

# Nanomaterials for Solar Energy Conversion: Dye-Sensitized Solar Cells Based on Ruthenium(II) *tris*-Heteroleptic Compounds or Natural Dyes

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## 1 Aims and Scope

Dye-sensitized solar cells, DSSCs, gained much attention since it is a simple and cheap device capable of converting the sunlight into electricity through a regenerative photoelectrochemical process. DSSCs overall efficiency attained up to 14% and it is estimated to last around 20 years. Besides the economic advantages, these devices can be transparent, which allows their use for distinct architectonic purposes such as facades of buildings. DSSCs are based on a nanocrystalline mesoporous semiconductor films sensitized by dyes, which are responsible for light harvesting and electron transfer, these processes start the energy conversion and are directly responsible for its overall efficiency.

This paper aims to review a specific class of synthetic dye, the *tris*-heteroleptic ruthenium sensitizers, which have been attracting much attention on the last years due to the possibility of tune their spectroscopic and electrochemical properties as well as to improve the stability of the device. The recent advances on the use of natural dyes as semiconductor sensitizers, from 2003 to 2016, are also reviewed.

## 2 Introduction

The use of fossil fuel based technologies is the major responsible for the continuous increase in the pollution and in the concentration of greenhouse gases. Renewable sources must have higher contribution on the energetic matrix in providing more energy available for the humanity in a short period, having low environmental

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impact [1, 2]. The interest on the conversion of environmentally friendly energy sources led to the development of several devices that took the advantage of the continuous evolution on several fields of research, which can result in new materials for already developed devices. For instance, the performance of direct methanol fuel cells, a well-known technology [3, 4] was improved due to the development of nanomaterials especially designed for the energy conversion process [5, 6] and their evolution allows the use of light to boost the process through a synergic arrangement [7–10].

The use of sunlight has been gaining much attention due to its abundance. For instance, it is possible to supply human energy needs up to year 2050 covering only 0.16% of the earth surface with 10% efficiency solar devices [1, 11]. There are several investigations on the conversion of sunlight in substances with more chemical energy than the reactants in a process that mimics the photosynthesis, this approach is known as artificial photosynthesis [12]. Most recently, the investigation on this research field is being called solar fuels and several papers were published describing photochemical approaches to produce high energy content substances, or fuels, from simple reactants such as water or  $\text{CO}_2$  [13–19].

Great interest is dedicated to an especially attractive device, the dye-sensitized solar cells, DSSC, since they are capable of converting the sunlight into electricity based on photoelectrochemical principles. The materials employed for the construction of these new solar cells are common and cheap and the procedures do not require controlled environment, thus clean rooms or any other sophisticated control can be avoided, consequently a very low production cost is estimated (less than 1 € per  $W_{\text{peak}}$ ) [20]. The use of new nanomaterials allows interesting features of these devices, such as transparency, possibility to have distinct colors, among others. These characteristics are very interesting for new applications of solar cells, since it can substitute glass windows and promote the co-generation of energy, or for any other architecture design.

Albeit the possible use of sensitization effect for solar energy conversion is known for a long time [21], the breakthrough of these solar cells was in 1991 when B. O'Regan and M. Grätzel published the use of nanocrystalline and mesoporous  $\text{TiO}_2$  film [22]. This film enhanced the light absorption due to its sponge-like characteristic which increases the surface area. The nanocrystallinity plays an important role on the electron injection and transport in these devices [23].

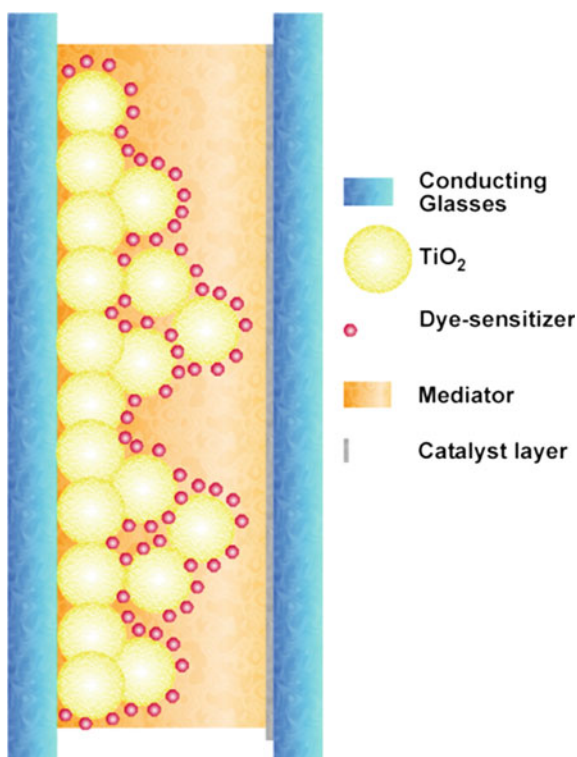
Since the paper of 1991, this field has been growing very fast and all the aspects of these solar cells are investigated [24–27]. In this review, the focus is on the development of *tris*-heteroleptic ruthenium (II) dyes as well as the use of natural extracts as a source of sensitizers. The absorption spectra and photoelectrochemical parameters published for these compounds since 2003 will be reviewed and discussed.

## 2.1 Dye-Sensitized Solar Cells—Principles and Operation

Dye-sensitized solar cells are prepared in a sandwich arrangement and are comprised by two electrodes, the photoanode and the counter electrode, Fig. 1. The photoanode is a conducting glass covered by a mesoporous and nanocrystalline  $\text{TiO}_2$  film, sensitized by the dye-sensitizers. The counter electrode is a conducting glass covered by a thin film of catalyst, such as platinum or graphite. Between these electrodes is placed a mediator layer, usually a solution of  $\text{I}_3^-/\text{I}^-$  in nitriles.

In order to promote the energy conversion, the sunlight is harvested by the dye-sensitizers leading to an excited state capable of inject an electron into the semiconductor conducting band. The oxidized dye is immediately regenerated by the mediator and the injected electron percolates through the semiconductor film, reaches the conducting glass, and flows by the external circuit to the counter electrode. The counter electrode is responsible for regenerating the oxidized specie of the mediator, reducing it by a catalyzed reaction using electrons from the external circuit. Since there is not a permanent chemical change for dye-sensitized solar cells, the estimated lifetime of these devices is 20 years [23].

**Fig. 1** Schematic arrangement of a dye-sensitized solar cell



## 2.2 Performance Experiments

Dye-sensitized solar cells are evaluated by several experimental approaches. For instance, the recombination processes or electron injection dynamics are investigated by time-resolved experiments [27–35], information about electron transport and electrical characteristics of  $\text{TiO}_2$  film can be obtained by electrochemical impedance spectroscopy [36]. Among several experiments used in evaluation of DSSCs, two experiments play an important role for investigation of dye performance, the current–voltage curves and photocurrent action spectra. Due to their importance, they are detailed in the next sections.

## 3 Current–Voltage ( $I \times V$ ) Curves

Current–voltage curves allow the access to one of the most important information about the prepared solar cells, the overall efficiency,  $\eta$ . Other important parameters such as the short-circuit current density,  $J_{\text{SC}}$ , open-circuit potential,  $V_{\text{OC}}$ , and fill factor,  $ff$ , are also determined by this experiment. In most cases,  $I \times V$  curves determined experimentally for dye-sensitized solar cells are similar to the schematic one, Fig. 2.

