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Review

Metal complex sensitizers in dye-sensitized solar cells

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Dedicated to Professor Michael Grätzel in recognition of his achievements.
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Contents

Abstract

A brief review of the investigation of solar energy conversion and the development of dye-sensitized thin-layer solar cells is presented, with the main focus on dyes, specially on d^6 metal complexes employed, since 1998, as photosensitizers of nanocrystalline semiconductors. An extensive literature coverage of the spectroscopic properties and the performance of solar cells employing a series of *cis*-[Ru(dcbH$_2$)$_2$LL′] species, in which dcbH$_2$ is 4,4′-(CO$_2$H)$_2$-2,2′-bipyridine and L and/or L′ are ancillary ligands, is presented along with non-carboxylic acid anchoring polypyridine-ruthenium complexes. The utilization of other d^6 metal complexes and natural extracts, with emphasis on Brazilian products, is also reviewed. A list of ligands with structures and a series of Tables summarize the collected data. The research and development on dye-sensitized solar cells conducted at our Laboratory of Inorganic Photochemistry and Energy Conversion at the University of São Paulo-Brazil is also covered in this context as a part of this special issue in homage to Prof. Grätzel.

Keywords: Dye-cells; Sensitizers; Dye-sensitized solar cells; Natural dyes; Energy conversion; Photoelectrochemical solar cells

Abbreviations: AN, acetonitrile; APCE, absorbed photon-to-current efficiency; Black Dye, [Ru(tcterpy)(NCS)$_3$]$^-$; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; Dye-cell, dye-sensitized solar cell; EG, ethylene glycol; EtOH, ethanol; ff, fill factor; FTO, fluorine doped tin oxide; HOAc, acetic acid; IPCE, incident photon to current efficiency; I_{sc}, short circuit current; ITO, indium doped tin oxide; MeOH, methanol; MLCT, metal to ligand charge transfer; 3-MPN, 3-metoxypropionitrile; N3, *cis*-[Ru(dcbH$_2$)$_2$(NCS)$_2$]; NMO, 3-methyl-2-oxazolidinone; PC, propylene carbonate; TBA, tetrabutylamonium; TCO, transparent conducting oxide; TFMS, trifluoromethylsulfonate; THF, tetrahydrofuran; V_{oc}, open circuit voltage; ε, molar absorptivity; η, quenching efficiency; η_{cell}, overall efficiency; λ, wavelength

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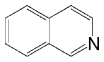
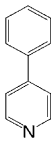
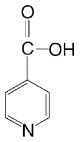
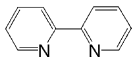
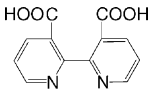
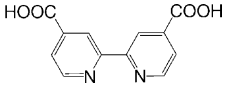
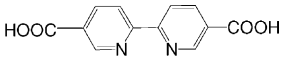
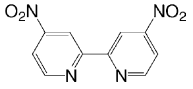
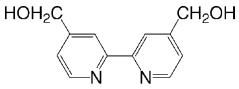
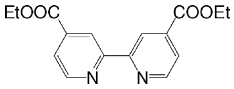
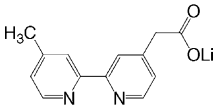
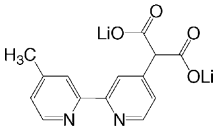
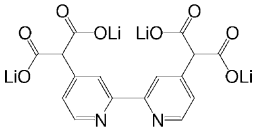
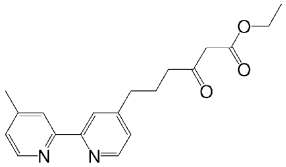
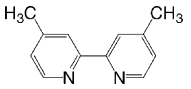
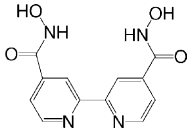
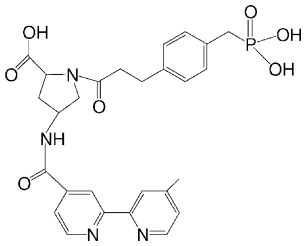
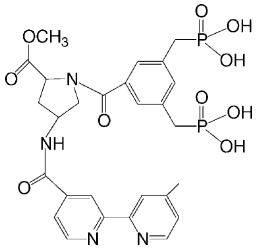
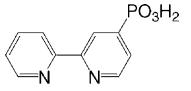
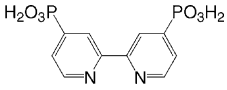
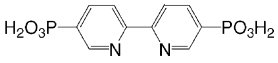
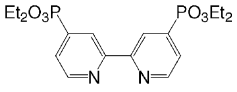
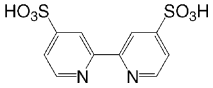
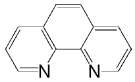
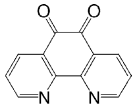
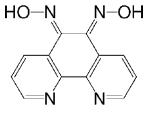
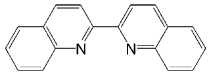
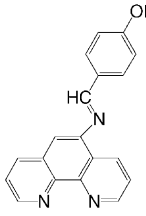
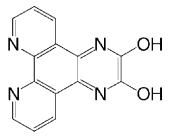
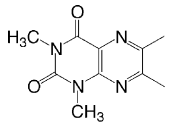
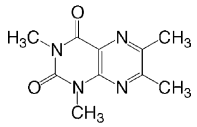
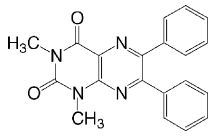
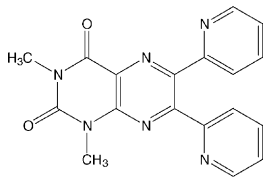
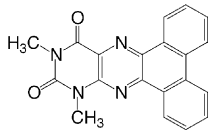
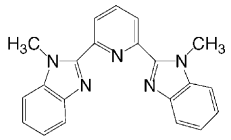
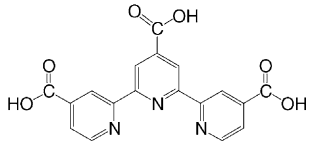
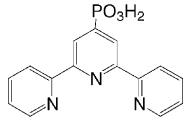
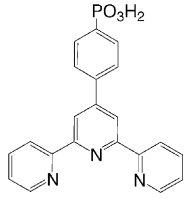
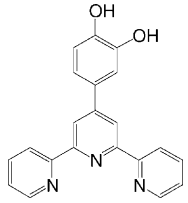
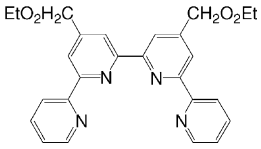
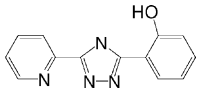
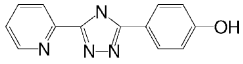
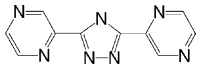
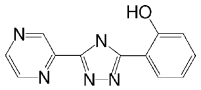
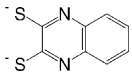
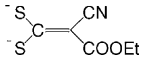
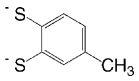
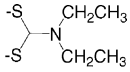
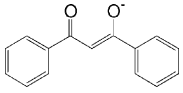
Ligands

Name	Abbreviation	Structure
Pyridine	py	
4-Thiopyridine	pySH	
Isoquinoline	isq	
4-Phenylpyridine	ppy	
4-Cyanopyridine	CNpy	
Isonicotinic acid	isn	
2,2′-Bipyridine	bpy	
3,3′-Dicarboxylic acid-2,2′-bipyridine	3,3′-dcbH$_2$	
4,4′-Dicarboxylic acid-2,2′-bipyridine	dcbH$_2$	
5,5′-Dicarboxylic acid-2,2′-bipyridine	5,5′-dcbH$_2$	
4,4′-Dinitro-2,2′-bipyridine	bpy-(NO$_2$)$_2$	
4,4′-Dihydroxymethyl-2,2′-bipyridine	bpy-(CH$_2$OH)$_2$	
4,4′-dicarboxylate-diethyl 2,2′-bipyridine	bpy-(CO$_2$Et)$_2$	
4-(Lithium carboxymethyl)-4′-methyl-2,2′-bipyridine	bpy-CH$_2$COOLi	
4-(1,1-Dilithiumcarboxymethyl)-4′-methyl-2,2′-bipyridine	bpy-CH(COOLi)$_2$	
4,4′-(1,1-Dilithiumcarboxymethyl)-2,2′-bipyridine	bpy-(CH(COOLi)$_2$)$_2$	
4-[4-Oxo-5-(ethoxycarbonyl)pentyl]-4′-methyl-2,2′bipyridine	bpy-acac	

Name	Abbreviation	Structure
4,4′-Dimethyl-2,2′-bipyridine	dmbpy	
4,4′-Dihydroxamic acid-2,2′-bipyridine	$dobH_2$	
3-Dihydroxy phosphinyl-*cis*-4-(4′-methyl-2,2′-bipyridine-4-carboxamido)-L-proline-*N*-carboxylic acid	pbp-pra	
3,5-Bis(dihydroxy phosphinyl)-*N*-(1,1-dimethoxycarbonyl)-*cis*-4-(4′-methyl-2,2′-bipyridine-4-carboxamido)-L-proline methyl ester	bpb-pra	
4-Phosphonic acid-2,2′-bipyridine	bpy-PO_3H_2	
4,4′-Biphosphonic acid-2,2′-bipyridine	bpy-$(PO_3H_2)_2$	
5,5′-Biphosphonic acid-2,2′-bipyridine	5,5′-bpy-$(PO_3H_2)_2$	
4,4′-Dietyl ester phosphonate-2,2′-bipyridine	bpy-$(PO_3Et_2)_2$	
2,2′-Bipyridine-4,4′-disulphonic acid-2,2′-bipyridine	dsbpy	
1,10-Phenanthroline	phen	
Phendione	phendione	
Phendioxime	phendioxime	
2,2′-Biquinoline	biquin	
4-([1,10]Phenanthrolin-5-yliminomethyl)-phenol	aphb	

