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Coordination Chemistry Reviews
196 (2000) 219–247

COORDINATION CHEMISTRY REVIEWS

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Energy conversion: from the ligand field photochemistry to solar cells

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Received 6 May 1998; accepted 24 August 1998

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Abstract

The investigation of photochemical and photophysical properties of coordination compounds as well as experiments on solar cells carried out in our Laboratory of Inorganic Photochemistry and Energy Conversion are outlined here. They are discussed in parallel with

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PII: S0010-8545(98)00212-4

the current state of knowledge in each topical area. Particular emphasis is given to the photochemical behavior of the $[Fe(CN)_5L]^{3-}$ complexes including the solvent dependence for the photosubstitution of both L and CN^-. The quantum yields for the photodissociation of a cyanide are also analyzed in terms of such effects as metric, topological, chelating and neighboring group effects on the photoinduced ring closure efficiency. The photophysics and photochemistry of some rhenium complexes are discussed, as well as some supramolecular photochemistry, in particular, ion-pair photochemistry of cobalt complexes and a covalently-linked Re–Ru system. Finally, the investigations on solar energy conversion and development of thin-layer solar cells based on sensitization of nanocrystalline TiO_2 semiconductor films by some ruthenium polypyridyl complexes are presented. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Ligand field photochemistry; Supramolecular photochemistry; Sensitization; Solar cells

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1. Introduction

The investigations in inorganic photochemistry carried out in our laboratory have followed several major trends in the field. Our initial studies had been focused on kinetics, electrochemistry and spectroscopy of some inorganic compounds, with emphasis on the reactivity of the ground state [1–13]. Later, studies of the photoreactivity of these compounds came as a natural step for subsequent investigations. As research in inorganic photochemistry has continued at an active pace into new and exciting areas, our interests have also been extended to supramolecular photochemistry and nanocrystalline semiconductor sensitization. Our interest grew gradually and slowly, but steadily, as a natural consequence of the growth of our programs, as well as from positive inputs through important collaborations. Professor Viktoria K.L. Osorio has thoroughly assisted the group on my leave and a very fruitful collaboration has emerged with Professor Carlo A. Bignozzi. Fortunately, undergraduate and graduate students working together as a highly motivated team, with enthusiasm and a similar aim, provided the driving force for our research in such an interdisciplinary area.

The basic spectroscopy, reactivity, and photochemistry of particular traditional metal complexes are still of interest in our research. These studies and the solid knowledge of their photophysical and photochemical properties have also proven to be fundamental to the exploitation of more complex chemical systems, as well as in applying these complexes in several new areas.

Several books [14–27] and some classic [28–34] and more recent review articles [35–38] have already discussed principles and novel advances in inorganic photochemistry, as well as applications in various areas. Many of them, including some chapters in basic textbooks [39–41], are intended for instructional or supplementary material for undergraduates or advanced undergraduates. It is also useful for graduates and educators to keep in touch with summaries of recent and ongoing research in inorganic photochemistry and to visualize research horizons in this field. Therefore, in this review, we have not attempted an exhaustive coverage of the literature on each subject. Rather, an introduction to the literature has been included to provide perspective for our representative experimental results and to place our own work in this field. Only the fundamental concepts required for the understanding of results arising from focused photochemical events will be presented.

This review deals initially with different types of photoreactions of coordination compounds, basically ligand field photochemistry and photoexcited electron and energy transfer. In a later section principles and experiments in solar energy conversion in thin-layer solar cells based on sensitization of the wide band-gap TiO_2 semiconductor films by some ruthenium(II) complexes of bipyridine dicarboxylic acid will be presented.

2. Photosubstitution and photoisomerization reactions

2.1. Photosubstitution

The absorption of light, usually visible or ultraviolet, by transition metal complexes results in excited states with new electronic configurations and properties. As a consequence, light absorption can initiate a number of different chemical reactions, some of them unusual and distinct from related thermal reactions of the ground state. In fact, the decay of excited states, both by physical processes or by chemical reactivity, is fundamentally related to the type of the state reached after light absorption and by what pathways the excited state uses to decay, either chemical to give new products, or physical to return to the ground state.