Short-circuit current density,  $J_{\text{SC}}$ , and open-circuit potential,  $V_{\text{OC}}$ , are the values determined by the intersection of  $I \times V$  curve to the current density axis. The voltage at this axis is zero, the short-circuit condition, thus the current is named for this condition. Analogous idea is applied for the determination of open-circuit potential, since the current at voltage axis is zero, open-circuit condition.

The maximum power output of a DSSC,  $P_{\text{max}}$ , is the highest value obtained for the multiplication of current density and voltage for each point of the  $I \times V$  curve and can be graphically expressed as the area covered by the orange rectangle in

**Fig. 2** Schematic current–voltage curve

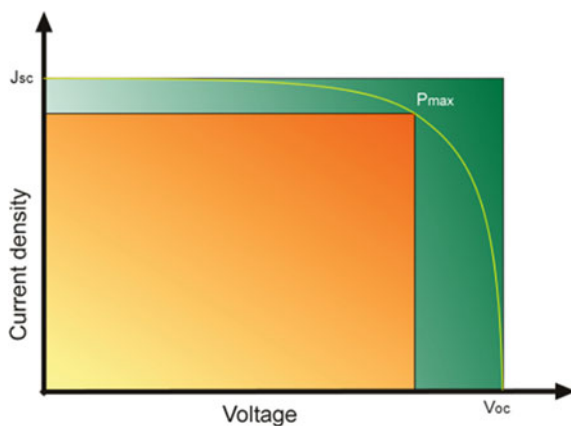


Fig. 2. On the other hand, the multiplication of  $V_{OC}$  by  $J_{SC}$  results in the maximum power output possible to be achieved for this DSSC and it can also be represented by the green rectangle of Fig. 2. The fill factor,  $ff$ , is named for the amount of the green rectangle which is filled by the orange one. Thus,  $ff$  express the electrical losses of DSSCs. Mathematically,  $ff$  can be determined by the ratio of  $P_{max}$  and the multiplication of  $J_{SC}$  by  $V_{OC}$ , Eq. 1.

$$ff = \frac{P_{max}(\text{mW cm}^{-2})}{J_{SC}(\text{mA cm}^{-2}) \cdot V_{OC}(V)} \quad (1)$$

Under simulated solar irradiation condition, (1 sun =  $P_{irr} = 100 \text{ mW cm}^{-2}$ ), the overall efficiency,  $\eta_{Cell}$ , can be determined by dividing  $P_{max}$  by the total incident light power,  $P_{irr}$ , Eq. 2, resulting in the percentage amount of solar light converted in electrical output.

$$\eta_{Cell}\% = \frac{P_{max}}{P_{irr}} \cdot 100\% \quad (2)$$

## 4 Photocurrent Action Spectra

Photocurrent action spectra exhibit the photoelectrochemical behavior of solar cells as a function of wavelength. For each wavelength, the incident photon-to-current conversion efficiency, IPCE, can be determined and the spectra are valuable to analyze the performance of new dyes prepared. IPCE values can be determined by a relationship that considers the energy and intensity of the incident light, the  $J_{SC}$  and Planck's constant, Eq. 3.

$$\text{IPCE}(\lambda) = \frac{J_{SC}}{P_{irr} \cdot e} \cdot \frac{hc}{\lambda} \quad (3)$$

- $J_{sc}$  Short-circuit photocurrent density ( $\text{A m}^{-2}$ );
- $h$  Planck's constant (J s);
- $c$  Speed of light ( $\text{m s}^{-1}$ );
- $\lambda$  Irradiation wavelength (nm);
- $P_{irr}$  Power of the incident light ( $\text{W m}^{-2}$ );
- $e$  Elementary charge (C).

For practical purposes, this equation can be simplified to Eq. 4.

$$\text{IPCE}\%(\lambda) = \left( 1239.8 \cdot \frac{J_{SC}(\text{mA cm}^{-2})}{P_{irr}(\text{mW cm}^{-2}) \cdot \lambda(\text{nm})} \right) \cdot 100\% \quad (4)$$

IPCE values are also related to some important parameters for DSSCs, such as light harvesting efficiency, LHE, electron injection quantum efficiency,  $\Phi_{\text{EI}}$ , and the efficiency of collecting electrons in the external circuit,  $\eta_{\text{EC}}$ , Eq. 5 [37]. The simple measurements, such as  $J_{\text{SC}}$  and  $P_{\text{irr}}$  allow the access to important information such as the electron injection quantum yield.

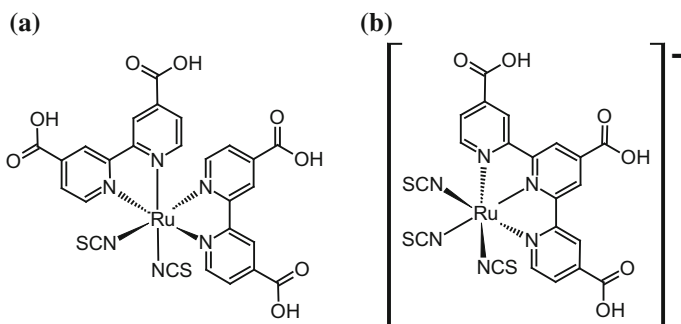
$$\text{IPCE}(\lambda) = \text{LHE} \Phi_{\text{EI}} \eta_{\text{EC}} \quad (5)$$

Photocurrent action spectra are valuable experiments to evaluate new dye-sensitizers since it is possible to directly associate the absorption response of the dye with the conversion efficiency. This is important information for designing new sensitizers.

## 4.1 Molecular Engineering

The design of new dye-sensitizers is based on joining in just one specie components capable of performing specific tasks. Using different ligands, it is possible to have excellent light harvesting, electron injection on semiconductor conducting band and fast regeneration by the mediator. A new molecule to be employed in DSSCs should fulfill some basic requirements such as having an intense absorption in the visible region, which corresponds to 44% of the incident sunlight on the earth's surface, having an anchoring group capable of promoting the chemical adsorption onto  $\text{TiO}_2$  surface, improving the electronic coupling between dye and semiconductor interface.

The first DSSC that exhibited  $\eta > 10\%$  employed *cis*-di(isothiocyanato)*bis*-(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II), N3, as dye-sensitizer [38]. After this dye, the complex *mer*-tri(isothiocyanato)(2,2',2''-terpyridyl-4,4',4''-tricarboxylic acid)ruthenium(II), black dye, was prepared and also successfully used as sensitizer [39], Fig. 3.



**Fig. 3** Structures of the N3 (a) and black dye (b) sensitizers

Due to the outstanding performance of N3 and black dye as dye-sensitizers, they can be used as models for molecular engineering of new dyes. Their chemical attachment onto  $\text{TiO}_2$  surface occur through the carboxylic acid groups of the 2,2'-bipyridine or of the 2,2',2''-terpyridine ligands. Particularly, the 4,4'-dicarboxylic acid-2,2'-bipyridine anchoring ligand is been widely employed among several other possible groups investigated and it has been considered the best one for ruthenium(II) sensitizers [40]. This ligand allows intimate electronic coupling between the dye excited state wave function and the semiconductor conducting band. Its lowest unoccupied orbital, LUMO, is the lowest one of the coordination compound and facilitates an efficient electronic transfer from excited dye molecules to titania nanocrystals [41].