Name	Abbreviation	Structure
2,3-Dihydroxydipyrido[3,2-*f*:2′,3′-*h*] quinoxaline	$dpq(OH)_2$	
2,4-(1,3-*N*,*N*′-Dimethyl)pteridinedione	dmp	
6,7-Dimethyl-2,4-(1,3-*N*,*N*′-dimethyl) pteridinedione	mdmp	
6,7-Diphenyl-2,4-(1,3-*N*,*N*′-dimethyl) pteridinedione	phdmp	
6,7-Bis(pyrid-2-yl)-2,4-(1,3-*N*,*N*′-dimethyl) pteridinedione	pydmp	
Dibenzo[*h*,*j*]-(1,3-*N*,*N*′-dimethyl)isoalloxazine	bIAlo	
2,6-Bis(1-methylbenzimidazol-2-yl)pyridine	bmipy	
4,4′,4″-Tricarboxylic acid-2,2′:6′,2″-terpyridine	tc-terpy	
4-Phosphonic acid-2,2′:6,2″-terpyridine	hp-terpy	
4′-(4-Phosphonic acid phenyl)-2,2′:6′,2″-terpyridine	ttp-PO_3H_2	
4′-(3,4-Dihydroxyphenyl)-2,2′:6′,2″-terpyridine	dhpt	

Name	Abbreviation	Structure
4′,4″-Diethoxycarbonyl-2,2′:6′,2″:6″,2‴-quaterpyridine	detOq	
3-(2-Hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole	2-ppt	
3-(4-Hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole	4-ppt	
3,5-Bis(pyrazin-2-yl)-1,2,4-triazole	bpzt	
3-(2-Hydroxyphenyl)-5-(pyrazin-2-yl)-1,2,4-triazole	2-ppzt	
Quinoxaline-2,3-dithiolate	qdt	
Ethyl-2-cyano-3,3-dimercaptoacrylate	ecda	
1,2-Benzenedithiolate	bdt	
3,4-Toluenedithiolate	tdt	
N,*N*′-Diethyldithiocarbamate	ddtc	
Acetylacetonate	acac	
3-Methyl-2,4-pentanedionate	mpdionate	
1,3-Diphenyl-1,3-propanedionate	dphdionate	

1. Introduction

An energy system infrastructure is fundamental for worldwide technological and economic achievements. In the 21st century, fossil fuel based energy has to be replaced by new energy systems by incorporating novel technologies derived from advancements in science [1]. Renewables are the perspective for future energy needs and the key to sustainable development.

Solar photovoltaic cells, capable of directly converting sunlight into electrical power, are one of the most promising devices in the search for sustainable and renewable sources of clean energy [2,3]. Although the field had been dominated in the last years of the past century by technology based on the solid-state p–n junction devices, a new generation of photovoltaics is now emerging. One of them is the dye-sensitized nanocrystalline solar cell [4–6], named by us as Dye-cell.

The Dye-cell is the result of exploiting several new concepts and materials, such as nanotechnology and molecular devices, and it is one of the new approaches for photovoltaic technology. This device is based on chemical concepts, in which the separation of charge carriers is kinetically controlled by the chemical reactions involved. The tasks of light absorption and charge carrier transport are separated in a Dye-cell by having the light absorbed by sensitizers (dyes) chemically attached to the surface of a nanostructured wide band-gap semiconductor (mesoporous oxides); they therefore do not require an intrinsic electric field.

The simple materials employed in production provide an efficient and low cost solar cell. Moreover, the process generates a very little residue. Thus among several other advantages, the low environmental impact [7,8] and reduced energy demand in the production of dye-sensitized solar cells [1] are certainly worth emphasizing [1,8,9].

In this special issue in homage to Prof. Grätzel, a brief review of thin-layer solar cells based on the sensitization of the wide band-gap TiO_2 semiconductor films by some metal complexes or natural dyes will be presented. The

main focus will be on dyes, specially on d^6 metal complexes employed during the last few years as photosensitizers of nanocrystalline semiconductors. Due to the page limit of this issue, an extensive literature coverage of spectroscopic properties and performance in solar cells has been limited for a series of ruthenium(II) complexes of bis(dicarboxylic acid bipyridine), *cis*-$[Ru(dcbH_2)_2LL']$, in which $dcbH_2$ is 4,4′-$(CO_2H)_2$-2,2′-bipyridine and L and/or L′ are ancillary ligands, and for ruthenium complexes with polypyridine ligands having non-carboxylic acid anchoring groups. The utilization of natural sensitizers, including several Brazilian natural products, as well as other d^6 sensitizers is also reviewed. A list of ligands and a series of tables summarize the data collected.

The research and development on dye-sensitized solar cells conducted at our Laboratory of Inorganic Photochemistry and Energy Conversion at the University of São Paulo-Brazil is also covered in this context as a part of this special issue to provide a perspective for some of our representative experimental results and to place our own work in this field.

The studies carried out in our Laboratory had been initially focused on kinetics, electrochemistry and spectroscopy of some inorganic compounds with emphasis on the reactivity of the ground state [10–22], followed by investigation on the photoreactivity of these compounds [11,23–27]. Our interests have also been extended to supramolecular photochemistry [28–30], photosensors [31–35] and nanocrystalline semiconductor sensitization [1,5,28,29,36–44]. This natural step had positive inputs through important collaborations established with Prof. Carlo A. Bignozzi and Prof. Thomas J. Meyer. A very important additional motivation resulted from very fruitful discussions maintained since 1997 with the Lausanne Group through Prof. Grätzel and Dr. Nazeeruddin.

During our visit in their Laboratory at EPFL in 1998, the ensuing discussion strongly encouraged us in our incipient investigation of natural dyes. Both their enthusiasm and similar objectives have provided a driving force for our research in such an interdisciplinary area.

2. Overview

The dye-sensitized solar cell is a particularly interesting case of an integrated chemical system [45,46], in which a device is designed and molecularly engineered to perform light conversion into electricity. It is a fascinating multidisciplinary topic of current interest and a very active research field, which has attracted wide attention in the last decade. It also illustrates an application that has evolved from fundamental investigation to the concept of specifically designed artificial molecular devices [47].

The device itself, operating principles, stability, theoretical background, state of the art, technology and manufacturability as well as historical overview have been the subject of recent reviews [1,9,48] and will not be covered here. Several books and other review papers [4,6,46,49–52] have already discussed different aspects of dye-sensitized solar cells, but two of them are particularly worthwhile for visualizing research horizons in this field [6,46]. Kalyanasundaram and Grätzel presented an instructional and wide coverage in their 1998 review [46]; this being one of the reasons for this work to focus on papers published from 1997/1998 up to now. Updated results and ongoing investigation can now be followed in this and other papers of this special issue; therefore, only the basic principles required for understanding the subjects discussed here will be briefly presented in this review.

Historically, chemically-based systems such as photogalvanic and photoelectrochemical cells have been developed [51,52] as an alternative to the conventional solid-state p–n junction photovoltaics for the conversion of solar energy into electricity.

The use of coordination compounds, such as $[Ru(bpy)_3]^{2+}$, as light absorbers, was one of the first approaches to convert low-energy starting materials into high-energy products in homogeneous cells, although with low efficiencies due to the fast recombination of the photoproducts in the solution [51].

Photoelectrochemical cells seemed to be the answer to accomplish this conversion, but early experiments resulted in low photocurrent generation [51,53]. The use of photostable wide band-gap semiconductors required high-energy light to create electron–hole pairs and the effectiveness of dye sensitization was restricted by the surface area of TiO_2 crystals, sub-monolayer coverage and low absorptivities [54]. It did however present advantages over direct band to band excitation of semiconductors due to the reduction of electron–hole recombination.

Semiconductors in mesoporous membrane type film with a high surface area led to an efficient light absorption by attached sensitizers and resulted in intensely colored photoanodes. Solar cells employing such photoanodes presented astonishing results, with photoresponse 1000 times higher for the nanostructured electrode [49,55]. In the early 1990s the development of extremely rough TiO_2 and an efficient photosensitizer led to photoelectrochemical solar cells recognized as an efficient device for conversion of solar energy into electricity [6].

In this approach, attached dyes, rather than the semiconductor itself, are the absorbing species. They inject electrons into the semiconductor conduction band upon excitation. These electrons are then collected at a conducting surface, generating photocurrent. As a result of this advance, the development of low-cost, efficient photochemical solar cells became possible [6,56].