Primary photochemical events that lead to a ligand substitution originate from ligand field excited states (LFES). These states result from an angular, rather than a radial, redistribution of the electron density in the excited state. It does not mean that substitution is achieved only by irradiating a complex at the ligand field transition energy. Initially produced excited states can interconvert through internal conversion and/or intersystem crossing to lower states or by thermal activation to upper states, which are responsible for the photoreaction. We shall have to consider that different types of absorption bands often overlap and an irradiation at a pre-determined wavelength does not necessarily lead to population of a selected excited state.

Ligand photosubstitution has several applications emphasized already in other articles [28–35], such as in synthesis and catalysis. Fundamental theories concerning metal-ligand bonding provided the impetus for the beginning of inorganic photochemistry.

In the early 80s, with an extensive study of the thermal reactivity of pentacyanoferrate(II) complexes [3–5,7,8], we started our first investigations regarding their photosubstitution behavior [2,42]. The photolabilization of L had already been reported for $[Fe(CN)_5L]^{n-}$ complexes with $L = CO$ [14,43,44], NO [14,45–47], CN^- [14,48,49] and aromatic nitrogen ligands [50]. This pattern was considered for a long time to be the only reactive decay channel for the deactivation of the excited states reached upon photolysis (Eq. (1)).

$$[Fe(CN)_5L]^{3-} + H_2O \xrightarrow{hv} [Fe(CN)_5H_2O]^{3-} + L \qquad (1)$$

In earlier work, the determination of quantum yields was accomplished by measuring continuous spectral changes due to the formation of the $[Fe(CN)_5(H_2O)]^{3-}$ product [44,46,48,49]. Since both the photoproduct and the starting complex have relatively low extinction coefficients, a high net conversion of starting material to product is required in order to measure the quantum yields. It is not surprising that direct spectral analysis did not produce reliable results. Therefore, the use of analytical reagents to trap $[Fe(CN)_5(H_2O)]^{3-}$ has been employed to improve its quantitative determination as a photoproduct [50,51]. However, in many cases, the thermal labilization of L becomes an additional complicating factor in obtaining reliable quantum yields, even when a dark sample is employed.

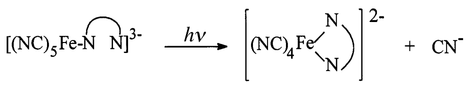
Our previous studies of cyanoferrate(II) species were fundamental in investigating systems for which the thermal process is negligible, and choosing the best analytical procedure to follow the photoreaction.

We employed the *N*-methylpyrazinium ion (Mpz^+) in order to trap the photoproduct. In addition to its remarkable thermal and photochemical stability, the $[Fe(CN)_5(Mpz)]^{2-}$ complex also exhibits a high extinction coefficient ($\varepsilon = 12.3 \times 10^3$ M^{-1} cm^{-1}) which increases the sensitivity of the photometric analysis, affording quantitative detection of the photoproduct for conversions up to 1%. The results obtained for the substitutionally inert $[Fe(CN)_5L]^{3-}$ with L = CO, PPh_3, $AsPh_3$, $SbPh_3$ and $P(OCH_3)_3$ are shown in Table 1 in comparison to other reported values.

The higher quantum yield for CO substitution in $[Fe(CN)_5CO]^{3-}$ is consistent with an appreciably longer lifetime for the low-lying $^3A_2$ excited state [52]. For the others, a reasonable explanation is that the low-lying ^3E excited state is responsible for the photoreaction [53].

The photochemistry of $[Fe(CN)_5NO]^{2-}$ has been intensively investigated [25,45–47,54–59], in part because of an interest in environmental studies on NO [60], and also for its use clinically as a vasodilator [56]. The quantitative determinations of its photoreactivity can have interference from a relatively large number of side thermal reactions [25,45,46,55,57].