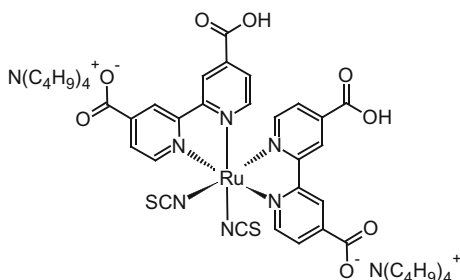
Great influence on the absorption spectra and molar absorptivities of compounds, emission maxima and quantum yields, as well as excited state lifetimes, in addition to the redox properties was observed as a function of the degree of protonation of the carboxylic acids of the ligand. These changes are directly responsible for the increase on photovoltaic performance of solar cells sensitized by N719, Fig. 4, which is the di-deprotonated N3 specie [42]. As a natural consequence, the use of compounds having one or more deprotonated carboxylic groups in the  $\text{dcBH}_2$  has been increasing [32, 41, 43–48].

In the case of N3, consequently of N719, the presence of two  $\text{dcBH}_2$  ligands results in absorption spectra which overlaps the visible region of the incident sunlight. The absorption bands have high molar absorptivity ( $\epsilon \sim 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), typical of metal-to-ligand charge transfer transitions,  $\text{MLCT}_{\text{d}\pi\text{Ru}-\pi^*\text{dcBH}_2}$ . The high molar absorptivity improves the light harvesting efficiency, allowing the absorption of almost all incident light in a few micrometers of optical length of the  $\text{TiO}_2$  film. Besides the bipyridine, the two isothiocyanate ligands in these complexes are valuable to promote the stabilization of the  $t_{2g}$  orbitals and result in a fine tuning of the energy levels of the complex.

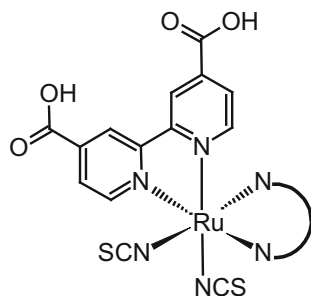
## 5 Ruthenium *tris*-Heteroleptic Complexes

The knowledge acquired understanding the structure of the N3 dye can be used for the development of several other complexes by using the molecular engineering [49]. Among several classes of compounds developed, ruthenium *tris*-heteroleptic

**Fig. 4** Structure of N719



**Fig. 5** General structure of  $cis$ -[Ru(dcbH<sub>2</sub>)(L)(NCS)<sub>2</sub>] dyes



complexes have been gaining attention on the last years due to the possibility of modulate their properties, just changing one of the polypyridinic ligands. This approach is very interesting for the development of new sensitizers. A comprehensive review about these compounds was also published in 2016 [50].

There are several classes of ruthenium *tris*-heteroleptic compounds described by the general formula  $cis$ -[Ru(dcbH<sub>2</sub>)(L)(NCS)<sub>2</sub>], Fig. 5, since each new ligand L and its derivatives can be a new class. In this work, our focus will be on 2,2'-bipyridine derivatives and 1,10-phenanthroline derivatives, even that several other compounds of this general formula are known [34, 51–53].

### 5.1 2,2'-Bipyridine Derivative Ligands

The search for high-efficiency ruthenium(II) dyes is focused on the development of complexes having high molar absorptivity, mainly in visible and near infrared region [54, 55]. A good light harvesting yield and a reduction on the film thickness, which imply reduction of transport losses in the nanoporous environment, result in higher open-circuit potentials and more efficient devices [56, 57]. Another approach is the development of dye-sensitizers capable of improving the lifetime performance of a dye-sensitized solar cell.

The first *tris*-heteroleptic ruthenium compounds investigated as dye-sensitizers are based on 2,2'-bipyridine derivatives and it is possible to observe three different approaches, following the bipyridine substituent. These subclasses are the amphiphilic, donor antenna, and thiophene compounds.

## 6 Amphiphilic Compounds

In 2003, a thermally stable DSSC was disclosed employing the amphiphilic Z907 sensitizer. Using this dye it was possible to prepare stable devices under prolonged thermal stress at 80°. However, the molar extinction coefficient of this sensitizer is



somewhat lower than that of the standard N719 dye. Meanwhile, a compromise between efficiency and high temperature stability has been noted for the Z907 sensitizer [58]. Subsequently, the concept of developing a high molar extinction coefficient, amphiphilic ruthenium sensitizer, was followed by other groups, with a motivation to enhance device efficiency [34, 59–62]. The absorption properties as well as the performance parameters determined for ruthenium *tris*-heteroleptic complexes having amphiphilic derivatives of 2,2'-bipyridine are listed in Table 1.

The absorption spectra of amphiphilic compounds usually exhibit two MLCT bands in the visible region, typical of ruthenium *bis*-bipyridyl compounds. Molar absorptivity values listed on Table 1 are similar to those determined for the complexes N3 or N719. This behavior is expected since the aliphatic substituents do not have significant influence in the chromophoric properties of the complexes.

Amphiphilic ruthenium *tris*-heteroleptic dye-sensitizers exhibit lower photoelectrochemical performance than determined for N3. The highest efficiency achieved by this class of dyes is 8.6% [60]. The advantage of these compounds is their long-term stability. These amphiphilic heteroleptic sensitizers have the ground-state  $pK_a$  of 4,4'-dicarboxy-2,2'-bipyridine higher than determined for N3, enhancing the chemical adsorption of the complex onto the  $TiO_2$  surface [61, 70, 71]. The structure of amphiphilic ligands decreases the charge density on the sensitizer, resulting in less electrostatic repulsion and higher amount of dye adsorbed. The hydrophobic substituent of 2,2'-bipyridine does not allow the presence of water molecules close to  $TiO_2$  surface, improving the stabilization of solar cells toward water-induced desorption of the dye. The redox potentials of these complexes are shifted toward a more positive electrochemical potential in comparison to the N3 sensitizer, increasing the reversibility of the ruthenium III/II couple, leading to higher electrochemical stability [61, 70, 71].

## 7 Donor Antenna Compounds

Complexes prepared with donor antenna substituents of 2,2'-bipyridine are an approach to improve the light absorption at the same time that the hydrophobic character is enhanced. The use of aromatic substituents can have this function since the aromaticity increases the light absorption and the existence of the hydrophobic chain allows the protection to dye desorption caused by water. The spectral and photoelectrochemical parameters of this class of dyes are listed in Table 2.

In most cases, it is observed higher molar absorptivities values in comparison to amphiphilic compounds or N3 or N719 dyes which can be ascribed to an extended  $\pi$ -cloud delocalized in the substituent. The higher light harvesting efficiency results directly in higher IPCE values as well as overall efficiency of the solar cell, Table 2.