The field experienced steady progress since then and dye-sensitized photoelectrochemical solar cells attained the required maturity to become a noteworthy device for production [9,57,58]. Due to the multitude of issues related to

dye-sensitized solar cells, investigations are currently spread over a wide range of fields. The research is supported by contributions from interdisciplinary domains in several aspects, such as molecular engineering and syntheses of new dyes, TCO and semiconductor materials, electrolyte media, long-term stability of the devices, theoretical studies of the photoconversion process and so on.

3. Dye-sensitized solar cells

Regenerative photoelectrochemical solar cells based on a thin-layer sandwich-type set-up containing a dye-sensitized nanocrystalline TiO_2 photoanode are now commercially feasible devices.

Dye sensitization has provided a successful solution to extending the absorption range of the cells to low-energy light with effective results. This approach presents advantages over the direct band-to-band excitation in conventional solar cells, since attached dyes, rather than the semiconductor itself, are the absorbing species and the processes of light absorption and charge separation are separated by the semiconductor/sensitizer interface preventing electron–hole recombination [28,29,59–67]. Electron injection from the photoexcited sensitizer into the semiconductor conduction band occurs with energy lower than the band gap, providing good sunlight harvesting by sensitizers (dyes) which exhibit broad absorption bands in the visible region.

A typical dye-sensitized solar cell is depicted in Fig. 1. The device is constituted of two transparent conducting oxide substrates, TCO, such as fluorine doped tin oxide, FTO, on glass or polymeric substrates [4,68]. One TCO is a photoanode, composed of a sensitizer adsorbed onto the surface of the nanocrystalline semiconductor electrode (typically nanostructured TiO_2), and the other a photoinert counterelectrode with a thin layer of a catalyst (for instance, platinum) sandwiching an electrolyte/relay medium (usually a solution containing the I_3^-/I^- pair).

n-TiO_2 is the most employed semiconductor material in dye-sensitized photoelectrochemical solar cells due to its favorable energetics, stability, low price and facile processing [68–71]. Semiconductor colloids are typically obtained via a sol–gel process from titanium isopropoxide or directly from commercial TiO_2. Whereas the preparation of colloids from Degussa TiO_2 is easier and faster, the isopropoxide hydrolysis method results in transparent to translucent semiconductor films [5]. Screen printing of TiO_2 sol followed by sintering around 450 °C are usually used to provide textured semiconductor substrates with nanocrystalline structure.

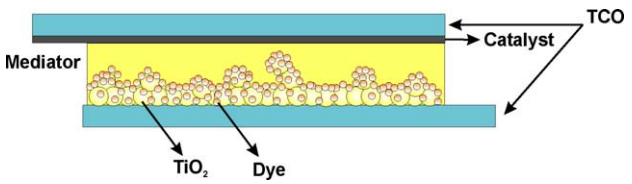


Fig. 1. Thin-layer sandwich-type solar cell and its components.

The sensitization of wide band gap nanocrystalline semiconductor oxides by dyes has been intensively investigated and a strategy to obtain both the photosensitizer and the interface through molecular engineering is one of the most attractive approaches to improve the performance of the cell. Thus, the following items of this review are dedicated to photosensitizers, with the main focus on metal complex sensitizers.

The photoexcitation of sensitizer and subsequent electron injection into the conduction band of the semiconductor allows population of the band using light of energy lower than the semiconductor band gap, and can provide a good match with the solar spectrum. The oxidized sensitizer (S^+) is quickly reduced back to S by the redox mediator couple, usually I_3^-/I^-, present in the electrolyte and this is, in turn, regenerated at the counter electrode, concluding the redox cycle. The reduction of I_3^- is catalyzed by small amounts of Pt deposited on the counter electrode. Therefore, in this regenerative electrochemical device, visible light is efficiently converted into electricity without any permanent chemical change.

The performance of the cell can be quantified on a macroscopic level with parameters such as Incident Photon to Current Efficiency, IPCE, open circuit photovoltage, V_{oc}, and the overall efficiency of the photovoltaic cell, η_{cell}. Several parameters such as the spectroscopic and redox properties of dyes, the efficiency of charge injection and the structural properties/characteristics of the semiconductor electrode to collect and direct electrons through the external circuit are relevant to determine the photocurrent values and will certainly be subjects of several reviews in this special issue.

4. Photosensitizers

An efficient photosensitizer should fulfill some requirements such as an intense absorption in the visible region, strong adsorption onto the semiconductor surface and efficient electron injection into the conduction band of the semiconductor. Moreover, it must be rapidly regenerated by the mediator layer in order to avoid electron recombination processes and be fairly stable, both in the ground and excited states. Many different compounds have been investigated for semiconductor sensitization, such as porphyrins [72,73,55], phthalocyanines [74–81], coumarin 343 [82,83], carboxylated derivatives of anthracene [84,85] and polymeric films. Among the photosensitizers investigated, transition metal complexes have been the best so far [1,46].

4.1. Metal complex sensitizers

Metal complexes sensitizers usually have anchoring ligands and ancillary ligands. Anchoring ligands are responsible for the complex adsorption onto the semiconductor

surface and are also chromophoric groups. Ancillary ligands are not directly attached onto the semiconductor surface and can be used for tuning the overall properties of the complexes.

Polypyridinic complexes of d^6 metal ions show intense metal to ligand charge transfer (MLCT) bands in the visible region with potential interest for promoting charge injection processes to the conduction band of wide band gap semiconductors, such as TiO_2, SnO_2 and ZnO. The energies of the MLCT states can be altered systematically by modifying the anchoring ligands as well as by changing the ancillary ligands or its substituents.

The wide possibilities to tune the MLCT energy led to the preparation of many different compounds that have been investigated for semiconductor sensitization. Among them, the best light-to-electricity conversion efficiency has been achieved by using ruthenium(II) polypyridyl complexes as TiO_2 sensitizers in dye-sensitized solar cells. Ruthenium polypyridinic complexes have been intensively employed as sensitizers due to their appropriate redox, spectroscopic, and excited-state properties [86–93]. In particular ruthenium(II) complexes with carboxylic pyridine derivatives are able to react readily with oxide surfaces to form the corresponding esters [46], presenting efficient adsorption onto the semiconductor surface and improved light harvesting efficiency, leading to fine results. Due to the page limit we will restrict our review to a series of ruthenium(II) complexes of bis(dicarboxylic acid bipyridine), $dcbH_2$, although remarkable performance has been observed for other ruthenium sensitizers such as $[Ru(tcterpy)(NCS)_3]^-$, the so called Black Dye [94–96].

4.1.1. Series of *cis*-$[Ru(dcbH_2)_2LL']$

Several studies have been carried out using $[Ru(dcbH_2)_2LL']$ as dyes. The main idea behind these complexes is to have a good anchoring ligand to allow an efficient adsorption onto semiconductor surface, while its properties can be tuned by using different ancillary ligands. Most efficient energy conversion has been observed using bis-(4,4′-dicarboxylic acid-2,2′-bipyridine), $(dcbH_2)_2$, as anchoring ligands leading to these complexes becoming one of the most important classes of photosensitizer investigated so far.

An outstanding result was reported in 1993 by Grätzel and co-workers with the *cis*-$[Ru(dcbH_2)_2(NCS)_2]$ photosensitizer, also known as N3 [97]. Since then it has been employed as a standard dye in several studies, especially to compare the performance of other dyes [43,88,98–101] or the results of modifications introduced in semiconductor composition/treatment [102], as noted in Table 1.

Ever since N3 was reported as a very efficient energy conversion dye, efforts have been made to either match or improve its performance. One approach that has been attempted by several investigators is the substitution of the NCS^- ancillary ligands. This search for efficient *cis*-$[Ru(dcbH_2)_2LL']$ sensitizers has led to a wide variety of new photosensitizers. Their spectroscopic properties are listed in Table 2, while their performance in solar cells is shown in Table 3. Even though the main focus is the performance, the data in Table 2 are also relevant as far as an understanding of these results is concerned.

Data presented in Table 3 point out that the substitution of the ancillary ligands has not, so far, improved the performance of the cells in terms of overall efficiency, η_{cell}, or IPCE values, even though the new dyes could be successfully employed as semiconductor sensitizers. On the other hand, these new photosensitizers usually provide a wider coverage of the solar spectrum, promoting light harvesting in a lower energy region. The MLCT bands are susceptible to a greater electron donating or withdrawing ability of the ancillary ligand as can be seen in a series of complexes using pteridinediones or diimine thiolates [91,105]. Such transitions are sensitive to changes made in the anchoring

Table 1
Photoelectrochemical data obtained with solar cell sensitized by *cis*-$[Ru(dcbH_2)_2(NCS)_2]$

V_{oc} (V)	I_{sc} (mA cm^{-2})	IPCE$_{max}$ (%)	ff	η_{cell} (%)	Remarks	Reference
		82.4				[102]
0.698	17.9	>80	0.56	7.4		[101]
0.662	14.5		0.55	6.8		[100]
0.640	16.5		0.65			[99]
0.55	10.4		0.52	2.99		[98]
0.70	15.0	80	0.74	7.8		[87]
0.57	18.4	67				[103]
	17.5–18.5	80				[104]
0.61	6.4		0.42	6.1		[88]
0.640	5.0		0.76	10.4	[a,b]	[97]
0.660	7.9		0.76	10.4	[a,c]	[97]
0.670	11.5		0.74	10.3	[a,d]	[97]
0.720	18.2		0.73	10.0	[a,e]	[97]

[a] AM 1.5, light intensity.
[b] 24.1 mW cm^{-2}.
[c] 38.2 mW cm^{-2}.
[d] 55.6 mW cm^{-2}.
[e] 96.0 mW cm^{-2}.