Cyanide photosubstitution had been expected to be less favored than for a neutral ligand [16] and had also been considered to be non-detectable [50]. Our study on the continuous photolysis of aqueous solutions of $[Fe(CN)_5(en)]^{3-}$ (en is 1,2-diaminoethane), in the presence of a large excess of the diamine ligand was the first example reported in the literature [42] which presented cyanide photolabilization as the reactive deactivation pathway. This work exploited the presence of the neighboring effect in the excited state, and explored the ability of the dangling, free amino group to capture a lower coordinate intermediate and effect ring closure after labilization of the Fe–CN bond. The presence of competing reactants within the coordination sphere of the metal enhanced the trapping of the vacant site before recombination with CN^- took place. The inertness of the photoproduct, the tetracyanoferrate(II) complex, due to the formation of the chelate (Eq. 2), enabled its further isolation and quantitative analysis.



(2)

A systematic study to correlate the structure of the aliphatic diamine $\widehat{NN}$ with quantum yields of the cyanide photosubstitution was further carried out [61] to assess the roles of factors such as metric, topological, chelating and neighboring group effects. Caused by the presence of the additional amine group available for coordination, the topological effect was useful to detect the CN^- release efficiently. The experiments showed the importance of a free NH_2 group, which assisted the dissociation of a cyanide from the metal by forming an incipient chelating ring in the excited state.

Table 1
Quantum yields for the photosubstitution of L for the $[Fe(CN)_5L]^{n-}$ complexes

Complex	λ_{irr}/nm	Φ	Remarks	Ref.
$[Fe(CN)_5CO]^{3-}$	300–370	0.9	[a]	[44]
	250	0.5	[a]	[44]
	366	0.23	Cyclic voltammetry[b], 0.50 M KCl	[2]
	366	0.37	[a,c]	[53]
$[Fe(CN)_6]^{4-}$	366	0.1	pH measurements	[77]
	254	0.1–0.2	[a], 6.8–9.9 pH range	[78]
	313	0.4	[a,d]	[78]
	365	0.5–0.9	[a], 1–4 pH range	[48]
$[Fe(CN)_5(AsO_3H_3)]^{3-}$	366	0.09	[a,d]	[51]
$[Fe(CN)_5(AsPh_3)]^{3-}$	366	0.15	[a,c]	[53]
$[Fe(CN)_5(SbPh_3)]^{3-}$	366	0.12	[a,c]	[53]
$[Fe(CN)_5(P(OMe)_3)]^{3-}$	366	0.14	[a,c]	[53]
$[Fe(CN)_5(PPh_3)]^{3-}$	313	0.14	[a,c]	[53]
	366	0.15		[53]
	404	0.12		[53]
$[Fe(CN)_5(P(OEt)_3)]^{3-}$	313	0.13	[a,c]	[79]
	365	0.11		[79]
$[Fe(CN)_5(NO)]^{2-}$	366	0.35	[a], pH 6	[46]
	436	0.18		[46]
	313	0.37	[a]	[54]
	436	0.18		[54]
	265	0.62	[a], in methanol	[55]
	313	0.63		[55]
	366	0.38		[55]
	436	0.38		[55]
	313	0.42	[a], in dimethylsulfoxide	[54]
	405	0.39		[54]
	436	0.33		[54]

[a] In aqueous solution, unless otherwise specified, following spectral changes.

[b] In the presence of the analytical ligand imidazole.

[c] In the presence of the analytical ligand Mpz^+.

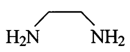
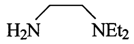
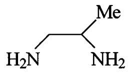
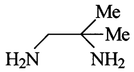
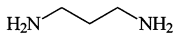
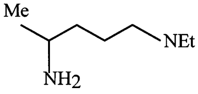
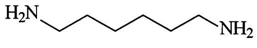
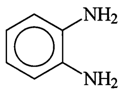
[d] In the presence of the analytical ligand nitrosobenzene.