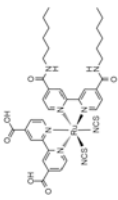
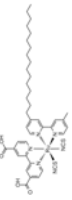
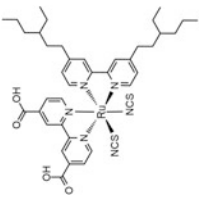
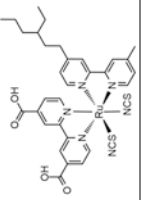
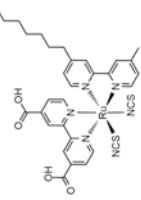
There are a few investigations on the use of  $\pi$ -excessive heteroaromatic rings as end groups in substituted bpy ligands [43, 44, 72]. The use of conjugated  $\pi$ -excessive heteroaromatic rings as end substituents donors directs the electron

**Table 1** Absorption properties and photoelectrochemical performance of ruthenium(II) *tris*-heteroleptic compounds having amphiphilic derivatives of 2,2'-bipyridine

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{\text{MAX}}/\text{nm}$ ( $\epsilon_{\text{MAX}}/\text{cm}^{-1}$ )	$V_{\text{oc}}/\text{V}$	$J_{\text{sc}}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/\text{nm}$ )	$ff$	$\eta_{\text{cell}}$ %	
Z907		Ethanol	295 (4.24); 312 (3.01); 385 (1.09); 526 (1.16)	0.73	12.5	80 (540)	0.67	6.2	[58]
CS9		DMF	296 (4.17); 366 (1.03); 518 (0.7)	0.63	14.59	60 (540)	0.62	5.68	[59]
NMK-2 <sup>a</sup>		Ethanol	295 (4.54); 312 (3.35); 383 (1.13); 524 (1.16)	0.7	14.7	—	—	6.8	[60]
NMK-3 <sup>a</sup>		Ethanol	296 (4.26); 312 (3.2); 384 (1.01); 525 (1.11)	0.7	15.5	—	—	7.4	[60]
NMK-5 <sup>a</sup>		Ethanol	296 (4.21); 312 (3.02); 384 (1.08); 525 (1.15)	0.75	16.2	90	—	8.6	[60]
KC-8 <sup>a</sup>		DMF	297 (4.54); 309 (2.74); 370 (1.25); 522 (1.26)	0.673	17.13	86	0.72	8.3	[61]
A597		DMF	313 (5.2); 397 (1.6); 539 (1.8)	0.778	11.83	57 (540)	0.78	7.25	[63]

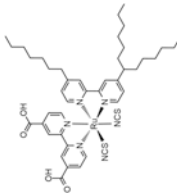
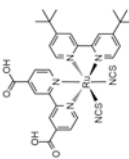
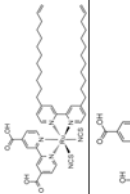
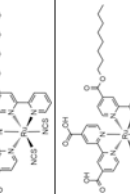
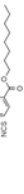
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Table 1 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4 L mol^{-1} cm^{-1}$ )	$V_{oc}/V$	$J_{sc}/mA cm^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}$ %	
C4		Ethanol	312 (2.6); 391 (0.9); 535 (0.9)	0.71	15.5	75 (500)	0.66	7.3	[64]
C5		Ethanol	296 (3.65); 314 (2.53); 384 (1.0); 528 (1.01)	0.72	16.7	—	0.64	7.7	[64]
CS27		DMF	299 (4.78); 369 (1.25); 517 (1.13)	0.63	3.0	45	0.77	1.46	[65]
CS28		DMF	299 (4.48); 370 (1.20); 518 (1.08)	0.66	7.0	80	0.72	3.28	[65]
CS32		DMF	298 (4.50); 370 (1.17); 518 (1.05)	0.66	6.7	80	0.67	2.95	[65]

(continued)

Table 1 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{oc}/V$	$J_{sc}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}\%$	
CS43		DMF	299 (5.43); 369 (1.34); 518 (1.20)	0.69	6.1	70	0.69	2.91	[65]
K005		Ethanol	316 (2.68); 418 (0.95); 537 (0.94)	0.553	9.35	—	0.720	3.72	[66]
Ru-C		—	—	0.68	11.1	—	0.67	5.1	[67]
RuC9		Acetonitrile/ <i>t</i> -butanol (1:1 v/v)	215; 294; 379 (0.99); 521 (1.14)	0.673	14.10	—	0.711	6.92	[68]
S8		Ethanol	315; 395; 535	0.60	13.02	—	0.69	5.36	[69]

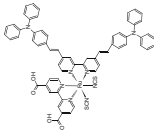
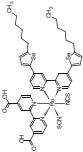
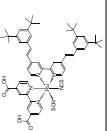
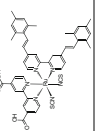
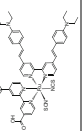
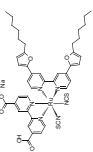
<sup>a</sup>These compounds were named after the initials of the first author of the reference cited

**Table 2** Absorption properties and photoelectrochemical performance of ruthenium(II) *tris*-heteroleptic compounds having donor antenna derivatives of 2,2'-bipyridine

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{oc}/V$	$J_{sc}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$\mathcal{F}$	$\eta_{cell}\%$	
LXJ1		DMF	309 (4.7), 353 (3.3), 549 (1.84)	0.715	16.50	83.7 (550)	0.745	8.80	[43]
IJ-1		Ethanol	218; 308 (5.0); 432 (4.3), 536 (1.9)	0.748	19.2	87	0.72	10.3	[56]
KW-2 <sup>a</sup>		DMF	310 (4.86); 373 (7.95); 550 (2.22)	0.685	3.42	—	0.42	0.99	[57]
KW-3 <sup>a</sup>		MeOH + 1 wt % KOH	307 (8.13); 429 (5.34); 524 (3.09)	0.735	4.03	—	0.46	1.37	[57]
KW-4 <sup>a</sup>		1:1 H <sub>2</sub> O; DMF + 1 wt% KOH	307 (3.88); 381 (1.28); 526 (1.13)	0.635	2.15	—	0.42	0.58	[57]

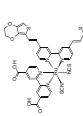
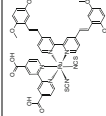
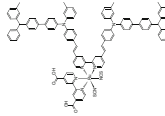
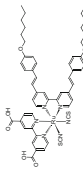
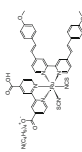
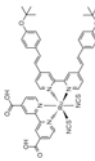
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Table 2 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{\text{MAX}}/\text{nm}$ ( $\epsilon_{\text{MAX}}/10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )	$V_{\text{oc}}/ \text{V}$	$J_{\text{sc}}/ \text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/\text{nm}$ )	$ff$	$\eta_{\text{cell}} \%$	
KW-5 <sup>a</sup>		1:1 H <sub>2</sub> O: DMF + 1 wt% KOH	304 (6.25); 423 (5.47); 544(2.27)	0.715	4.30	—	0.43	1.31	[57]
C105		DMF	309 (3.90); 353 (3.2); 420(1.84); 550 (1.84)	0.747	18.9	95 (520)	0.744	10.06	[72]
HRD-1		DMF	543 (1.93)	0.59	10.9	60	0.78	4.93	[70]
HRD-2		DMF	532 (1.61)	0.60	10.5	64	0.78	4.91	[70]
HRS-2		Ethanol	431 (5.93); 542 (2.81)	0.697	17.47	85 (552)	0.711	8.65	[71]
C102		DMF	305; 341; 407; 547 (1.68)	0.740	17.80	82 (550)	—	9.5	[44]

(continued)

Table 2 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{oc}/V$	$J_{sc}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}\%$	
AB-I <sup>a</sup>		Ethanol	314; 388; 538 (1.6)	0.663	19.1	87	0.72	9.1	[55]
N945		1:1 acetonitrile: <i>tert</i> -butanol	400 (3.4); 550 (1.9)	0.728	17.96	61	0.71	9.29	[73]
KCS-I <sup>a</sup>		DMF	310 (8.49); 440 (5.34); 540 (2.67)	0.757	9.6	—	0.35	3.4	[74]
K-19		DMF	310 (5.0); 350 (4.8); 410 (1.8); 545 (1.8)	0.718	13.2	—	0.745	7.1	[32]
K-73		DMF	310; 350; 410; 545	0.748	17.22	85 (540)	0.649	9.5	[32]
K77		DMF	310; 346; 546 (1.94)	0.737	17.5	90 (550)	0.696	9.0	[75]