Table 2
Spectroscopic parameters of *cis*-[Ru(dcbH$_2$)$_2$LL′] evaluated as photosensitizers

Complex	Solvent	λ_{max} (nm) (ε_{max} (10^4 M^{-1} cm^{-1}))	Reference
[Ru(dcbH$_2$)$_2$(dmp)]Cl$_2$	EtOH	314 (1.68), 362 (sh), 514 (0.22)	[105]
[Ru(dcbH$_2$)$_2$(mdmp)]Cl$_2$	EtOH	246 (3.0), 316 (2.57), 364 (1.7), 550 (0.75)	[105]
[Ru(dcbH$_2$)$_2$(phdmp)]Cl$_2$	EtOH	314 (2.67), 366 (0.84), 410 (sh), 552 (0.33)	[105]
[Ru(dcbH$_2$)$_2$(blAlo)]Cl$_2$	EtOH	314 (1.55), 388 (0.615), 532 (0.52)	[105]
[Ru(dcbH$_2$)$_2$(pydmp)]Cl$_2$	EtOH	300 (0.34), 355 (0.22), 440 (0.75), 512 (0.56)	[105]
[Ru(dcbH$_2$)$_2$(aphb)]	DMF	350, 466	[98]
poly[Ru(dcbH$_2$)$_2$(aphb)	DMF	350, 476	[98]
[Ru(dcbH$_2$)$_2$(CNpy)(H$_2$O)]$^{2+}$	AN	310, 490	[39]
[Ru(dcbH$_2$)$_2$(CNpy)(H$_2$O)]$^{2+}$/TiO$_2$		500	
Ru(dcbH$_2$)$_2$(qdt)	EtOH/MeOH	310 (2.58), 403 (0.94), 476 (0.86), 517 (0.88)	[91]
Ru(dcbH$_2$)$_2$(ecda)	EtOH/MeOH	313 (3.21), 402 (1.75), 500 (0.84), 582 (0.98)	[91]
Ru(dcbH$_2$)$_2$(bdt)	EtOH/MeOH	309 (3.23), 463 (0.95), 662 (0.21)	[91]
Ru(dcbH$_2$)$_2$(tdt)	EtOH/MeOH	307 (3.20), 470 (0.96), 670 (0.20)	[91]
[Ru(dcbH$_2$)$_2$(isq)$_2$]$^{2+}$/TiO$_2$	MeOH	220, 305, 362, 471	[37,38]
[Ru(dcbH$_2$)$_2$(ppy)(H$_2$O)]$^{2+}$		∼525	
[Ru(dcbH$_2$)$_2$(ppy)(H$_2$O)]$^{2+}$/TiO$_2$	MeOH	252, 313, 378, 519	[36,38]
[Ru(dcbH$_2$)$_2$(ppy)$_2$]$^{2+}$		∼500	
[Ru(dcbH$_2$)$_2$(ppy)$_2$]$^{2+}$/TiO$_2$	MeOH	253, 307, 366, 485	[36,38]
[Ru(3,3′-dcbH$_2$)$_2$(NCS)$_2$]	DMF	572	[103]
[Ru(5,5′-dcbH$_2$)$_2$(NCS)$_2$]	DMF	585	[103]
[Ru(dcbH$_2$)$_2$Cl$_2$]	EtOH	304, 380, 540	[88]
[Ru(dcbH$_2$)$_2$(acac)]Cl	NaOH/MeOH	309 (5.35), 384 (1.46), 525 (1.35)	[106]
[Ru(dcbH$_2$)$_2$(mpdionate)]Cl	NaOH/MeOH	310 (5.10), 386 (1.41), 532 (1.21)	[106]
[Ru(dcbH$_2$)$_2$(dphdionate)]Cl	NaOH/MeOH	309 (5.76), 378 (1.37), 514 (1.37)	[106]
Ru(dcbH$_2$)$_3$Cl$_2$	H$_2$O	303, 352, 458	[88]
[Ru(dcbH$_2$)$_2$(4-ppt)]	AN	495	[107]
[Ru(dcbH$_2$)$_2$(2-ppt)]	AN	495	[107]
[Ru(dcbH$_2$)$_2$(bpzt)]	AN	475	[107]
[Ru(dcbH$_2$)$_2$(2-ppzt)]	AN	475	[107]
[Ru(dcbH$_2$)$_2$(ddtc)]	EtOH	312 (3.35) 364 (0.97), 548 (1.13)	[108]
Ru(dcbH$_2$)$_2$(NCS)$_2$	EtOH	314 (4.94) 398 (1.31), 538 (1.31)	[108]

Bibliography since 1998.

group, dcbH$_2$, and the distinct positioning of the carboxylic group can also promote absorption shifts [103] and be conveniently employed to tune the spectroscopic response of the sensitizer.

The proper selection of the ancillary ligands L and L′ in these complexes, provides the suitable energetic control of the properties of the species. Different compounds with appropriate characteristics can be molecularly engineered enabling the design of efficient sensitizers of TiO$_2$ for photoelectrochemical solar cells. The two ancillary ligands, coordinated to the non-attached side of the dye, can be conveniently replaced in order to adjust or tune the absorption bands to low-energy wavelengths, thus enhancing its spectroscopic response to the visible light [37,38,109–112].

The contribution of our group in the design of photosensitizers has been based on our experience in molecularly engineering metal complexes and a knowledge of their photophysics and photochemical properties [28,29]. For instance, based on the properties previously described for Re(I) carbonyl complexes with isoquinoline, isq, and 4-phenylpyridine, ppy [113,114], we have prepared a series of *cis*-[Ru(dcbH$_2$)$_2$LL′] complexes (Fig. 2) in which L and/or L′ are substituted pyridines, such as *cis*-[Ru(dcbH$_2$)$_2$(isq)$_2$]$^{2+}$ and *cis*-[Ru(dcbH$_2$)$_2$(ppy)$_2$]$^{2+}$,

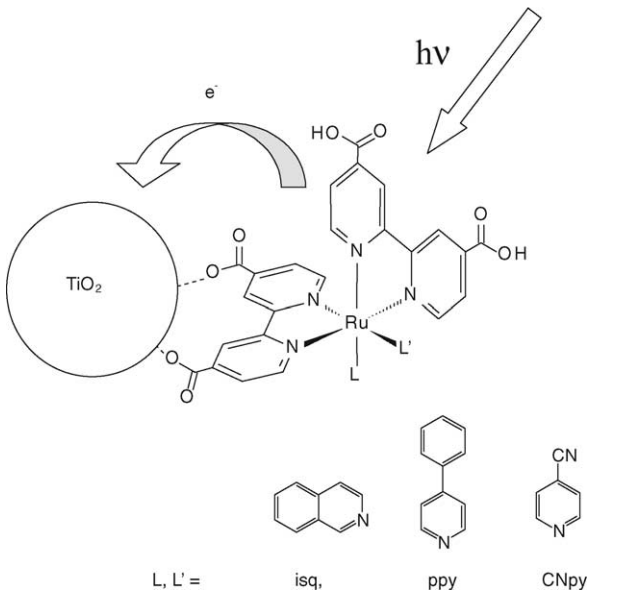


Fig. 2. Schematic representation of interfacial electron transfer following light absorption for *cis*-[Ru(dcbH$_2$)$_2$LL′] with some ancillary ligands.

Table 3
Photoelectrochemical data obtained with solar cell sensitized by *cis*-[Ru(dcbH$_2$)$_2$LL′]

