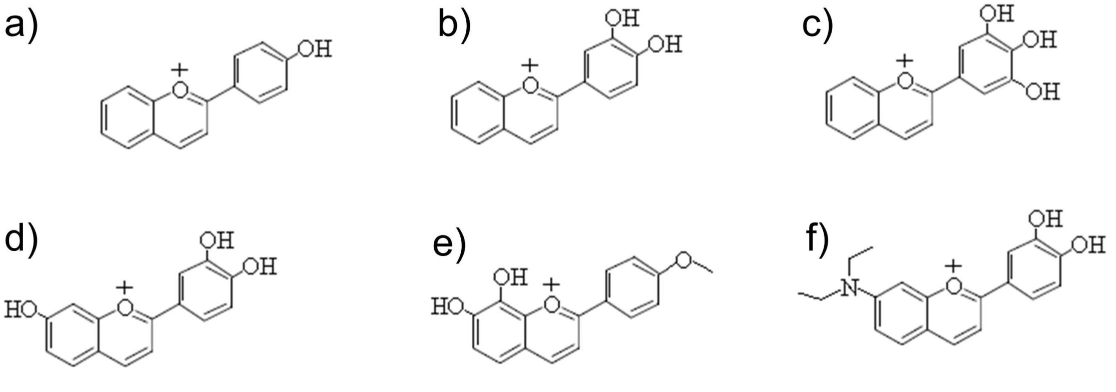


Fig. 25 *Chemical structures of synthetic flavylium ions. a) 4'-hydroxyflavylium;b) 3',4' dihydroxyflavylium; c) 3',4',5'-trihydroxyflavylium; d) 3',4',7-trihydroxyflavylium; e) 7,8-dihydroxy-4'-metoxyflavylium; f) 7-diethylamine-3',4'-dihydroxyflavylium.*

Further bio-inspired strategy mimics the light harvesting antenna (LHA) effect developed by different natural photosynthetic systems,[564,565] such as the green sulfur bacterial chlorosome,[566] the Pcb (*prochlorococcus* chl-a_2/b binding) protein[567] or the light-harvesting complex of photosystem II (LHC-II),[568] the purple bacterial light-harvesting complexes 1, 2 and 3 (LH1-LH3)[569] and many others. Despite the wide structural differences of LHA, influenced by the different habitats in which the diverse LHA systems exist, their light harvesting mechanism exploits similar principles.[570] During this process, light absorption followed by charge separation and efficient energy transfer to a reaction center (RC) are performed by molecular pigments. Natural LHAs are composed by a central molecular core (*i.e.*, RC) associated with an array of peripherical pigments, (antenna, A).[565] The role of the antenna is twofold: it collects the solar radiation and, through energy transfer, transfers the excitation energy[570] to the RC, where charge separation takes place.[570]

The energy transfer process can take place via Förster[571] or Dexter[572] mechanisms which, mainly differ in length scale (*i.e.*, the donor-acceptor distance, R_{DA}). In the Förster model the energy released from an excited light-sensitive molecule (donor) excites a second chromophor (acceptor) through nonradiative dipole-dipole coupling (coulombic interaction) and efficiencies (*i.e.*, the ratio of acceptor emission intensity to that of the donor)[573] sensitive to R_{DA}. Therefore, Förster energy is a short and intermediate range process (10-100Å)[571,574,575,576,577] mainly restricted to a singlet-singlet energy transfer.[571] Differently, Dexter mechanism[572] is a double electron exchange between the donor and the acceptor, depending strongly on the spatial overlap of their molecular orbitals. Thus, it is a very short range process (<10Å) decaying exponentially with R_{DA}.[572] Furthermore, Dexter mechanism can promote both singlet-singlet and singlet-triplet excited-state energy transfers.[572] A useful feature for energy transfer from fluorescent organic antenna to transition metal complex sensitizer.[578]

The knowledge gained in the field of natural photosynthesis[579,580] constitutes a valuable help to overcome the limits (*i.e.*, low ε, weak absorptivity, etc.) of LHE efficiency in the sensitization of wide-bandgap semiconductor for solar cells applications. In fact, in a DSSC the sensitizer is usually the sole light collector, and the cell J_{SC} strongly depends on the fraction of the light absorbed relatively to the whole incident solar flux on the photoanode. Thus, any improvement in the LHE constitutes a viable way in increasing the cell performances (*i.e.,* $J_{SC,}$ $V_{OC,}$ FF, IPCE and η).

The "antenna effect" concept introduced by Balzani and Lehn[581] was first used in DSSCs by Scandola and co-workers in 1990 [Ref. 582] which, proposed the use of a antenna/sensitizer structure based on trinuclear ruthenium polypyridine complex in order to increase the LHE of sensitized TiO_2-semiconductor. Since then, the inspiration of photosyntesis has prompted a considerable interest in the use of organic pigments for solar-energy applications and significant amount of artificial molecular and supramolecular architectures have been constructed and investigated.[583,584,585,586,587,588,589,590] In Ru(II)-complexes based DSSCs, the low ε ($\sim 10^{-4}$ $M^{-1}cm^{-1}$)[36,83,220,221,225] value and the weak absorptivity in the near-IR region, see section 4.1, remain the main weakness for LHE. Differently, in spite of their narrow absorption wavelength bandwidth, several vegetable dyes show intense π–π* transitions and wide tunability over a large electromagnetic spectral region, making them suitable candidates in the multichromophores sensitizer molecular devices (panchromatic effect).[591]