(continued)

Table 2 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{\text{MAX}}/\text{nm}$ ( $\epsilon_{\text{MAX}}/10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )	$V_{\text{oc}}/\text{V}$	$J_{\text{sc}}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/\text{nm}$ )	$ff$	$\eta_{\text{cell}}\%$	
Z-910		Acetonitrile	410 (1.7); 543 (1.69)	0.777	17.2	87 (520)	0.764	10.2	[33]
KC-5 <sup>a</sup>		DMF	313 (3.88); 392 (1.17); 537 (1.19)	0.695	15.8	75	0.66	7.01	[61]
KC-6 <sup>a</sup>		DMF	314 (3.36); 390 (1.11); 531 (1.12)	0.676	15.47	63	0.71	7.42	[61]
KC-7 <sup>a</sup>		DMF	312 (3.39); 393 (1.12); 533 (1.21)	0.676	16.11	79	0.7	7.62	[61]
MH06		DMF	390 (4.07); 541 (2.15)	0.642	15.07	70	0.692	6.70	[76]
MH11		DMF	414 (5.16); 547 (2.7)	0.671	19.70	90	0.664	8.78	[76]

<sup>a</sup>These compounds were named after the initials of the first author of the reference cited



injection in the excited state and enhances the oscillator strength resulting in significant increases in the short-circuit photocurrent [55].

The higher molar absorptivity in the visible region can be understood by the influence of the different delocalized  $\pi$ -systems integrated in the bipyridyl donor antenna ligands. The reason for the lower absorption of the standard N719 dye in this region is the absence of any these groups [57].

## 8 Thiophene Compounds

Ruthenium(II) sensitizers having 2,2'-bipyridine with thiophene substituents have higher molar absorptivity than observed for the previous classes of compounds. For instance, the compound KW-1 has  $\epsilon_{515} = 3.56 \text{ L mol}^{-1} \text{ cm}^{-1}$  [57], much higher than the ones determined for N3 or N719 dyes. As it is observed for the donor antenna class of compounds, the higher light harvesting efficiency results in higher IPCE values and consequently improves the overall performance of the solar cell, Table 3.

Ruthenium(II) thiophene compounds gained special attention after C101 dye has set a new DSSC efficiency record of 11.3–11.5% and became the first sensitizer to triumph over the well-known N3 dye [44]. In comparison to its analogues C102 or C105, in which the thiophene is replaced by furan, or selenophene, respectively, the molar absorptivity increases in the order of  $\text{Se} > \text{S} > \text{O}$ . This sequence it is consistent with the electropositivity trend and the size of the heteroatoms of five-member conjugated units. The LUMO energy sequence of the spectator ligand is  $\text{O} > \text{S} > \text{Se}$ , which explains this behavior [72].

Another important dye employing thiophene derivatives is CYC-B1, which exhibits a remarkably high light-harvesting capacity of up to  $2.12 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  [40]. After the development of the CYC-B1 dye, several ruthenium dyes were synthesized by incorporating thiophene derivatives into the ancillary ligand and DSSC cells based on these dyes exhibited excellent photovoltaic performances [45, 46, 77, 78].

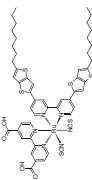
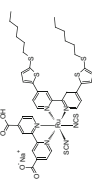
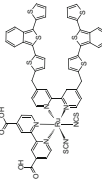
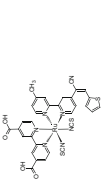
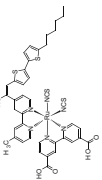
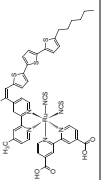
The extensive use of polythiophene is due to its similarity to a *cis*-polyacetylene chain bridged with sulfur atoms. The “bridging sulfur atoms” could effectively provide aromatic stability to the polyacetylene chain while preserving the desirable physical properties, such as high charge transport. The facile functionalization of thiophene groups also offers relatively efficient synthetic solutions to solubility, polarity, and energetic tuning. Furthermore, sulfur has greater radial extension in its bonding than the second-row elements, such as carbon. Therefore, thiophene is a more electron-rich moiety and incorporation of thiophene onto bipyridine ligands raises the energy levels of the metal center and the LUMO of the ligands [80]. As a consequence, the band resulting from charge transfer from the metal center to the anchoring ligand is redshifted, and upon illumination of the sample, the electrons on the metal center are transferred to the anchoring  $\text{dcBH}_2$  ligand, where electrons can move to the outer circuit through the  $\text{TiO}_2$  particles more efficiently [40].

**Table 3** Absorption properties and photoelectrochemical performance of ruthenium(II) *tris*-heteroleptic compounds having thiophene derivatives of 2,2'-bipyridine

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4 L mol^{-1} cm^{-1}$ )	$V_{oc}/V$	$J_{sc}/mA cm^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$\mathcal{F}$	$\eta_{cell}$ %	
CYC-B1		DMF	312 (3.58); 400 (4.64); 553 (2.12)	0.65	23.92	77.5	0.55	8.54	[40]
CYC-B3		DMF	350; 400; 544 (1.57)	0.669	15.7	64.1 (520)	0.705	7.39	[77]
CYC- B7		DMF	345 (3.55), 412 (4.35), 551 (2.19)	0.788	17.4	76 (530)	0.654	8.96	[78]
CYC-B11		DMF	305(4.5), 388(5.40), 554 (2.42)	0.714	16.1	95 (580)	0.69	7.9	[45]
CYC-B13		DMF	295 (8.6); 397 (3.4); 547 (1.93)	0.728	10.26	90 (550)	0.68	5.1	[46]
C101		DMF	305; 341; 407; 547 (1.75)	0.746	5.42	89 (580)	0.833	11.3	[44]

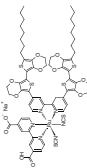
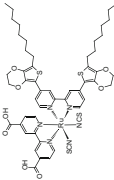
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Table 3 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{OC}/V$	$J_{SC}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}$ %	
C104		DMF	312 (5.4); 368 (4.5); 553 (2.05)	0.76	17.87	85 (580)	0.776	10.53	[62]
C106		DMF	310 (3.95); 348 (3.1); 550 (1.87)	0.749	18.28	90 (520–640)	0.772	10.57	[41]
KW-1 <sup>a</sup>		DMF	301 (4.58); 369 (3.51); 515 (3.56)	0.625	1.06	—	0.46	0.31	[57]
RT-1 <sup>a</sup>		DMF	301 (3.04); 368 (2.28); 529 (1.41)	0.58	6.0	—	0.70	2.45	[79]
RT-2 <sup>a</sup>		DMF	300 (4.34); 445 (2.88); 551 (1.68)	0.57	5.3	—	0.75	2.84	[79]
RT-3 <sup>a</sup>		DMF	305 (4.56); 388 (3.15); 563 (2.76)	0.54	4.5	—	0.76	1.85	[79]
(continued)									

(continued)

Table 3 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{OC}/V$	$J_{SC}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}$ %	
C107		DMF	310 (3.9); 453 (5.43); 552 (2.8)	0.739	19.8	92 (550)	0.751	10.7	[47]
SJW-E1		DMF	310; 360; 546 (1.87)	0.669	21.6	72.6 (550)	0.626	9.02	[77]

<sup>a</sup>These compounds were named after the initials of the first author of the reference cited

## 8.1 1,10-Phenanthroline Derivative Ligands

Besides 2,2'-bipyridine derivatives, 1,10-phenanthroline and its derivatives are gaining attention to be used in *cis*-[Ru(dcbH<sub>2</sub>)(L)(NCS)<sub>2</sub>] sensitizers. Their similarity to 2,2'-bipyridine and the advantage of having an extended  $\pi$ -conjugated structure led to a great potential to be employed as ancillary ligands [81]. This class of compounds still having few complexes reported in DSSCs, and their spectral as well as photoelectrochemical parameters are listed in Table 4.