Complex	V_{oc} (V)	I_{sc} (mA cm^{-2})	IPCE$_{max}$ (%)	ff	η_{cell} (%)	Reference
[Ru(dcbH$_2$)$_2$(dmp)]Cl$_2$	0.289	0.315	33.24	0.55	2.0	[105]
[Ru(dcbH$_2$)$_2$(mdmp)]Cl$_2$	0.330	0.400	42.21	0.61	3.2	[105]
[Ru(dcbH$_2$)$_2$(phdmp)]Cl$_2$	0.420	0.604	63.74	0.38	3.8	[105]
[Ru(dcbH$_2$)$_2$(blAlo)]Cl$_2$	0.320	0.390	41.15	0.45	2.2	[105]
[Ru(dcbH$_2$)$_2$(pydmp)]Cl$_2$	0.212	0.220	48.36	0.65	2.5	[105]
[Ru(dcbH$_2$)$_2$(aphb)]	0.58	5.5		0.48	1.51	[98]
poly[Ru(dcbH$_2$)$_2$(aphb)]	0.34	2.1		0.48	0.33	[98]
[Ru(dcbH$_2$)$_2$(CNpy)(H$_2$O)]$^{2+}$			∼60			[38,39]
Ru(dcbH$_2$)$_2$(qdt)	0.595	11.1	45	0.70	3.7	[91]
Ru(dcbH$_2$)$_2$(ecda)	0.580	5.4	30	0.65	2.0	[91]
Ru(dcbH$_2$)$_2$(bdt)	0.540	2.1	7	0.66	0.7	[91]
Ru(dcbH$_2$)$_2$(tdt)	0.504	1.1		0.70	0.4	[91]
[Ru(dcbH$_2$)$_2$(isq)$_2$]$^{2+}$			∼40			[37,38]
[Ru(dcbH$_2$)$_2$(ppy)(H$_2$O)]$^{2+}$			>50			[38]
[Ru(dcbH$_2$)$_2$(ppy)$_2$]$^{2+}$			∼40			[38]
[Ru(3,3′-dcbH$_2$)$_2$(NCS)$_2$]	0.47	8.0	21			[103]
[Ru(5,5′-dcbH$_2$)$_2$(NCS)$_2$]	0.49	7.8	37			[103]
[Ru(dcbH)$_2$Cl$_2$]	0.57	2.6		0.38	2.1	[88]
[Ru(dcbH$_2$)$_2$(acac)]Cl	0.674	13.20	>50	0.68	6.0	[106]
[Ru(dcbH$_2$)$_2$(mpdionate)]Cl	0.677	8.56		0.67	3.9	[106]
[Ru(dcbH$_2$)$_2$(dphdionate)]Cl	0.689	8.67		0.68	4.0	[106]
Ru(dcbH$_2$)$_3$Cl$_2$	0.52	1.0		0.37	0.7	[88]
[Ru(dcbH$_2$)$_2$(ppt)]			∼60			[107]
[Ru(dcbH$_2$)$_2$(2-ppt)]			∼60			[107]
[Ru(dcbH$_2$)$_2$(bpzt)]			∼65			[107]
[Ru(dcbH$_2$)$_2$(2-ppzt)]			∼55			[107]

Bibliography since 1998.

as *n*-TiO$_2$ sensitizers, which resulted in efficient photoelectrochemical solar cells [37]. The use of ancillary ligands enables the possibility to tune the spectroscopic response of the dyes [37], and our first sensitizer *cis*-[Ru(dcbH$_2$)$_2$(isq)$_2$]$^{2+}$ showed good light harvesting and efficient electron injection, successfully converting visible light to electrical output with IPCE values as high as 50% up to 550 nm [37]. A higher efficiency has been observed for *cis*-[Ru(dcbH$_2$)$_2$(ppy)(H$_2$O)]$^{2+}$ and *cis*-[Ru(dcbH$_2$)$_2$(CNpy)(H$_2$O)]$^{2+}$, where CNpy is 4-cyanopyridine [38]. The results obtained with these molecular sensitizers showed performance much better than those obtained with the same ancillary ligands, i.e. L = L′. Interestingly, the heteroleptic complex, with different ancillary ligands, led to considerably higher IPCE values and a broader spectroscopic response at longer wavelengths in comparison to the homoleptic one, as can be observed in Fig. 3. One approach for a molecular design of efficient photosensitizers is the control of the number of azine ancillary ligands, which play an important role in spectroscopic sensitivity, tuning the overall properties of the complexes [37,38].

All these compounds have broad absorption spectra with intense MLCT bands overlapping the solar spectrum, along with suitable photoelectrochemical properties. The carboxylic groups provide for strong adsorption of the dye to the TiO$_2$ surface and the necessary electronic coupling between the charge transfer excited state of the sensitizer and the wavefunction of the semiconductor conduction band. As a consequence, excitation of these complexes with visible light results in a very fast electron transfer through the carboxylic groups to the semiconductor as described in the literature [115–118]. Fig. 2 illustrates the electron injection into the semiconductor from these photosensitizers with some ancillary ligands employed in our studies.

The excited state properties of *cis*-[Ru(dcbH$_2$)$_2$(ppy)$_2$]$^{2+}$ were also investigated by laser flash photolysis [119], showing that the kinetics of charge recombination is much slower than the ultrafast electron injection. The difference of several orders of magnitude between these processes is essential to the successful operation of the photoelectrochemical cell.

Further examination of charge recombination and quenching processes, following the electron transfer across the excited dye/semiconductor interface, has been investigated with *cis*-[Ru(dcbH$_2$)$_2$(CNpy)(H$_2$O)]Cl$_2$ attached to TiO$_2$ films. These time-resolved experiments emphasized the importance of the efficient capture of the oxidized dye by the electron relay in solution to direct the electron transport process to the desired pathway preventing the recombination of the injected electron with the oxidized sensitizer. The analysis of experiments on TiO$_2$ photoanodes functionalized with [Ru(dcbH$_2$)$_2$(CNpy)(H$_2$O)]$^{2+}$ and other dye species has shown a linear correlation between the quenching efficiency, η, and the IPCE parameters.

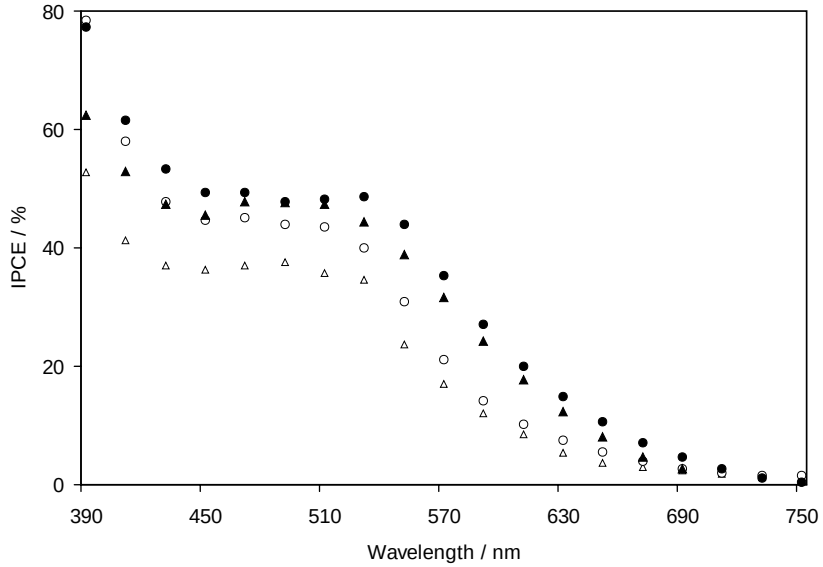


Fig. 3. Photocurrent action spectra of solar cells employing $[Ru(dcbH_2)_2(ppy)(H_2O)]^{2+}$ (●), $[Ru(dcbH_2)_2(ppy)_2]^{2+}$ (○), $[Ru(dcbH_2)_2(isq)_2]^{2+}$ (△), and $[Ru(dcbH_2)_2(CNpy)(H_2O)]^{2+}$ (■) as TiO_2 sensitizers.

4.1.2. Non-carboxylic acid anchoring group ruthenium complexes

Several reports have already discussed the results obtained for ruthenium complexes having non-carboxylic acid anchoring groups, such as phosphonic acids, catechol, etc. [88,120–124].

Spectroscopic parameters and performance data for ruthenium complexes with non-carboxylic acid anchoring polypyridines, in dye-sensitized solar cells, are listed in Tables 4 and 5, respectively.

The phosphonic acid group has been the more investigated groups among those studied for anchoring photosensitizers onto TiO_2 [88,120,123,124], as an alternative to carboxylic acid residues. The best performance was obtained with phosphonic terpyridine complexes with IPCE values up to 70%; these appear to be promising candidates to compete with carboxylated analogous [130]. Further modifications on the phosphonated-terpy ligand, made by introducing a phenyl group close to the attaching group, provided an even better complex to sensitize TiO_2 with an IPCE as high as 75.6%.

Recently, a new class of complexes, *cis*-$[Ru(dobH_2)_2L_2]$, where $L = Cl^-$ or H_2O, having the hydroxamic acid, $dobH_2$ = 4,4′-$(CONHOH)_2$-2,2′-bipyridine, as an anchoring group (Fig. 4) has been synthesized [43]. These new photosensitizers exhibit intense, broad MLCT absorption, covering a wide range of visible light. Solar cells sensitized by these complexes resulted in $I_{sc} = 4.58\,mA\,cm^{-2}$, $V_{oc} = 0.595\,V$ and ff = 0.56 for *cis*-$[Ru(dobH_2)_2Cl_2]$ and in $I_{sc} = 4.36\,mA\,cm^{-2}$, $V_{oc} = 0.612\,V$ and ff = 0.59 for *cis*-$[Ru(dobH_2)_2(H_2O)_2]^{2+}$. The data clearly point out that these new dyes are strongly adsorbed to the mesoporous TiO_2 and promote efficient electron injection to the semiconductor conduction band upon light absorption.

4.1.3. Other d^6 complexes

Most of the work in dye-sensitized solar cells has focused on Ru(II) polypyridine complexes mainly because of their intense charge transfer absorption across the whole visible range and ease of tunability of redox properties. Research has also been extended to other charge transfer d^6 complexes such as Fe(II) [133,134], Re(I) [135] and Os(II) [136,137]. Their spectroscopic and photoelectrochemical data are listed in Tables 6 and 7, respectively.