A critical factor in the design of a photosynthetic LHA system is the choice of the individual components (sensitizer and antenna) as well as their geometrical arrangement.[592] Amongst synthetic organic multi-pigments arrays, porphyrinic assemblies have proved their potentiality for DSSCs purpose.[304,584,593,594,595,596] In these systems, the light absorption by an antenna pigment is followed by singlet-singlet excited-state energy transfer process towards the porphyrin nucleo which, in turn injects the excited electrons into anchored TiO_2 semiconductor.[597] In addition, other pigments such as carotenoids,[583] coumarins,[598] cyanine,[599] xanthenes[600] and perylene dyes[601,602] that, absorb in spectral regions where porphyrins have low ε values, can be covalently bound to the main porphyrin macrocycle to enhance its LHE. As an example, synthetic covalent perylene-imide/porphyrins dyes have shown high LHE in the spectral blu-green region (*i.e.,* between the porphyrin Soret and Q-bands (450-500 nm)).[603,604,605] A similar idea was exploited by Hupp and Lee[606] using in DSSC a bichromophore (dyad) zinc-porphyrin/boron-dipyrrin (4,4-difluoro-4-bora- 3a,4a-diaza-s-indacene, (Bodipy)) with Bodipy acting as LHA molecule to fill out the blue-green region of the spectrum. As a result of the larger solar spectral coverage, the Zn-porphyrin/Bodipy based cell has shown a η=1.55%, nearly twice compared to that of the Zn-porphyrin based reference cell (η =0.84%).[606]

In 2011 Odobel and co-workers[591] realized a trichromopheric sensitizer (triad) consisting of covalently linked Bodipy, Zn-Pr and squaraine units.[591] The first two chromophoric subunits (Bodipy and Zn-Pr) act as LHA while the squaraine behaves as sensitizer for electron injection into TiO_2. In such a way, the assembled supramolecular architecture covered a wide window of the solar spectrum, combining the absorption properties of the individual components (see **Fig. 26**). Moreover, the triad absorbs in a range of wavelength (*e.g.*, ~650nm) not covered both by Ru-based and vegetable dyes, see Fig. 27. The triad (Bodipy/Zn-Pr/Squaraine) based DSSC has shown higher η (3.9%) compared to those of squaraine alone (3%) and Bodipy/Zn-Pr (3.6%).[591]

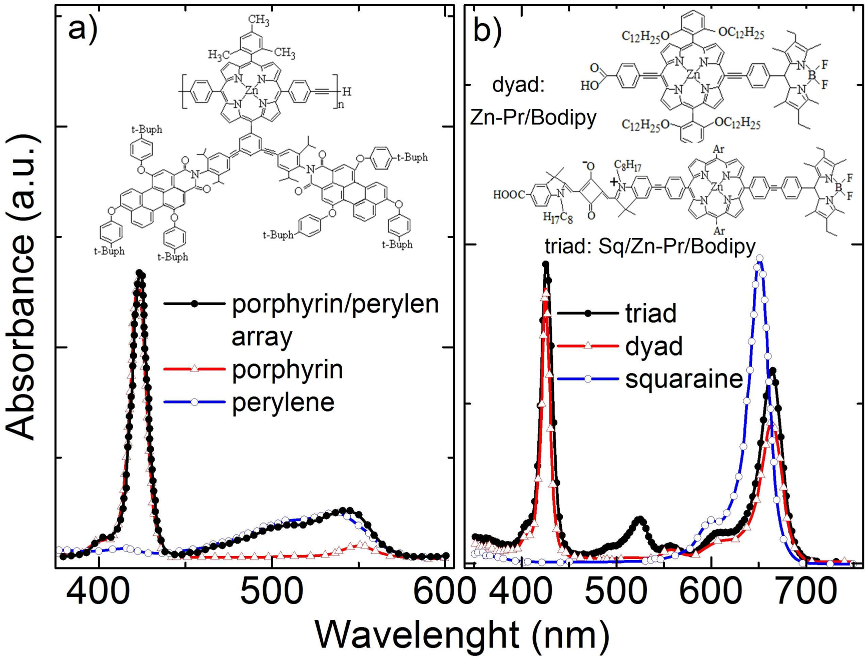


Fig. 26: *a) Absorption spectra of porphyrinin-perylene arrays (black dots), perylene (blue dots) and porphyrin monomers (red triangles). The chemical structure of porphyrin/perylen array shown as inset. b) Absorption spectra of triad Bodipy/Zn-Pr/Squaraine chromopher together with those of the respective monomeric and dimeric units is also shown. The chemical structures of dyad and triad are shown as inset (Adapted from refs. 591 and 607).*