The use of phenanthroline derivatives in ruthenium(II) sensitizers leads to properties favorable to the energy conversion processes and can increase the DSSCs performances, which have shown promising results [48, 82, 83].

The comparison on the properties of the complex NOK-1 [83] with N3 indicates that the substitution of the 2,2'-bipyridine derivative by 1,10-phenanthroline does not exhibit better performance or absorption properties. On the other hand, the complexes YS5 and AVM-2 exhibit higher absorbance and also had better performance than the complexes N719 and N3 under the same conditions [48, 86], indicating that this is a promising class of compounds to be investigated. Their higher efficiency was ascribed to an enhancement of electron injection. This effect is due to the reduction of dihedral angle between phenanthroline and its substituents (phenyl or carbazole) on the excited state, allowing the electron injection through the thermalized triplet excited state.

## 9 Natural Dyes

Faster, cheaper, low-energy way alternative for ruthenium sensitizers are natural dyes and these compounds have been gaining much attention. Natural dyes can be obtained from fruits, flowers, or leaves and are suitable for educational purposes [91–93] or are an environmentally friendly alternative for dye production since a long-term stability of DSSC using these sensitizers has been demonstrated [94].

On the last years, these natural dyes solar cells experienced a great transformation, focusing on alternatives to improve the performance of such DSSCs [95–102], and special attention is given for dye cocktails [103–106] or co-sensitization approach [107]. There are also several papers describing the use of natural dyes in solid, or quasi-solid, solar cells [108, 109] or using semiconductors such as ZnO [110–112] in such DSSCs, as well as their use on investigations of electron injection/recombination processes. In this chapter, it is presented only the results reported on natural dye-sensitizers used in DSSCs having TiO<sub>2</sub> as semiconductor and liquid mediator.

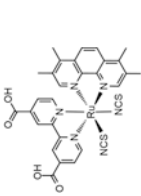
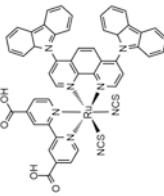
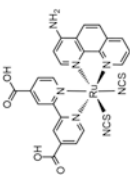
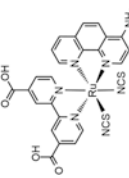
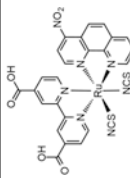
The absorption properties and photoelectrochemical performance of natural dye-sensitized solar cells reported since 2003 are listed in Table 5.

**Table 4** Absorption properties and photoelectrochemical performance of ruthenium(II) *tris*-heteroleptic ruthenium compounds having 1,10-phenanthroline derivatives

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4 L mol^{-1} cm^{-1}$ )	$V_{oc}/V$	$J_{sc}/mA cm^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}$ %	
Y55		DMF	283(5.68), 308 (3.95), 362 (0.81), 522 (1.71)	0.749	14.52	64.6 (540)	0.557	6.05	[48]
AR25		DMF	420; 518(6.58)	0.69	9.6	61 (520)	0.39	2.6	[82]
NOK-1 <sup>a</sup>		0.01 M NaOH aqueous solution	267 (5.7); 309 (2.9); 400 (1.0); 492(1.2)	0.65	15.3	74	0.67	6.7	[83]
NOK-2 <sup>a</sup>		0.01 M NaOH aqueous solution	275 (5.7); 310 (3.5); 374 (1.8); 492 (1.1)	0.62	11.7	54	0.73	5.3	[83]
FC-1 <sup>a</sup>		Acetonitrile	430 (1.3); 535 (1.0)	0.683	12.72	60 (515)	0.55	4.60	[84]

(continued)

Table 4 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance						References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{oc}/V$	$J_{sc}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}\%$		
AVM-1 <sup>a</sup>		Acetonitrile	420 (1.3); 535 (0.8)	0.627	11.9	50 (505)	0.67	5.0	[85]	
AVM-2 <sup>a</sup>		Ethanol	330 (2.0); 375 (1.4); 525 (1.8)	0.76	15.6	79 (500)	0.716	8.6	[86]	
AR24a		DMF	420 (1.2); 546 (0.9)	0.48	1.45	—	0.31	0.22	[87]	
AR24b		DMF	415 (1.0); 545 (0.9)	0.46	0.98	—	0.31	0.14	[87]	
AR27a		DMF	403 (0.5); 538 (0.7)	0.44	5.26	—	0.34	0.8	[87]	

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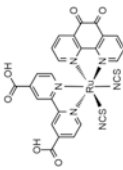
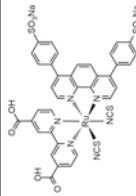
Table 4 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance					References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4 L mol^{-1} cm^{-1}$ )	$V_{oc}/V$	$J_{sc}/mA cm^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}$ %	
AR27b		DMF	400 (0.5); 535 (0.7)	0.44	0.79	—	0.35	0.13	[87]
HJ1		Methanol	304 (1.33); 428 (0.52), 516 (0.57)	0.67	9.65	—	0.44	2.83	[88]
CYC-P1		DMF	302 (3.9); 380 (3.8); 518 (0.8)	0.64	14.92	—	0.63	6.01	[89]
CYC-P2		DMF	304 (2.3); 423 (2.2); 530 (0.4)	0.55	9.8	—	0.64	3.42	[89]

(continued)



Table 4 (continued)

Abbreviation	Structure	Absorption properties		Photoelectrochemical performance						References
		Solvent	$\lambda_{MAX}/nm$ ( $\epsilon_{MAX}/10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ )	$V_{OC}/V$	$J_{SC}/\text{mA cm}^{-2}$	IPCE <sub>MAX</sub> % ( $\lambda/nm$ )	$ff$	$\eta_{cell}\%$		
K27		DMF	292 (4.8); 380 (1.3); 524 (1.1)	0.55	7.19	—	0.63	2.51	[90]	
K28		DMF	308 (5.4); 380 (1.0); 476 (1.6); 522 (1.8)	0.50	5.59	—	0.60	1.69	[90]	

<sup>a</sup>These compounds were named after the initials of the first author of the reference cited

**Table 5** Absorption properties and photoelectrochemical performance of natural dye-sensitized solar cells reported since 2003