The metric factor determined how efficiently these effects acted on the photosubstitution of the cyanide ion. The highest quantum yield for the complexes studied, 0.110, was obtained with 1,3-diaminopropane (tn) due to its having the best geometrical fit. A pronounced decrease in the extent of ring closure was observed for complexes with longer chain size diamine ligands, reaching the lowest value, 0.025, for 1,6-diaminohexane. The results shown in Table 2 emphasize the importance of molecular organization [62] prior to the occurrence of the photochemical reaction.

2.2. Solvent cage effect

We have also reported the first example of a pentacyanoferrate(II) exhibiting wavelength dependent quantum yields for release of a cyanide [63], shown in Table 2.

Table 2
Quantum yields for the ring closure process after the CN^- release in the $[Fe(CN)_5(\widehat{NN})]^{3-}$ complexes

L	λ_{irr} / nm	Φ
	313	0.236
	334	0.232
	365	0.084
	404	0.025
	434	0.022
	365	0.087
	365	0.088
	313	0.228
	334	0.229
	365	0.095
	404	0.030
	434	0.028
	365	0.100
	313	0.230
	334	0.226
	365	0.110
	404	0.032
	434	0.028
	313	0.113
	334	0.110
	365	0.058
	404	0.028
	434	0.023
	365	0.025
	365	0.100

This work emphasized the importance of cage recombination in substitutional photochemistry. An analog to this phenomenon in charge-transfer (CT) photochemistry is the competition that exists between geminate recombination and solvent cage escape. This model has been shown to be consistent with a significant number of available experimental results for other systems [64–66], particularly those of d^6 Co(III) complexes [67–75].

Fig. 1 depicts the efficiency of photochemically induced ring closure as a function of the excitation wavelength for the 1,3-diaminopropane derivative. Also shown is a Gaussian deconvolution of the electronic spectrum. There are electronic transitions from the $^1A_1$ ground state to give either a singlet charge-transfer ^1CT and/or a ligand field $^1E(1)$ state, depending on the irradiation wavelength. Irradiation at 404 or 434 nm populates exclusively the $^1E(1)$ state. An increasing population of ^1CT is expected when shorter irradiation wavelengths are employed, and it is almost the exclusive process with 313 nm excitation.

For the $[Fe(CN)_5(\widehat{NN})]^{3-}$ systems, the highest quantum yields were obtained for 313 or 334 nm excitations, indicating a more efficient escape from the solvent cage [63]. On the other hand, the low quantum yields measured for the 404 or 434 nm irradiations are associated with an efficient recombination of the primary photoproducts. In the latter case, the ^3E state is the only one responsible for the photoreaction, while the participation of higher-energy states is likely for shorter wavelengths. Alternatively, a higher intersystem crossing efficiency leads to efficient deactivation from the ^1CT state.

These facts show that the cage recombination does occur in ligand photosubstitution reactions following heterolytic bond scission. The effects in $[Fe(CN)_5(\widehat{NN})]^{3-}$ are more pronounced than that for Co(III) complexes [65–71] and observable even in pure water.

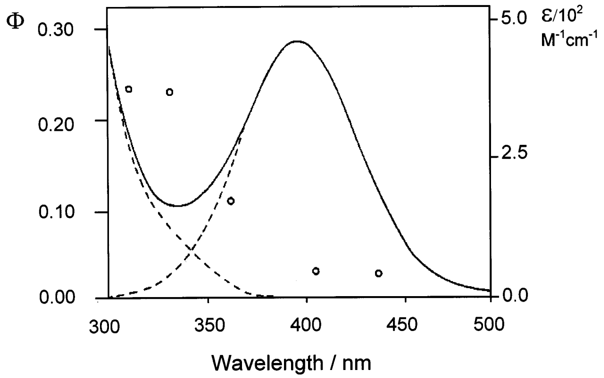


Fig. 1. Quantum yields for the ring closure process in the $[Fe(CN)_5(tn)]^{3-}$ complex for 313, 334, 365, 404 or 434 nm irradiation. The dashed line represents the Gaussian deconvolution of the electronic spectrum.