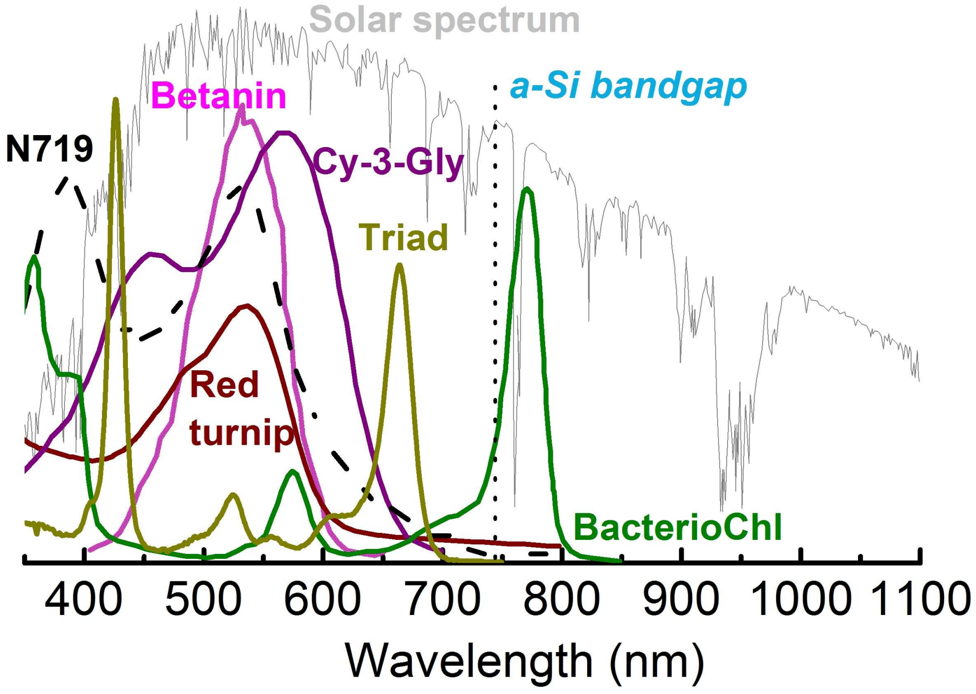


Fig. 27 *Representative absorption spectra of typical vegetable dyes, anthocianins (cyanidin 3-glucoside-Cy-3-Gly-), betalains (betanin and red turnip), chlorophylls (bacterioChl) and synthetic analogues (triad) reviewed in this article plotted against the solar spectrum (grey line). The absorption spectrum of ruthenium-based dye (N719), dashed line, is also reported for comparison. The approximate positions of the band-gap of amorphous silicon (a-Si), vertical dot line, is also shown.*

7 Scaling-up and costs

The final goal of any PV technology development is the scaling-up of lab cells to the specific size required by target applications. Nowadays PV systems are utilized in different contests: conventional PV plant, space solar power,[608,609] building integrated PV (BIPV),[610,611,612] energy harvester for sensors and other information and communication technology devices,[613,614] etc. Concerning DSSC, the good response to low illumination conditions[615] and diffuse light,[616] reduced angular dependence of efficiency[617] and the capacity to easily tune colour and transparency of the cell[618] make them well suited for BIPV[619,620] and indoor applications.[615]

The scaling-up from the lab size cells (less than 1cm^2) to large area cells or modules, is usually associated with a reduction of performances (*i.e.* η).[621] This lowering in η is due primarily to the increase of the internal voltage drop caused by sizeable increases in the series resistances. The *Rs* of TCO (>7 Ohm/□)[65] is not negligible and induces considerable reduction of the FF already for cells larger than 1 cm^2. Such issue is common to all PV technologies and several module architecture have been developed to mitigate this scaling problem.[622,623,624,625] Being electrochemical devices, however, specific problems arises for scaling up DSSCs, such as the management of the liquid electrolyte. For DSSC mainly four module architecture have been proposed, one for parallel connection and three for series connection of the cells (W-type, Z-type and monolithic),[622] see Fig. 28.

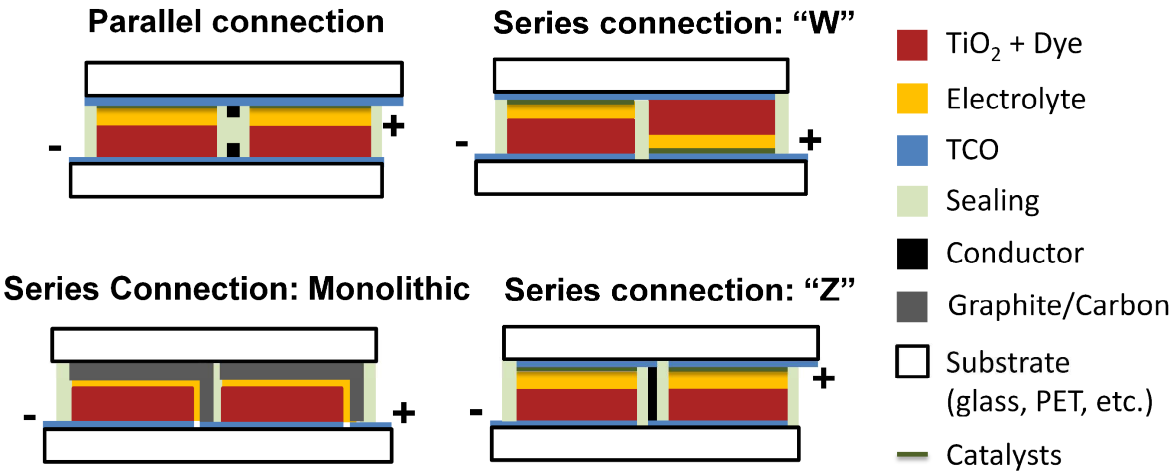


Fig. 28 *Connection schemes of DSSCs in a module.*

In parallel connection, similarly to c-Si PV technology, metal fingers are used to collect the generated current. However, metal finger corrosion can be induced by the electrolyte.[626] For this reason peculiar encapsulation strategies for metal grids have been developed for DSSC.[627,628,629,630,631] In Z-type series connected DSSC module the anode of the cell is connected to the cathode of the adjacent cell through a vertical metal contact.[623,624,625]Also in this case, vertical metal contact should be properly sealed to prevent the corrosive action of the electrolyte. This corrosive effect of the electrolyte is mitigated in the "metal-free" W and monolithic architectures. W connection exploits the bi-facial property of DSSC that is the ability to operate with front or rear illumination. In this architecture one cell (front illuminated cell) is connected to the adjacent cell, which is oriented in the opposite direction (back illuminated cell), thus eliminating the metal vertical connection of the Z-scheme. Such kind of architecture suffers of cell unbalance being the front illuminated cell typically more efficient than the back illuminated one.[632,633] For this reason, a careful design of the module should be consider.[634,635,636,637] Finally, in the monolithic architecture the printed back contact is used also for interconnecting adjacent cells.[638,639] Usually, carbon materials such as carbon black,[640,641] graphite,[642] graphite/carbon black[643,644] and graphene sheet/carbon[645] are used for the back contact even though other opaque or transparent materials can be used, also adopting vacuum-based deposition techniques (thermal evaporation, sputtering etc.).[639]