Extract of	Dye	Medium	$\lambda_{\text{max}}$ (nm)	$V_{\text{oc}}/V$	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	$ff$	$\eta_{\text{cell}}$ (%)	References
Red cabbage	Anthocyanin	Water	550	0.52	0.68	0.70	0.50	[113]
Rosella flower ( <i>Hibiscus sabdariffa</i> L.)	Anthocyanin	Water	520	0.404	1.63	0.57	0.37	[114]
Blue pea flower ( <i>Clitoria tematea</i> )	Anthocyanin	Water	580, 620	0.372	0.37	0.33	0.05	[114]
<i>Canna indica</i> flower	Anthocyanin	Water and Ethanol	513	0.54	0.82	0.59	0.29	[115]
		TiO <sub>2</sub>	530	—	—	—	—	
<i>Salvia splendens</i> flower	Anthocyanin	Water and ethanol	507	0.558	0.7	0.61	0.26	[115]
		TiO <sub>2</sub>	516	—	—	—	—	
Cowberry	Anthocyanin	Water and ethanol	522	0.556	0.4	0.54	0.13	[115]
		TiO <sub>2</sub>	531	—	—	—	—	
<i>Solanum nigrum</i>	Anthocyanin	Water and ethanol	539	0.54	1.01	0.51	0.31	[115]
		TiO <sub>2</sub>	564	—	—	—	—	
<i>Rhododendron arboretum zeylanicum</i>	Anthocyanin	Ethanol	538	0.4020	1.15	0.637	0.29	[116]
<i>Sesbania grandiflora</i> Scarlet	Anthocyanin	Ethanol	544	0.4067	4.40	0.569	1.02	[116]
<i>Hibiscus rosasinensis</i>	Anthocyanin	Ethanol	534	0.4003	4.04	0.633	1.02	[116]
<i>Hibiscus surattensis</i>	Anthocyanin	Ethanol	545	0.3921	5.45	0.535	1.14	[116]
<i>Nerium oleander</i>	Anthocyanin	Ethanol	539	0.4088	2.46	0.591	0.59	[116]
<i>Ixora macrothyrsa</i>	Anthocyanin	Ethanol	537	0.4031	1.31	0.568	0.30	[116]
Black rice ( <i>Oryza sativa</i> L. indica)	Anthocyanin	Ethanol	560	0.551	1.142	0.52	—	[117]
<i>Rosa xanthina</i>	Anthocyanin	Ethanol	560	0.492	0.637	0.52	—	[117]
Maple leaves	Anthocyanin	Ethanol	536	0.65	1.0	0.60	0.4	[118]
Red Sicilian orange	Anthocyanin	Water	515	0.340	3.84	0.5	—	[119]
Skin of eggplant	Anthocyanin	Water	522	0.350	3.40	0.4	—	[119]
Skin of jaboricaba	Anthocyanin	Ethanol	535	0.66	2.6	0.62	—	[120]
Begonia	Anthocyanin	Ethanol	540	0.537	0.63	0.722	0.24	[121]

(continued)

Table 5 (continued)

Extract of	Dye	Medium	$\lambda_{\text{max}}$ (nm)	$V_{\text{oc}}/V$	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	$ff$	$\eta_{\text{cell}}$ (%)	References
Violet	Anthocyanin	0.1 M HCl— ethanol	546	0.498	1.02	0.645	0.33	[121]
Blackberry	Anthocyanin	—	—	0.320	5.85	0.57	1.07	[122]
Mulberry	Anthocyanin	TiO <sub>2</sub>	553	0.42	0.86	0.43	—	[123]
Red mulberry	Anthocyanin	—	—	0.340	4.45	0.64	0.99	[122]
Radicchio	Anthocyanin	—	—	0.322	5.05	0.55	0.90	[122]
Giacchè grapes	Anthocyanin	—	—	0.333	3.06	0.56	0.57	[122]
<i>Erythrina variegata</i>	Anthocyanin	Ethanol	451; 492	0.48	0.78	0.55	—	[124]
Chaste tree fruit	Anthocyanin	TiO <sub>2</sub>	555	0.39	1.06	0.48	—	[123]
Cabbage-palm fruit	Anthocyanin	TiO <sub>2</sub>	552	0.44	0.37	0.61	—	[123]
Dragon fruit ( <i>Hylocereus polyrhizus</i> )	Anthocyanin	Water	535	0.22	0.20	0.30	0.22	[125]
Bitter leaf ( <i>Vernonia amygdalin</i> )	Anthocyanin	Ethanol	400	0.38	0.50	0.89	0.96	[126]
Red onion ( <i>Allium cepa</i> )	Anthocyanin	Water	520	0.44	0.51	0.48	0.14	[127]
Henna ( <i>Lawsonia inermis</i> )	Anthocyanin	Ethanol	518	0.61	1.87	0.58	0.66	[128]
Red frangipani flowers	Anthocyanin	Ethanol	530	0.50	0.94	0.65	0.301	[129]
<i>R. chinensis</i>	Anthocyanin	—	—	0.54	0.80	0.66	0.29	[130]
<i>Delonix regia</i>	Anthocyanin	TiO <sub>2</sub>	538	0.30	1.33	0.39	0.317	[131]
<i>Eugenia jambolana</i>	Anthocyanin	TiO <sub>2</sub>	543	0.35	1.49	0.48	0.505	[131]
<i>Panica granatum pleniflora</i>	Anthocyanin	—	—	0.62	0.40	0.61	0.15	[132]
<i>Consolida orientalis</i>	Anthocyanin	—	—	0.60	0.56	0.53	0.18	[132]
<i>Clematis orientalis</i>	Anthocyanin	—	—	0.42	0.22	0.49	0.05	[132]
Strawberry	Anthocyanin	—	—	0.47	1.33	0.37	0.229	[133]
<i>Luffa cylindrica L.</i>	Anthocyanin	Ethanol	420; 450	0.52	0.44	0.60	0.13	[134]
Purple corn (husk)	Anthocyanin	—	—	0.46	3.57	0.64	1.06	[135]

(continued)

Table 5 (continued)

Extract of	Dye	Medium	$\lambda_{\text{max}}$ (nm)	$V_{\text{oc}}/V$	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	$ff$	$\eta_{\text{cell}}$ (%)	References
Purple corn (cob)	Anthocyanin	—	—	0.48	3.42	0.62	1.01	[135]
Purple corn (silk)	Anthocyanin	—	—	0.48	3.25	0.62	0.96	[135]
Red tamarind ( <i>T. indica</i> )	Anthocyanin	Methanol	525	0.532	0.35	0.67	0.14	[136]
Calafate fruit	Anthocyanin	Water	525	0.47	6.2	0.36	—	[120]
		TiO <sub>2</sub>	545	—	—	—	—	
Raw beet	Betalain	TiO <sub>2</sub>	470	0.22	2.00	0.51	0.19	[137]
		Water	535	—	—	—	—	
Red turnip	Betalain	Water	484, 536	0.425	9.5	0.37	1.7	[138]
		TiO <sub>2</sub>	450	—	—	—	—	
Wild silician prickly pear	Betalain	TiO <sub>2</sub>	460	0.375	8.20	0.38	1.19	[138]
Red <i>Bougainvillea glabra</i>	Betalain	Water	482, 535	0.26	2.34	0.74	0.45	[139]
Violet <i>Bougainvillea glabra</i>	Betalain	Water	547	0.23	1.86	0.71	0.31	[139]
Red <i>Bougainvillea spectabilis</i>	Betalain	Water	480	0.28	2.29	0.76	0.48	[139]
Violet <i>Bougainvillea spectabilis</i>	Betalain	Water	535	0.25	1.88	0.73	0.35	[139]
Cactus fruits ( <i>O. dillenii</i> )	Betalain	Methanol	517	0.521	1.09	0.69	0.47	[136]
Kelp	Chlorophyll	Ethanol	460	0.441	0.433	0.62	—	[117]
Wormwood	Chlorophyll	Ethanol	432	0.67	2.3	0.56	0.9	[118]
Bamboo leaves	Chlorophyll	Ethanol	432	0.67	1.9	0.56	0.7	[118]
Pomegranate leaves	Chlorophyll	Ethanol	412, 665	0.560	2.05	0.52	0.597	[140]
Perilla	Chlorophyll	Ethanol	665	0.522	1.36	0.696	0.50	[121]
Petunia	Chlorophyll	Ethanol	665	0.616	0.85	0.605	0.32	[121]
China loropetal	Chlorophyll	Ethanol	665	0.518	0.84	0.626	0.27	[121]
Chinese rose	Chlorophyll	0.1 M HCl— ethanol	516	0.483	0.90	0.619	0.27	[121]