Table 3
Quantum yields for the ring closure process for the $[Fe(CN)_5(tn)]^{3-}$ complex at different excitation wavelengths and mixed-solvent compositions

	η/Cp	ε	Φ_{313}	Φ_{334}	Φ_{365}	Φ_{404}	Φ_{434}
Glycerol (wt.%)							
0.00	0.89	78.54	0.230	0.226	0.110	0.032	0.028
10.73	1.18	75.80	0.205	0.082	0.082	0.028	0.026
19.30	1.51	74.05	0.190	0.075	0.075	0.021	0.020
38.25	2.97	69.32	0.182	0.127	0.060	0.014	0.014
57.34	7.45	63.37	0.134	0.098	0.035	0.012	0.012
61.85	9.90	61.75	0.095	0.063	0.018	0.010	0.010
CH_3CN (wt.%)							
0.00	0.89	78.54	0.230	0.226	0.110	0.032	0.028
22.08	0.97	69.22	0.195	0.163	0.064	0.025	0.019
53.60	0.73	53.96	0.230	0.178	0.072	0.024	0.017
66.48	0.60	48.30	0.244	0.197	0.077	0.028	0.020

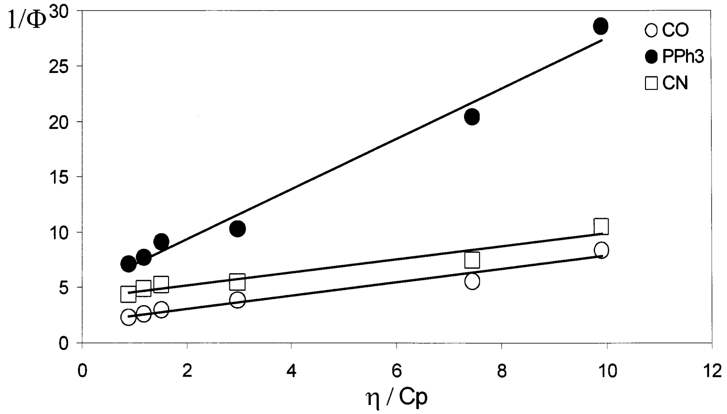


Fig. 2. Reciprocal of quantum yields for the photosubstitution of CO, PPh_3 and CN^-, respectively, in $[Fe(CN)_5CO]^{3-}$, $[Fe(CN)_5PPh_3]^{3-}$ and $[Fe(CN)_5(tn)]^{3-}$ vs. viscosity of water–glycerol mixtures.

We have also investigated the influence of the solvent in water–glycerol and water–acetonitrile mixtures on the quantum yields for ring closure in $[Fe(CN)_5(tn)]^{3-}$ in order to analyze the role of the solvent in the conceptual framework of the cage model. The data displayed in Table 3 and Fig. 2 point out the importance of solvent viscosity on the magnitude of the quantum yield [76]. Despite the fact that viscosity dominates the observed trend, a good correlation between quantum yields and the reciprocal of the solvent dielectric constant was observed, as can also be seen in Fig. 3.

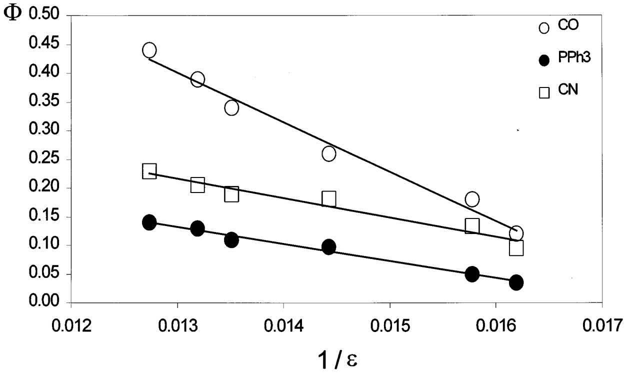


Fig. 3. Quantum yields for the photosubstitution of CO, PPh_3 and CN^-, respectively, in $[Fe(CN)_5CO]^{3-}$, $[Fe(CN)_5PPh_3]^{3-}$ and $[Fe(CN)_5(tn)]^{3-}$ vs. the reciprocal of dielectric constant of water–glycerol mixtures.