The scaling up concepts presented above have been widely applied in DSSC sensitized with Ru-based dyes and industrialization activities are well advanced. G24 Power is commercialising flexible DSSC modules while companies like Toyota-Aisin, TDK, Fujikura, Sony, DongJing-Semichem and others are in the pre-industrialization phase.[622] Moreover, quite recently there have been several announcements about IEC61646 endurance tests cleared by some Ru- and organic-based DSSC cells and modules.[646,647,648] This demonstrate the maturity of the DSSC technology also with respect to the severe stress test presented in the IEC norm originally developed for conventional thin-film PV technology.

While Ru- and Organic-dyes DSSC modules are well developed and first commercial applications have been launched on the market, limited example of DSSC modules sensitized with vegetable dyes have appeared. Fig. 29 shows some example of modules sensitized with both vegetable dyes and N719. Efficiency of the modules based on vegetable sensitizer is ~1% while the N719 one is ~5%.

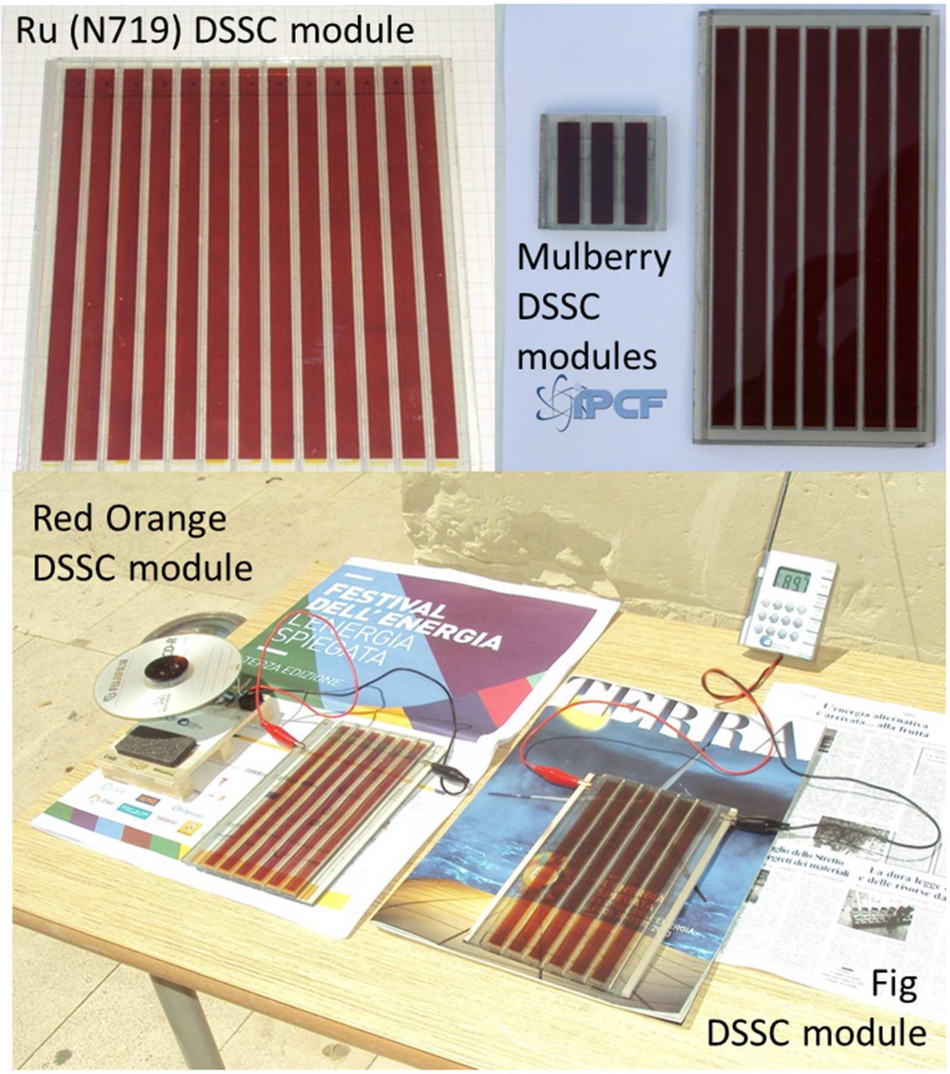


Fig. 29 *Ru-based and vegetable dye DSSC modules realized at the Centre for Hybrid and Organic Solar Energy (CHOSE) in collaboration with CNR-IPCF.*

The main reason for this scarce interest for scaling up of DSSC made with vegetable dye is mainly due to the low η shown, up to now, by the vegetable dyes (see Table 4 and Table 5).

However, the low cost of vegetable dyes may compensate, in view of performance/price ratio, their lower η with respect to Ru-based DSSC. To better define this issue it is necessary to quantify the price of the cell per peak output power (Wp).