In recent studies, osmium complexes have also been found to be efficient photosensitizers in nanocrystalline TiO_2-based solar cells [136,137]. Osmium polypyridine complexes appear to be promising candidates for further optimization due to some potential advantages relative to their Ru analogues, as shown by impressive results with the $dcbH_2$ chromophoric ligand Os(II) complexes [136,137]. Replacement of the ruthenium metal center with osmium extends the light absorption and spectroscopic response of nanocrystalline TiO_2 photoanode to higher wavelength values without reducing photoelectrochemical energy con-

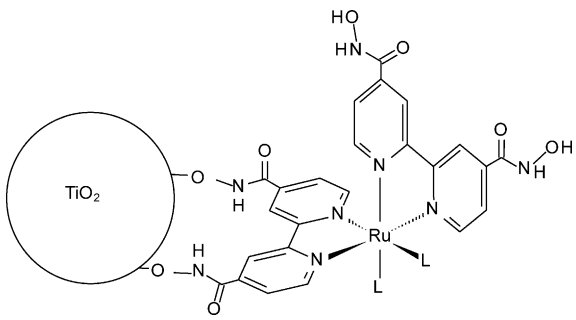


Fig. 4. Schematic representation of the hydroxamic acid anchoring group complexes, *cis*-$[Ru(dobH_2)_2L_2]$, attached on TiO_2.

Table 4
Spectroscopic parameters for ruthenium photosensitizers with non-carboxylic acid anchoring group ligands

Complex	Solvent	λ_{max} (nm) (ε_{max} ($10^4\,M^{-1}\,cm^{-1}$))	Reference
cis-[Ru(dobH$_2$)(H$_2$O)$_2$]	DMF	393, 561	[44]
cis-[Ru(dobH$_2$)Cl$_2$]	DMF	405, 576	[44]
Ru(bpy-(PO$_3$Et$_2$)$_2$)$_2$Cl$_2$	H$_2$O[a]	308 (1.99), 379 (0.41), 528 (0.44)	[125]
Ru(bpy-(PO$_3$H$_2$)$_2$)$_2$CN$_2$	H$_2$O[a]	245 (1.2), 297 (3.12), 453 (0.56)	[125]
Ru(5,5′-bpy-(PO$_3$H$_2$)$_2$)$_2$CN$_2$	H$_2$O[a]	250 (1.97), 293 (5.53), 461 (0.454)	[125]
Ru(bpy-(PO$_3$H$_2$)$_2$)$_2$NCS$_2$	H$_2$O[a]	303 (3.396), 360 (0.786), 494 (0.7)	[125]
Ru(5,5′-bpy-(PO$_3$H$_2$)$_2$)$_2$NCS$_2$	H$_2$O[a]	250 (2.446), 299 (5.523), 351 (0.59), 515 (0.473)	[125]
Ru(detOq)(NCS)$_2$	DMF	658 (0.98), 613 (1.10), 488 (1.43), 360 (2.89), 289 (4.67)	[126]
[Ru(bpy)$_2$(pySH)$_2$]	EtOH	246 (1.2), 297 (1.8), 423 (3.9)	[127]
[Ru(bpy)$_2$(pySH)$_2$/ZnO		460	
[Ru(bpy)$_2$(pyS$^-$)]	EtOH	249 (3.4), 296 (3.7)	[127]
[Ru(bpy)$_2$(pyS$^-$)]/ZnO		440	
[(bpy)$_2$Ru(dpq(OH)$_2$)]$^{2+}$	AN	252 (3.5), 286 (8.78) 453 (1.56)	[128]
Ru(dsbpy)$_3$Cl$_2$	H$_2$O	297 (8.71), 330 (1.58), 458 (1.70)	[88]
Ru(dmbpy)$_2$(dsbpy)Cl$_2$	EtOH	287 (8.32), 463 (1.58)	[88]
Ru(dsbpy)$_2$Cl$_2$	EtOH	296 (3.80), 379 (1.12), 551 (0.69)	[88]
Ru(dsbpy)$_2$(NCS)$_2$	EtOH	303 (3.55), 367 (1.02), 523 (1.0)	[88]
[Ru(bpy)$_2$(bpy-CH$_2$COOLi)](PF$_6$)$_2$	AN	456 (1.846)	[124]
[Ru(bpy)$_2$(bpy-CH(COOLi)$_2$)](PF$_6$)$_2$	AN	456 (1.920)	[124]
[Ru(bpy)$_2$(bpy-(CH(COOLi)$_2$)$_2$)](PF$_6$)$_2$	AN	456 (1.750)	[124]
[Ru(bpy)$_2$(bpy-(PO$_3$H$_2$)$_2$)]$^{2+}$	AN	456	[122]
[Ru(bpy)$_2$(pbp-pra)]$^{2+}$	AN	458	[122]
[Ru(bpy)(bpb-pra)]$^{2+}$	AN	458	[122]
[Ru(dmbpy)(DMSO)$_2$]Cl$_2$	EtOH	288 (0.94) 364 (0.21)	[109]
[Ru(ttp-PO$_3$H$_2$)(dmbpy)(NCS)]	EtOH	503 (0.898)	[121]
[Ru(ttp-PO$_3$H$_2$)(phen)(NCS)]	EtOH	497 (0.992)	[121]
[Ru(ttp-PO$_3$H$_2$)(biquin)(NCS)]	EtOH	572 (1.014)	[121]
Ru(bmipy)(bpy-PO$_3$H$_2$)(NCS)	MeOH	298 (4.46), 316 (2.44), 344 (2.98), 360 (3.70), 496 (1.13)	[129]
[Ru(hp-terpy)(dmbpy)(NCS)]	EtOH	494 (0.87)	[130]
Ru(dmbpy)$_2$(bpy-acac)(PF$_6$)$_2$	CH$_2$Cl$_2$	462 (1.22)	[131]

Bibliography since 1996.
[a] 0.1N H$_2$SO$_4$.

version performance. Thus the performance of solar cells might be improved through the use of charge transfer sensitizers with high spin-orbit coupling constant metal centers. In these systems, direct population of low-energy ^{3}MLCT states is less forbidden, allowing an intensity increase of the corresponding charge transfer bands at the limit of the visible-near infrared regions [1].

Although rhenium polypyridine compounds are not well optimized for the harvesting of sunlight, these compounds may serve as useful probes for interfacial electron transfer processes due to their interesting redox, geometric and optical properties. The characteristic Re(II/I) reduction potential provides a larger driving force for donor oxidation. The facial geometry typical for Re(I) tricarbonyl complexes may provide a better molecular control of the orientation of the dye. Lower IPCE values for [Re(CO)$_3$(dcbH$_2$)(py)]TFMS and [Re(CO)$_3$(bpy)(isn)]TFMS in comparison to analogous Ru(II) complexes are due to the larger fraction of light transmitted, although the absorbed photon-to-current efficiency (APCE) is unity within experimental error.

The [Fe(dcbH$_2$)$_2$(CN)$_2$] complex can sensitize nanocrystalline TiO$_2$ in a dye-sensitized solar cell with $V_{oc} = 0.360$ V, $I_{sc} = 0.29\,mA\,cm^{-2}$ and IPCE around 10–11% [133]. Although, the reported photocurrents and photovoltages were much smaller than those with Ru(II) complex sensitizers, [Fe(dcbH$_2$)$_2$(CN)$_2$] exhibits relatively high quantum yield for the sensitization of nanocrystalline TiO$_2$. As iron is a common and cheap metal, it can provide a very economical alternative to ruthenium in sensitizing complexes [134].

4.2. Natural sensitizers

Fruits, flowers or leaves have been employed as sources of natural photosensitizers. Several reports, which are also suitable for educational purposes [42,43,139,140], have emphasized the use of extracts of these sources as a faster, cheaper, low-energy and environmentally friendly alternative for production of dye-sensitized solar cells [41–43,138].

Natural dyes reported as sensitizers of solar cells are listed with their spectroscopic data in Table 8 and their performance in solar cells in Table 9.

Anthocyanins, which can be found easily in strongly colored fruits, such as berries or plums as well as flowers, are the natural dyes most extensively investigated as photosensitizers. The strongly colored extracts have high concentrations of anthocyanins, mainly cyanidine (Fig. 5) and its derivatives, such as cyanidin-3-glucoside and cyanidin-3,5-diglucoside [41–43,139–141,143].