The overall quantum yield reflects the balance between solvent and irradiation wavelength effects. While the wavelength dependence accounts for different efficiencies of primary radical formation in the initial step before deactivation occurs, the dependence on medium parameters is related to the dynamics of deactivation for the formation of the final photoproduct. The characteristics of the medium can shift the balance from one pathway to another, tuning the efficiency of the photochemical process.

We have further investigated the influence of glycerol on the CO or PPh_3 photolabilization. This photoreactivity pattern had been characterized as wavelength independent [53]. According to the literature [44], the back reaction for the $[Fe(CN)_5CO]^{3-}$ complex was not expected to be as important as for the $[Fe(CN)_6]^{4-}$ complex due to the more efficient escape of the CO from the solvent cage when compared to that of CN^-. The CO ligand was considered to diffuse with high efficiency due to its low solubility in water [44]. The results in Table 4 and Fig. 2 show that solvent recombination does occur to a high degree, ruling out the hypothesis previously stated [44]. The data showed that the recombination is not

Table 4
Quantum yields for the photolabilization of L for the $[Fe(CN)_5L]^{3-}$ complexes at 313 nm excitation

Glycerol (wt.%)	η/Cp	ε	$[Fe(CN)_5CO]^{3-}$	$[Fe(CN)_5PPh_3]^{3-}$
0.00	0.89	78.54	0.44	0.14
10.73	1.18	75.80	0.39	0.13
19.30	1.51	74.05	0.34	0.11
38.25	2.97	69.32	0.26	0.097
57.34	7.45	63.37	0.18	0.049
61.85	9.90	61.75	0.12	0.035
79.52	43.40	54.34	0.067	0.010

negligible, and its importance enhances with the increase of viscosity, which dominates the observed solvent dependence for these systems [80].

2.3. Photoisomerization

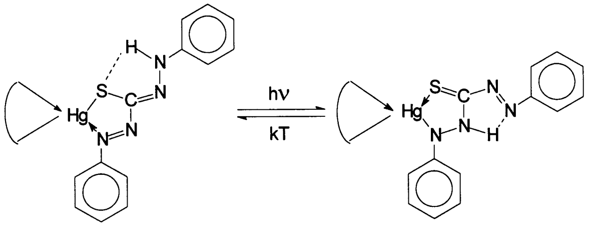
Although the photoisomerization processes that we have been investigating do not necessarily involve ligand substitution, they will be reported in this section.

It is not common to find intraligand photoreactions following metal complex irradiation, although such processes are one of the most important contributions of the photochemistry of coordination compounds [32]. It is also a way to promote endergonic chemical reactions photochemically, through a metal complex assisted ligand conversion. Wrighton et al. [81–84] and Whitten et al. [85–87] have reported some very interesting results on this subject, analyzing *trans* → *cis* isomerization of styrylpyridines coordinated to some carbonyl metal complexes, such as $[W(CO)_5L]$, $[Ru(bpy)_2(L)_2]^{2+}$, where bpy is bipyridine, and related compounds.

Our first work related to this subject concerned photochemical and kinetic studies on mercury dithizonate, $[Hg(HDz)_2]$, where HDz is diphenylthiocarbazone, exploring its photochromic properties [88].

This complex, as many metal dithizonate complexes, undergoes a remarkable color change after being irradiated by visible light, which is reversed in the dark [89–91]. At first, interested in a chemical demonstration that could be useful in teaching [88], and would be also involved in a first exhibition demonstrating energy conversion in the inaugural event of the USP Museum of Science and Technology [92], the reaction caught our attention and brought us to this interesting system.

The study was initiated by following the kinetics of the back reaction after the photochemical event represented in Eq. 3. The quantum yield of the photoreaction was also determined by continuous photolysis.



(3)

The rate constants were determined at several temperatures, as well as the quantum yield values [88,93]. The vivid color change from orange to blue due to the photochemical isomerization has been used for years in our undergraduate course [93] to demonstrate photochromism, and it has been extended to the determination of rate constants. The thermal first-order decay of the excited state has been useful for experiments involving kinetics of coordination compounds that allow an evaluation of activation parameters in temperature dependence measurements.