It is widely recognized that the performance/price ratio will play a pivotal role in future choice of various PV devices. Concerning the DSSC technology, there are four major material costs, namely the mesoporous TiO_2, dye, and electrolyte and, with less extend, the catalysts. Moreover, similarly to thin-film PV technologies, the cost of TCO is not negligible with respect to the other components and should be considered as the ultimate cost of the module when all the other material costs are scaled in large productions.[254]

For DSSC productions of the order of few MWp/year it has been estimated that 15-20% of the total module cost is related to the dye while the cost of TiO_2 impacts for ~11-14 %.[649,650,651] This shows that the photoanode (considering also the TCO) is already covering half of the cost of DSSC modules. However, cost estimation strongly depends on the dye used for sensitizing the mesoporous TiO_2. In particular ε will dictate the quantity of dye needed for sensitization as well as the thickness of TiO_2. The relation between cost of a DSSC photoanode and the properties of materials used to fabricate it can be derived by considering the Lambert-Beer expression of the absorbance (A)

$$A = \varepsilon \cdot c \cdot d \qquad (15)$$

where c [mol/cm^3] is the concentration of dye in the TiO_2 layer and d [cm] the TiO_2 layer thickness. Equation (15) can also be written in terms of dye-uptake $\Gamma = cd$

$$A = \varepsilon \cdot \Gamma$$

A well-designed photoanode should have and absorbance $A > 1$ in order to absorb (in the range of the dye absorption spectrum) the major part of the electromagnetic radiation impinging on the cell. By using the equation of Calogero *et al.*[39] we can derive the cost per Watt-peak, $P_{tot}^{Dye}(€/W_p)$ of the dye:

$$P_{tot}^{Dye} = \left(\frac{A \cdot M_{Dye} \cdot P_{mass}^{Dye}}{\varepsilon \cdot I_{AM1.5} \cdot \eta} \right) \qquad (16)$$

where $M_{Dye}(g/mol)$ is the molecular mass of the dye, $P_{mass}^{Dye}(€/g)$ the price per mass of the dye, $I_{AM1.5}(W/m^2)$ the light power density and η the efficiency of the cell.

Equation 16 defines the cost of the dye, however, when a different dye is used, ε varies and consequently a different thickness of TiO_2 is needed to achieve the same absorbance. This will impact on the total cost of the cell, being the TiO_2 cost not negligible.

By using an approach similar to that described above for the dye, we can express the cost of the TiO_2 per Wp as:

$$P_{tot}^{TiO_2} = \left(\frac{A \cdot \rho_{TiO_2} \cdot P_{mass}^{TiO_2}}{R \cdot \varepsilon \cdot c \cdot I_{AM1.5} \cdot \eta} \right) \qquad (17)$$

where $R = \left(\frac{\text{Volume of sintered TiO}_2 \text{ layer}}{\text{Volume of deposited TiO}_2 \text{ paste}} \right)$ (typically R=0.1-0.15), $P_{mass}^{TiO_2}(€/g)$ the price per mass of TiO_2 paste and $\rho_{TiO_2}(g/cm^3)$ is the density of TiO_2 paste.

The total cost of the photoanode $P_{tot}^{PhA}(€/W_p)$ [€/W] (excluding the cost of the glass) is:

$$P_{tot}^{PhA} = \frac{A \cdot M_{Dye} \cdot P_{mass}^{Dye}}{\varepsilon I_{AM1.5} \cdot \eta} + \frac{A \cdot \rho_{TiO_2} \cdot P_{mass}^{TiO_2}}{R \cdot \varepsilon \cdot c \cdot I_{AM1.5} \cdot \eta} = \frac{A}{\varepsilon \cdot I_{AM1.5} \eta}\left[M_{Dye} \cdot P_{mass}^{Dye} + \frac{\rho_{TiO_2} \cdot P_{mass}^{TiO_2}}{R \cdot c} \right] \quad (18)$$

Beside TiO_2 and dyes other materials are needed for fabricate a DSSC. As shown in Fig. 28 we need to consider also the costs of front and rear glasses with FTO, electrolyte, catalyst (usually Pt), conductor (usually Ag) and sealing.

A comparison of material costs per Wp for the three classes of dyes (Ru-based, organic and vegetable) is shown in **Fig. 30**, where the results are obtained from the values reported in Table 6 and Table 7. To quantify material costs we used available prices for kg-size batch of TiO_2 [652] and g-size for dye batches.[652,653,654]

Costs of FTO coated glasses, Pt-catalyst, Ag-contacts are those reported in Ref. [651] while the cost for a high temperature thermoplastic sealant (DuPont Bynel) is from Ref. [653]. Here we consider an use of 0.091 m^2 of sealant per each square meter of DSSC module.

Table 6: Values of several parameters used for cost estimation.

Parameter	***Value***
TiO_2 paste density ($g \cdot cm^{-3}$)	0.82
R	0.15
Price of TiO_2 paste (€$\cdot kg^{-1}$)[651]	2500
Price of two TCO (€/m^2)[651]	16
Price of solvent-based electrolyte (€/l)[653]	1250
Price of Pt-catalyst (€/m^2)[651]	0.8
Price of Ag conductor (€/m^2)[651]	5.6
Price of sealant (€/m^2)[653]	15
Light Power density ($W \cdot m^{-2}$)	1000
Absorbance (A)	1.5

Table 7: Values of several dye-dependent parameters used for cost estimation.