Table 5
Photoelectrochemical data obtained with ruthenium photosensitizer with non-carboxylic acid anchoring group ligands

Dye	V_{oc} (V)	I_{sc} (mA cm^{-2})	IPCE$_{max}$ (%)	ff	η_{cell} (%)	Reference
cis-[Ru(dobH$_2$)(H$_2$O)$_2$]	0.612	4.36		0.59		[44]
cis-[Ru(dobH$_2$)Cl$_2$]	0.595	4.58		0.56		[44]
Ru(bpy-(PO$_3$H$_2$)$_2$)$_2$Cl$_2$			~20			[125]
Ru(bpy-(PO$_3$H$_2$)$_2$)$_2$CN$_2$			~50			[125]
Ru(5,5′-bpy-(PO$_3$H$_2$)$_2$)$_2$CN$_2$			~65			[125]
Ru(bpy-(PO$_3$H$_2$)$_2$)$_2$NCN$_2$	0.490	5	~75	0.67		[125]
Ru(5,5′-bpy-(PO$_3$H$_2$)$_2$)$_2$NCN$_2$			~45			[125]
[Ru(detOq)(NCS)$_2$]	0.654 ± 0.050	18 ± 0.5	~75	0.65 ± 0.05		[126]
[Ru(bpy)$_2$(pySH)$_2$]/ZnO	0.019	0.036	2.9			[127]
[Ru(bpy)$_2$(pyS$^-$)$_2$]/ZnO	0.0321	0.045	5.6			[127]
[(bpy)$_2$Ru(dpq(OH)$_2$)]$^{2+}$			~17.5			[128]
Ru(bpy)$_2$(NCS)$_2$	0.360	1.2		0.51	0.34	[132]
Ru(bpy-(NO$_2$)$_2$)$_2$(NCS)$_2$	0.024	0.056				[132]
Ru(bpy-(CO$_2$Et)$_2$)$_2$(NCS)$_2$	0.380	1.8		0.47	0.5	[132]
Ru(bpy-(CH$_2$OH)$_2$)$_2$(NCS)$_2$	0.510	10		0.48	3.8	[132]
Ru(dsbpy)$_3$Cl$_2$	0.52	1.4		0.34	0.9	[88]
Ru(dmbpy)$_2$(dsbpy)Cl$_2$	0.53	1.3		0.37	0.9	[88]
Ru(dsbpy)$_2$Cl$_2$	0.51	1.3		0.42	1.1	[88]
Ru(dsbpy)$_2$(NCS)$_2$	0.52	0.5		0.36	0.4	[88]
[Ru(dhpt)(NCS)$_3$]$^-$	0.617	3.25	20	0.75	1.5	[123]
[Ru(bpy)$_2$(bpy-CH$_2$COOLi)](PF$_6$)$_2$	0.245	0.83	34 ± 5			[124]
[Ru(bpy)$_2$(bpy-CH(COOLi)$_2$)](PF$_6$)$_2$	0.400	2.55	45 ± 5			[124]
[Ru(bpy)$_2$(bpy-(CH(COOLi)$_2$)$_2$)](PF$_6$)$_2$	0.380	3.00	48 ± 5			[124]
[Ru(bpy)$_2$(bpy-(PO$_3$H$_2$)$_2$)]$^{2+}$			0.23 ± 0.05			[122]
[Ru(bpy)$_2$(pbp-pra)]$^{2+}$			0.02 ± 0.01			[122]
[Ru(bpy)(bpb-pra)]$^{2+}$			<0.001			[122]
[Ru(bpy)$_2$(phendione)]PF$_6$			34			[120]
[Ru(bpy)$_2$(phendioxime)](PF$_6$)$_2$			27			[120]
[Ru(ttp-PO$_3$H$_2$)(dmbpy)(NCS)]	0.653	4.73	75.6	0.705		[121]
[Ru(ttp-PO$_3$H$_2$)(phen)(NCS)]	0.625	1.88	45.4	0.814		[121]
[Ru(ttp-PO$_3$H$_2$)(biquin)(NCS)]	0.445	0.368	1.74	0.750		[121]
Ru(bmipy)(bpy-PO$_3$H$_2$)(NCS)	0.60	8.6	55	0.70	4.1	[129]
[Ru(hp-terpy)(dmbpy)(NCS)]			~70			[130]
[Ru(dmbpy)$_2$(bpy-acac)](PF$_6$)$_2$	0.487	2.02	0.292			[131]

Bibliography since 1996.

Table 6
Spectroscopic parameters of other d^6 metal complexes evaluated as photosensitizers

Complex	Solvent	λ_{max} (nm) (ε_{max} (10^4 M^{-1} cm^{-1}))	Reference
Os(dcbH$_2$)$_2$(CN)$_2$	EtOH[a]	382 (1.40), 508 (1.44), ~680 (0.368)	[136]
Os(dcbH$_2$)$_2$(NCS)$_2$	EtOH	412 (1.43), 530 (1.51), ~780 (0.5)	[136]
[Os(dcbH$_2$)$_2$Cl$_2$]$^{2+}$	EtOH	448 (1.68), 494 (1.48), ~640 (0.4)	[136]
[Os(dcbH$_2$)$_3$]$^{2+}$	EtOH	442 (1.01), 496 (2.02), ~640 (0.6)	[136]
TBA$_4$[Fe(dcbH$_2$)$_2$(CN)$_2$]	EtOH	590	[134]
	3-MPN	594	[134]
	CCl$_4$	595	[134]
	DMSO	621	[134]
TBA$_4$[Fe(dcbH$_2$)$_2$(CN)$_2$]/TiO$_2$	EtOH	610	[134]
	3-MPN	608	[134]
	CCl$_4$	596	[134]
	DMSO	638	[134]
[Re(CO)$_3$(dcbH$_2$)(py)]TFMS	AN	380 (0.44)	[135]
[Re(CO)$_3$(bpy)(isn)]TFMS	AN	350 (0.53)	[135]

Bibliography since 1998.
[a] In EtOH with 1 mM pyridine and 1 mM pyridinium triflate.

Table 7
Photoelectrochemical data obtained with solar cell sensitized by other d^6 metal complexes

Dye	V_{oc} (V)	I_{sc} (mA cm^{-2})	IPCE$_{max}$ (%)	ff	Reference
$Os(dcbH_2)_2(CN)_2$	0.569	11.6		0.62	[136]
$Os(dcbH_2)_2(NCS)_2$	0.360	2.1		0.55	[136]
$[Os(dcbH_2)_2Cl_2]^{2+}$	0.540	7.7		0.66	[136]
$[Os(dcbH_2)_3]^{2+}$	0.514	10.0		0.69	[136]
$TBA_4[Fe(dcbH_2)_2(CN)_2]$	0.360	0.29	10–11		[133]
$[Re(CO)_3(dcbH_2)(py)]$TFMS			~0.9		[135]
$[Re(CO)_3(bpy)(isn)]$TFMS			~0.5		[135]

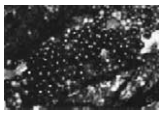
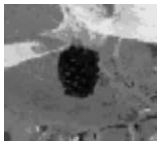
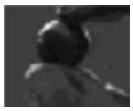
Bibliography since 1998.

The maximum absorption of anthocyanin extracts ranges from 510 to 548 nm depending on the fruit or the solvent employed. In most cases bathochromic shifts are observed after attachment to the semiconductor (Fig. 6). Chemical adsorption of the anthocyanins is stated to be the result of its alcohol bound protons which condense with the hydroxyl groups present at the TiO_2 nanostructured surface, as shown in Fig. 5a. The attachment can also be enhanced by a chelating contribution to the Ti(IV) ions, Fig. 5b [142].

Dai and Rabani in their studies with pomegranate extracts reported the successful use of an aqueous mediator layer [142]. Another interesting behavior has been observed with gallic acid and catechol. These compounds do not present charge transfer transitions bands in solution, however after their adsorption onto semiconductor surface they present a strong absorption band. This behavior is due to the chelating effect enhancing their binding onto TiO_2 surface [146].

Most natural dye-sensitized solar cells have been evaluated by short circuit current, I_{sc}, and open circuit voltage, V_{oc}, measurements as can be observed in Table 9.

Table 8
Spectroscopic parameters of natural extracts evaluated as photosensitizers since 1997

Extract of	Medium	λ_{max} (nm)	Reference
 Jaboticaba's skin	EtOH	538	[43]
	TiO_2	548	[43]
 Chaste tree fruit	EtOH	548	[41]
	TiO_2	555	[41]
 Mulberry	EtOH	543	[41]
	TiO_2	553	[41]
 Cabbage-palm fruit	EtOH	545	[41]
	TiO_2	552	[41]
 Java Plum	EtOH	536	[42,43]
	TiO_2	550	[42,43]
Blackberries	H_2O	517	[141]
California Blackberries	MeOH/ HOAc/H_2O	520[a]	[143]
	TiO_2	532	[143]
Pomegranate seeds	TiO_2	560	[142]
	H_2O	510–520	[142]
Pomegranate fruit	H_2O	520	[138]
	TiO_2	560	[138]

[a] Molar absorptivity = 3.5×10^4 L mol^{-1} cm^{-1} [144].

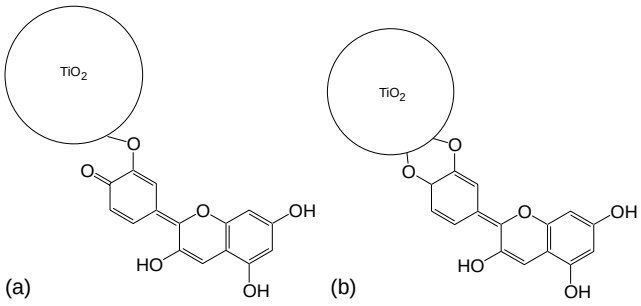


Fig. 5. Schematic representation of anthocyanin attachments onto TiO_2 surface.