(continued)

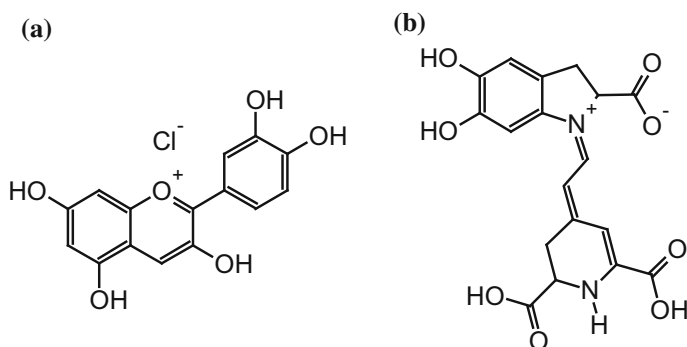
Table 5 (continued)

Extract of	Dye	Medium	$\lambda_{\text{max}}$ (nm)	$V_{\text{oc}}/V$	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	$ff$	$\eta_{\text{cell}}$ (%)	References
Spinach	Chlorophyll	Ethanol	437	0.55	0.47	0.51	0.131	[141]
Ipomoea	Chlorophyll	Ethanol	410	0.54	0.91	0.56	0.278	[141]
<i>Festuca ovina</i>	Chlorophyll	Methanol	420; 660	0.54	1.18	0.69	0.46	[142]
Shiso	Chlorophyll	Water and Ethanol	440; 600	0.55	3.56	0.51	1.01	[143]
<i>Ficus reusa</i>	Chlorophyll	Ethanol	670	0.520	7.85	0.29	1.18	[144]
<i>Rhoeo spathacea</i>	Chlorophyll	Ethanol	670	0.496	10.9	0.27	1.49	[144]
<i>Garcinia subelliptica</i>	Chlorophyll	Ethanol	670	0.322	6.48	0.33	0.691	[144]
<i>Aneithum graveolens</i>	Chlorophyll	Ethanol	666	0.579	0.965	0.40	0.22	[145]
Parsley ( <i>Petroselinum crispum</i> )	Chlorophyll	Ethanol	666	0.445	0.535	0.34	0.07	[145]
Arugula	Chlorophyll	Ethanol	666	0.599	0.788	0.42	0.20	[145]
Green algae	Chlorophyll	Ethanol	666	0.559	0.397	0.44	0.10	[145]
<i>U. pinnatifida</i>	Chlorophyll	—	—	0.36	0.8	0.69	0.178	[146]
Curcumin	Polyphenol	Ethanol	430	0.53	0.53	0.72	0.41	[113]
Tangerine peel	Polyphenol	Ethanol	446	0.592	0.74	0.631	0.28	[121]
Flowery knotweed	Polyphenol	Ethanol	435	0.554	0.60	0.627	0.21	[121]
<i>Reseda luteola</i>	Polyphenol	—	—	0.64	0.54	0.64	0.22	[132]
<i>Berberis integerrima</i>	Polyphenol	—	—	0.56	0.004	0.53	0.01	[132]
<i>Reseda gredensis</i>	Polyphenol	—	—	0.53	0.14	0.71	0.07	[132]
<i>Consolida ajacis</i>	Polyphenol	—	—	0.55	1.68	0.65	0.60	[132]
<i>Salvia sclarea</i>	Polyphenol	—	—	0.37	0.10	0.54	0.02	[132]
Mallow	Polyphenol	Ethanol	660	0.60	0.69	0.55	0.215	[133]
Erythrina	Carotenoid	Ethanol	451	0.484	0.776	0.55	—	[117]
Capsicum	Carotenoid	Ethanol	455	0.412	0.225	0.63	—	[117]
Achiote seed	Carotenoid	Chloroform	440, 475, 500	0.56	0.53	0.66	0.19	[147]

(continued)

Table 5 (continued)

Extract of	Dye	Medium	$\lambda_{\text{max}}$ (nm)	$V_{\text{oc}}/V$	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	$ff$	$\eta_{\text{cell}}$ (%)	References
Fructus lycii	Carotenoid	Ethanol	447; 425	0.689	0.53	0.466	0.17	[121]
Marigold	Carotenoid	Ethanol	487	0.542	0.51	0.831	0.23	[121]
Yellow rose	Carotenoid	Ethanol	487	0.609	0.74	0.571	0.26	[121]
Ivy gourd fruits	Carotenoid	Ethanol	458; 480	0.64	0.24	0.49	0.076	[129]
<i>K. japonica</i>	Carotenoid	—	—	0.59	0.56	0.68	0.22	[130]
<i>Adonis flammæa</i>	Carotenoid	—	—	0.59	0.40	0.66	0.16	[132]
Red perilla	—	—	—	0.51	0.39	0.67	0.27	[113]
Herba artemisiae scopariae	—	Ethanol	669	0.484	1.03	0.682	0.34	[121]
Bauhinia tree	—	Ethanol	665	0.572	0.96	0.660	0.36	[121]
Lithospermum	—	Ethanol	520	0.337	0.14	0.585	0.03	[121]
Mangosteen pericarp	—	Ethanol	—	0.686	2.69	0.633	1.17	[121]
Rose	—	Water	—	0.595	0.97	0.659	0.38	[121]
Lily	—	Water	—	0.498	0.51	0.667	0.17	[121]
Coffee	—	Water	—	0.559	0.85	0.687	0.33	[121]
Broadleaf holly leaf	—	Water	—	0.607	1.19	0.654	0.47	[121]



**Fig. 6** Structure of anthocyanidin (a), a flavinic ion of anthocyanin, and betanidin (b), a betalain compound

The most investigated classes of natural dyes are the anthocyanins, commonly found in red-purplish fruits or flowers; or betalains, Fig. 6. Besides these compounds, other sensitizers have also been investigated [148].

Betalain from raw beet, red turnip, and wild sicilian prickly pear have also been used as natural sensitizers and they have presented a good photoelectrochemical response, however these cells have low  $V_{OC}$ , with overall efficiency up to 1.7% and reasonable stability [138]. It was also observed the improvement on the photoelectrochemical performance due to changes on pH as well as in the presence of additives in the mediator layer [122].

Other classes of natural dyes, such as chlorophyll, polyphenol, etc., were also investigated, but the photoelectrochemical parameters were not as good as those observed for anthocyanins or betalains. Several reviews were published and describe the performance of these other classes of dyes along to those presented here [149–153].

## 10 Conclusion

The energy needs will be supplied by alternative sources and dye-sensitized solar cells are one of the most promising devices for this application since they are cheap and environmentally friendly. The investigation of dye-sensitizers is fundamental issue on the development of these devices and one of the most promising alternatives is the use of ruthenium *tris*-heteroleptic dyes sensitizers to modulate or enhance their photoelectrochemical performance. The investigation on natural extracts to be employed as dye-sensitizers has also been attracting much attention in the last years. They can be an alternative to further reduction of the production costs of these revolutionary devices.

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