Parameter	***Ru-Dye***	***Organic***	***Chlorophylls***	***Anthocyanins***	***Betalains***
Extinction Coefficient ($M^{-1} \cdot cm^{-1}$)	15000	30000	100000	40000	65000
Dye Molecular Mass M (g/mol)	1198	922	609	647	551
Concentration Dye onto TiO_2 ($mol \cdot cm^{-3}$)	10^{-4}	10^{-4}	10^{-4}	$5x10^{-5}$	$5x10^{-5}$
Price per mass dye (€$\cdot g^{-1}$)	60*	600[#]	0.13[¶]	0.24[¶]	0.10[¶]
η (%)	10	10	4	1	2.7

Dyes cost estimated from * Ref. [653], [#] Ref. [652], [¶] Ref. [654].

Fig. 30 shows very different prices and relative distribution of the cost between materials for the different families of sensitizer. Let us first consider the photoanode comprising the TiO_2 and dye. The cost of some Ru-based dyes is below 1 €/Wp (see Fig. 30), however the low ε value requires a thick (~10 mm) TiO_2 layer. This consequently increases the TiO_2 cost per Wp, which is slight above 1 €/Wp, (see Fig. 30). As reported in Sect. 4.1 and Sect. 4.2, organic dyes have a larger ε with respect to Ru-dyes. This permits a reduction of the cost per Wp of the TiO_2 layer for organic dye-based DSSCs. Nevertheless, the cost of organic dyes[652] is about 10 times larger than the Ru-dyes[653], see Table 7, making the total cost of the photoanode above 3 Wp/€. For what concerns the vegetable dyes, they have a negligible cost of the dye itself.[654] However, when η, ε and TiO_2 surface coverage are taken into account, the price per Wp of the photoanode of anthocyanins is larger with respect to both organic and Ru-based dyes, mainly due to the lower dye concentration onto TiO_2 and η, see Fig. 30. Contrary, although batalains have the same dye concentration onto TiO_2 of the anthocyanins, the higher η and ε make betalain a much cheaper material for DSSC applications, see Fig. 30. Nevertheless, amongst vegetable dyes, chlorophylls have the highest η, ε and TiO_2 surface coverage, see Table 7. This determines a reduction of the cost of the TiO_2 layer per Wp of photoanodes sensitized with chlorophylls.

When the costs of the other materials needed to fabricate the DSSC are considered, we observe that all the devices based on vegetable dyes present a higher impact of these additional costs on the total price-per-Watt with respect to those based on Ru and organic dyes. This is due to the lower η of vegetable dyes, with respect to the synthetic organic and inorganic ones. As shown in Fig. 30, electrolyte costs have the largest impact on devices based on vegetable dye even though both sealing and glass contributes substantially to the final cost. By comparing the costs of all the DSSC families we can see that the use of chlorophylls may contribute to the reduction of the price per Wp of this PV technology. We stress the fact that the presented costs estimation is only based on the material costs, without considering the stability of the cells and thus endurance tests, which could significantly modify the price of the cells for applications requiring long timescale.

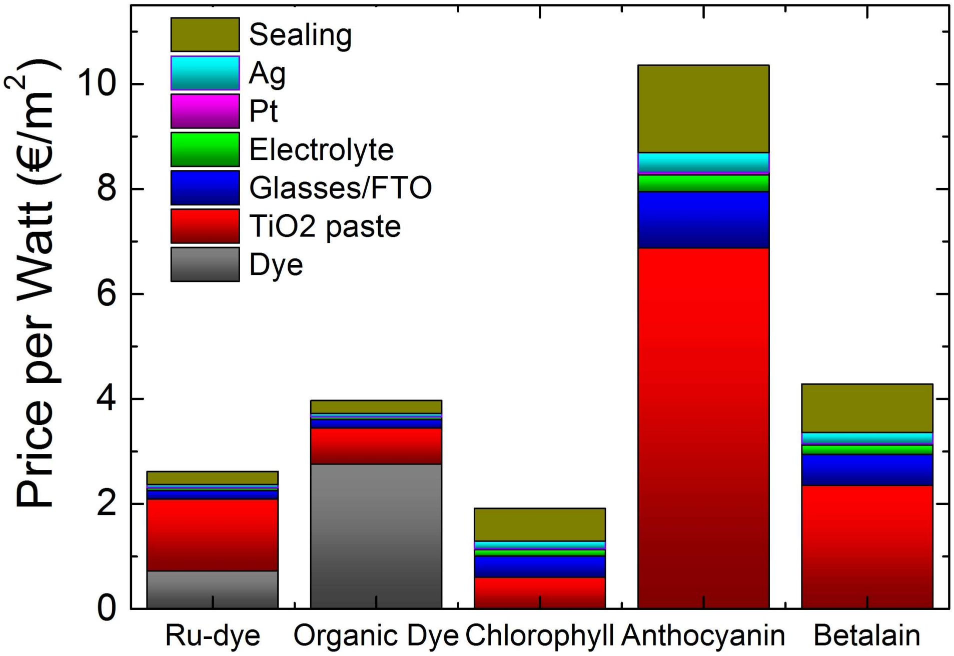


Fig. 30 *Price per Wp of DSSCs sensitized with Ru-Dye (N719), a synthetic organic dye (D35) and three different vegetable dyes, chlorophyll, anthocyanin and betalain. The price for Wp of dyes (grey)* TiO_2 *past (red), glasses-TCO (blue), electrolyte (green), Pt catalyst (magenta), Ag conductor (cyan) and sealing (olive) is reported.*

8 Outlook

The thought of imitating nature has been a dream for scientists over the centuries. In particular, the study of natural dyes remains an attractive and challenging goal contributing to a solution for future alternative environmentally sustainable energy conversion as predicted by G. Ciamician in his New York speech of 1912, "The photochemistry of the future" where he stated "…forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."[655]