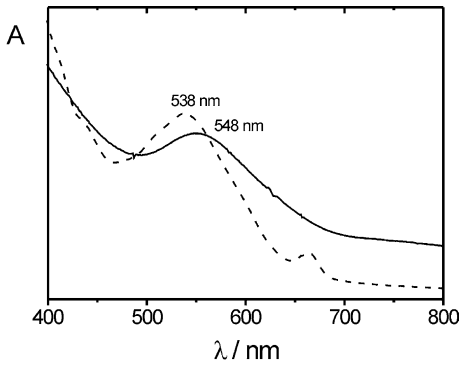


Fig. 6. Absorption spectra of an ethanolic extract of Jaboticaba's skin before (– – –) and after being adsorbed onto TiO_2 surface (—).

Table 9
Photoelectrochemical data obtained with solar cell sensitized by anthocyanin natural extracts evaluated as photosensitizers

Extract of	Medium[a]	V_{oc} (V)	I_{sc} (mA cm^{-2})	Reference
Jaboticaba's skin	AN/NMO	0.59	2.8	[43]
Chaste tree fruit	AN/NMO	0.39	2.1	[41]
Mulberry	AN/NMO	0.42	1.7	[41]
Cabbage-palm fruit	AN/NMO	0.44	0.74	[41]
Java Plum	AN/NMO	0.71	4.6	[42]
Blackberries, raspberries, pomegranate seeds	EG	0.3–0.5	1–2	[139]
Blackberries, raspberries, pomegranate seeds	EG	0.3–0.5	1–2	[140]
Blackberries		0.30	1	[141]
California Blackberries[b]	EG or PC	0.4–0.5	1.5–2.2	[143]
California Blackberries[b]	EG or PC	0.4–0.43	1–1.2	[143]
Pomegranate fruit	H_2O pH 2.8	0.30–0.44	0.45–2.2	[142]
	EtOH	0.41, 0.48	2.1, 0.48	[142]
Pomegranate fruit	H_2O	0.46		[142]
Pomegranate fruit	H_2O	0.45		[138]
Anthurium	H_2O	0.435	2.9	[145]
	AN	0.480	3.2	[145]

Bibliography since 1997.
[a] Electrolyte I_3^-/I^-.
[b] The extract was purified to obtain only anthocyanin compounds.

Anthocyanin photosensitizers usually exhibit a photovoltage between 0.3 and 0.71 V and photocurrent values ranging from 0.45 and 4.6 mA cm^{-2}. However, few studies have included the overall efficiency, which ranges from 0.5 to 1% [139,140,143], and IPCE value up to 19% at the maximum absorbance [143].

The performance of natural extracts are usually better than those obtained by using commercial or purified analogous compounds. The improved natural dye performance is probably due to a mixture of dyes present in such extracts [138]. Different dyes promote light harvesting in distinct wavelengths and have particular electron injection quantum yields leading to the enhancement of photocurrent and photovoltage [142].

The great biodiversity found in Brazil, with special emphasis in the Amazon and Northeast regions, has led our group to analyze the feasibility of using the extracts of plants widely spread over the Brazilian territory. The results obtained with Java Plum (Eugenia jambolana Lam), Jaboticaba's skin (Mirtus cauliflora Mart), cabbage-palm fruit (Euterpe oleracea Mart), among others, have already proved the possibility of using these common Brazilian fruits as alternative dye sources. For instance, an outstanding $I_{sc} = 2.8$ mA cm^{-2} and $V_{oc} = 0.59$ V, as well as fill factor of 0.48, obtained from the current-voltage profile shown in Fig. 7, for extract of Jaboticaba's skin, have encouraged us to continue searching for new natural dyes sources [41–43].

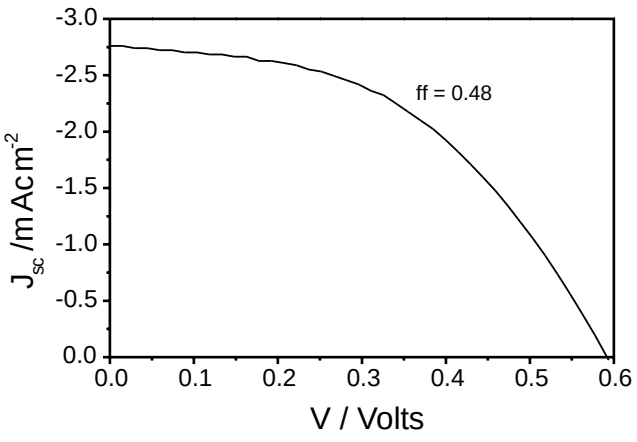


Fig. 7. Current–potential curve for solar cells incorporating a photoanode sensitized by extract of Jaboticaba's skin.

5. Closing remarks

The dye-sensitized solar cell is considered the new generation solar cell for the 21st century and is a fast growing multidisciplinary subject. Since its first announcement in 1991, using the concept of chemisorbed dye on the surface of mesoporous TiO_2 photoelectrode with a roughness factor of 1000, the efficiency has increased from the initial 7.1% to a presently certified efficiency of over 10% under standard AM 1.5 solar radiation. Increasing stability and improvements on manufacturing techniques, as well as the announcement of the commercial production should direct investments by several companies in this renewable energy technology in their search for a clean energy business.

A photoelectrochemical solar cell based on the dye-sensitization of *n*-TiO_2 represents an example of an integrated chemical system for energy conversion. The sensitization of a wide band gap semiconductor oxide film of nanocrystalline morphology, stable against pho-

tocorrosion, allows the efficient harvesting of sunlight with near quantitative conversion of incident photons into current.

5.1. Work on Dye-cell at the IQ/USP, Brazil

At the *Laboratory of Inorganic Photochemistry and Energy Conversion* in the Chemistry Institute of the University of São Paulo (IQ/USP), we are working on several aspects related to the Dye-cell technology, including developing the pathway from fundamental academic scientific knowledge acquired from research to technological innovation and intellectual protection by patents. A straightforward example of the association of both molecularly engineered chemical systems and photoinduced tasks for energy conversion is represented by our results with the photoelectrochemical solar cell based on dye-sensitization of *n*-TiO_2. Compounds with the general formula *cis*-[$Ru(dcbH_2)_2LL'$] (Fig. 2) where L/L′ = substituted pyridines and H_2O, were successfully employed as molecular sensitizers in such cells [36–38].

Preparation of colloidal TiO_2 using distinct methods has also been tested giving reliable and very useful results. Spin-coating and painting techniques have been employed for the deposition of TiO_2 films over TCO substrates. Homogeneous semiconductor films with controlled transparency, which were successfully used as dye-sensitized photoanodes in solar cells, have been obtained with the convenient choice of TiO_2 preparation techniques. Thin-film properties, such as thickness and transparency, were also controlled through the deposition technique [5].

The electron transfer process across the excited dye/semiconductor interface, as well as the charge recombination and quenching processes, were further investigated by transient UV–vis absorption spectra on dye-sensitized TiO_2 films deposited onto glass substrates. A fast quenching of the oxidized complex in the presence of iodide emphasized the importance of a proper concentration of donor species in the redox mediator for the effective regeneration of the oxidized sensitizer [39,119].

Molecular engineering of the *cis*-[$Ru(dcbH_2)_2LL'$] compounds, with different L,L′ ancillary ligands, that fulfill several requirements and act as panchromatic charge transfer sensitizers for wide band gap semiconductor solar cells is still a challenging task, but in continuous study. Our investigation efforts now progress also towards the development of new synthetic dyes and to the discovery of natural dyes to be efficiently used as semiconductor sensitizers. Sunlight harvesting and energy conversion to electricity assisted by a new class of complexes, *cis*-[$Ru(dobH_2)_2LL'$], having two hydroxamic acid groups as an anchoring site to be attached on the mesoporous nanostructured surface of the semiconductor oxide, have been reported [44]. The idea of using these complexes resulted from a discussion with Dr. Nazeeruddin, as they may provide a novel class of molecular sensitizers by engineering various ancillary ligands to modulate their properties conveniently in order to better absorb visible light to be converted into electrical output. Recent papers of our group also reported successful use of extract of Brazilian fruits as a natural sensitizer in photoelectrochemical solar cells [40–43].

Conducting plastic materials have also been tested to replace a rigid TCO as the electrode substrate in association with a polymeric gel as an electrolyte medium resulting in wholly flexible solar cells [147].

The development of solar cells became the main subject of a special program called CIUPE (Inter-institutional Collaborative Program for Strategic Researches), which was supported by the University of São Paulo and attracted researchers from several areas. It involved mainly discussions on subjects related with renewable energy sources and the development of photovoltaics and has provided encouragement for cooperative efforts among several different laboratories [5].

Our project “Dye-sensitized solar cells: Dye-cells” already has three patents and has been select by the Brazilian Ministry of Science and Technology (MCT) as an innovative project/product in the energy sector, and took part during the whole year of 2002 in a series of events entitled “Exhibition of Innovative Technological Products for Energy Production”. As a result several companies have contacted us and showed interest in the Dye-cell as the photovoltaic technology for the New Millennium.

Although ascending, the development of photovoltaic solar energy in Brazil is considerably recent and its contribution as an alternate energy source is still incipient. However, due to its geographic characteristics, large territorial area, favorable tropical climate and the existence of several remote communities not provided with an electrical energy network, photovoltaics is the most feasible alternative, when the environmental and the resources conservation are considered, to solve at least some of these specific Brazilian energy needs.

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