Within the energy-harvesting field, DSSCs represent the most remarkable example of biomimetic devices, directly inspired by the photosynthesis. Many different types of synthetic and natural dyes have been investigated and a large set of data on the relationship between their chemical structure and PV performance of DSSCs have been collected. Despite the literature on the subject and notable progress made in power-conversion efficiency, there is still a long way to go before vegetable-based DSSCs can be considered an alternative to other PV technologies[656]. While it would be beneficial to use vegetable dyes because they are more abundant, cheaper and eco-friendly with respect to synthetic metal-complexes and/or organic dyes, the efficiency of DSSCs sensitized by vegetable pigments is still lower than that achieved by the aforementioned synthetic dyes. The highest efficiency of DSSCs based on vegetable dye extracts, as reported in Fig. 31, is still lower than 5% for chlorophyll-based DSSC. Nevertheless, as discussed in section 7, chlorophylls as sensitizers are less expensive than Ru-dyes (~18%) or synthetic organic dyes (~45%), see **Fig. 30**. Thus, in terms of performance/cost ratio, some vegetable dyes based DSSC, such as those sensitized with chlorophyll, have a potential advantage over both Ru-based and synthetic organic DSSCs. Even though vegetable dyes based DSSC have a lower efficiency, see Fig. 31, they could be used in some niche applications, *e.g.*, indoor applications[657] (diffuse light) for powering small systems and home appliances, battery chargers for portable devices or educational demonstrators, where they can in principle compete with silicon-based solar cells. Nevertheless, to make natural pigmentation a solution of choice for DSSC technology, additional efforts are needed as briefly outlined below.

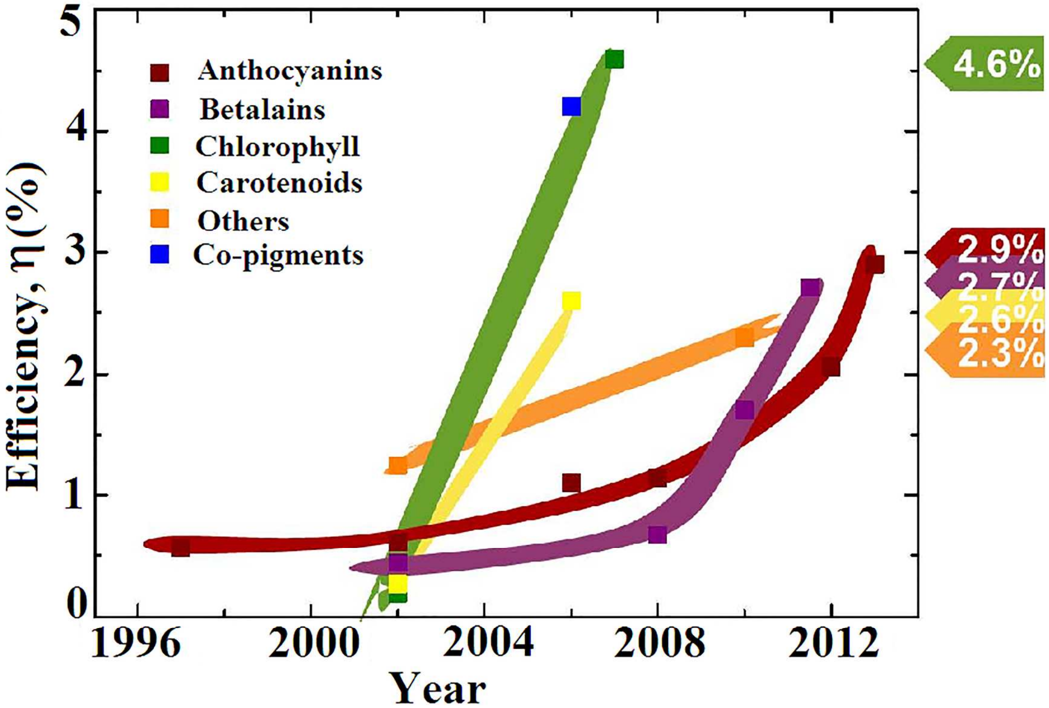


Fig. 31 *Progressing solar energy conversion efficiency of vegetable dye-based DSSCs from 1997 to 2014. Wine coloured squares anthocyanins, data taken from Refs. [39,47,48,337,436,440]; purple squares betalains data taken from Refs. [41,49,50,337], green squares chlorophylls, data taken from Refs. [337,346]; yellow squares carotenoids, data taken from Refs. [539]; orange squares other vegetable dyes data taken from Refs. [337,510] and blue square co-pigment (chlorophyll-carotenoids) data taken from Ref. [540]. The data on the right axis refer to state-of-the-art vegetable dye-based DSSC efficiency.*

Efficient natural sensitizers, as well as artificial ones, need to fulfill stringent properties such as harvesting light in wide range of the solar spectrum, bind strongly to the semiconductor nanoparticles and, upon excitation, efficiently inject electrons into the semiconductor conduction band. Moreover they require a rapid regeneration by the electrolyte and should exhibit a high V_{OC} and high stability. Usually, the low V_{OC} value, affecting the wide majority of vegetable dye-based DSSCs, is ascribed to a shift of the TiO_2 Fermi level, which follow the adsorption of natural dye onto semiconductor layer, and to the dark current;[41] and future research should address these two issues. Moreover, the dye structure is another fundamental parameter that affects the DSSCs performance. Steric hindrance of the dye molecules limits their ability to uniformly bind to the semiconductor surface, affecting the electron transfer process at the photoanode. Dye aggregation is another critical issue that deserves further investigation. Indeed, dye aggregation on the semiconductor layer produces high absorbance which does not directly translate into efficient electrons injection. Several kinds of additives such as chenodeoxycholic acid,[289,303] or other compounds with either long alkyl chains (e.g., hexadecylmalonic acid)[658] or bulky groups (*e.g.*, dineohexyl bis(3,3-dimethylbutyl)) phosphinic acid[659] can be exploited as co-adsorbant avoiding the dye aggregation on the semiconductor layer.

Another key point to be addressed in the development of vegetable dye-based DSSCs is the electrolyte. Indeed, unlike “conventional” DSSCs (based on synthetic organic/inorganic dyes), where enormous effort has been made to develop efficient electrolytes, natural dye-based DSSC still require optimization. A number of electrolyte additives have been developed for DSSC based on synthetic dyes to enhance the efficiency of the cell and to stabilize its PV performances. Carboxylic (*e.g.*, hexadecylmalonic acid) and phosphonic acid derivatives (*e.g.*, decylphosphonic acid) have been used to reduce carrier recombination, preserving dye integrity. 4-*tert*-butylpyridine and N-methylbenzimidazole are commonly used as electrolyte additives, suppressing the dark current thus improving the efficiency of the cell.[235,660] However, vegetable dyes such as anthocyanins, are pH sensitive, making additives such as 4-*tert*-butylpyridine or similar compounds less desirable. In fact, the basic nature of 4-*tert*-butylpyridine influences the dye molar extinction coefficient thus affecting the optical absorption properties (*i.e.*, a red-shift in the absorption spectrum). Moreover, the 4-*tert*-butylpyridine addition shifts the conduction band edge toward negative potentials and thus covers the surface, minimizing the recombination losses from the dark currents. The addition of various cations on the electrolyte has been investigated and found to increase the PV performance of DSSCs. For example, Li I the form of LiI intercalates in the TiO_2 nanoparticles due to its small size or strongly adsorbs at their surface. The presence of Li, can cause a positive shift in the flatband of TiO_2 with a consequent reduction of V_{OC}, and can also accelerate the rate of oxidized dye reduction by I^-.

A common problem, not isolated to intrinsic to vegetable pigments in DSSC technology, is the back electron injection from the TiO_2 to the oxidized dye. The creation of interfaces between the dye and the semiconductor could be a viable solution to overcome such issues. For example, a Schottky barrier, which is a potential energy barrier for electrons at the metal–semiconductor junction, produced by inserting a metal layer between the semiconductor nanoparticles and the dye could be a possible strategy to reduce the back electron transfer.[661]

Metal layers, *e.g.,* gold nanoparticles can also enhance charge separation in DSSCs[662], due to their ability to accept and conduct the current from the excited state of natural dyes to TiO_2, thus preventing charge recombination. Unfortunately, the main problem relies on the anchoring of the vegetable dye to metal nanoparticles layer, affecting the electron transfer efficiency from the dye to the nanoparticles themselves. A solution could be the use of molecular layers as bridge structure, able to anchor with the nanoparticles and at the same time linking the vegetable dye.

The successful use of vegetable dyes in DSSCs not only depends on the identification of the right pigments, but also on the ability to modify on-demand their photo-electrochemical properties. Although optimization of vegetable dyes is in progress, exploiting functional groups to improve the charge transfer between the dye and electrolyte mediator and from the dye to the semiconductor layer surface,[663] a lot more effort is still required. The exploitation of carbon-based nanomaterials (*e.g.*, graphene and carbon nanotubes) to modify the architecture of the semiconductor film could improve the electron lifetime thus reducing the dark current at the photoanode. Preliminary results[664] , *i.e.,* the incorporation of graphene in the anthocyanin dye mixture and the subsequent co-adsorption onto the titanium nanoparticles to suppress electron recombination, suggest that this could be a route worthy of further study. Another area where carbon-based nanomaterials can strongly contribute in the improvement of DSSCs is the replacement of expensive Pt counter electrodes.

Panchromatic systems are often used successfully in DSSCs because of their capability to harvest a broader portion of the solar spectrum in comparison to individual dyes. Vegetable dyes are ideal systems for such a task due to their large variety and complementary absorption properties. Unfortunately vegetable pigments, while they absorb well over a broad spectrum they tend to have low efficiencies. An advanced panchromatic system could be developed preparing a double layer (bicolor photoanode)[665], exploiting a similar approach to the one used in photography for the preparation of color films.

The photo-stability of vegetable dyes-based DSSCs is another crucial point that requires further investigation.[666] Indeed, the dye must be capable of many redox cycles (turnover higher than 10^6, *i.e.*, number of cycles that a dye molecule can support within a cell calculated from the ratio of dye regeneration rate by electrolyte and oxidative dye degradation rate) without undergoing decomposition. Nature supplies a large variety of vegetable dyes, designed to protect fruits and flowers in different ways, *e.g*., antioxidant activity, and scientists working in this field are called to exploit them alone or in mixture (co-pigmentation) to enhance the stability and efficiency of vegetable dye-based DSSCs. The use of UV and anti-reflective filters also improve dye reliability light reflection. Another route toward the increase of dye photo-stability could be the use of co-pigmentation and/or the use of additives linking the dye with the semiconductor layer without affecting the photo-electrochemical properties while still preserving the stability against heating or undesired redox reactions.[667]

Life-cycle analyses now available for conventional DSSC PV systems[668,669] show a limited environmental impact of such PV technology and vegetable dyes are expected to decrease such impact even further.

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