Another isomerization process, an intraligand photoreaction, has also been explored by investigating the behavior of the salt $[Re(CO)_3(phen)(t\text{-bpe})]PF_6$, where

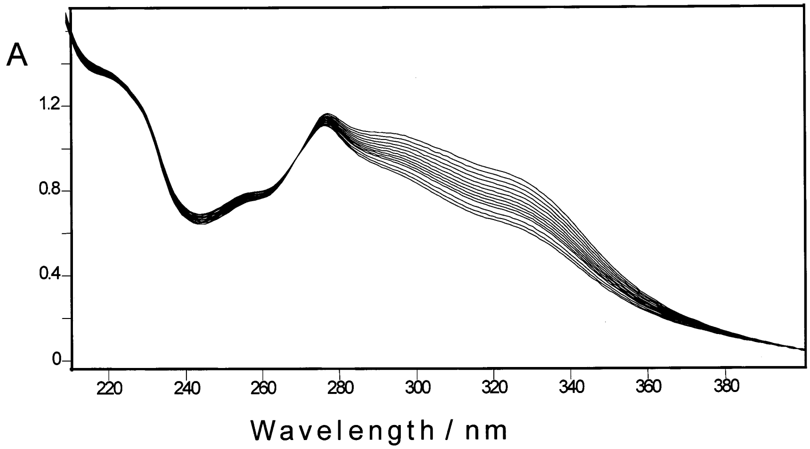


Fig. 4. Spectral changes during the 313 photolysis of 1.67×10^{-4} M [Re(CO)$_3$(phen)(t-bpe)]PF$_6$ in CH$_3$OH. $T = 298$ K, $\Delta t_{irr} = 5$ s.

t-bpe = *trans*-1,2-bis(4-pyridyl)ethylene and phen = phenanthroline, in experiments carried out at several different wavelengths [94]. The absorption spectrum of the complex, in comparison with the spectra of the free and protonated ligand, reveals that the lowest excited state has substantial metal-to-ligand charge-transfer (MLCT) character.

The irradiation of the free protonated or non-protonated ligands shows that the isomerization takes place with quantum yield of 0.04–0.4, depending on the solvent and excitation wavelength, as shown by direct irradiation or by sensitization [85,86,95]. Spectral changes accompanying the *trans–cis* isomerization exhibit very clear isosbestic points [94].

Similar behavior can be observed for the coordinated ligand when methanolic solutions of the complex are irradiated at 313 or 334 nm, as shown in Fig. 4. Photoexcitation at 365 nm leads to a less efficient isomerization process, showing that the reactive deactivation pathway is competing with deactivation to the low lying MLCT states for the decay of the excited state [96]. This deactivation process becomes evident in experiments performed in methanolic solutions of [Re(CO)$_3$(phen)(t-bpe)Fe(CN)$_5$]$^{2-}$ [94]. The formation of the binuclear complex leads to the appearance of a new Fe^{II} → t-bpe MLCT low energy transition ($\lambda_{max} = 600$ nm). No isomerization process can be detected after the coordination of the Fe(CN)$_5^{3-}$ moiety, even at 313 nm excitation, showing an effective deactivation pathway to MLCT states [94].

This study showed that in spite of the nature of the low lying excited state, the red-shifted absorption of the complex compared with the free ligand can be exploited to achieve the photoinduced isomerization by irradiation in the low energy region, where free t-bpe does not absorb. This kind of intraligand photoreaction represents an important contribution by the complex in photoassisting a conversion of the ligand to a thermodynamically unstable product.

3. Photoexcited electron and energy transfer

Charge-transfer photochemistry is related to many practical problems that range from synthesis to energy conversion. This is a large field with several books [97–99], published with numerous reviews and articles continuously emerging in addition to those which have already been cited. These processes have proven to be useful to test models of electron transfer theories and obtain unique information about individual electron transfer steps [100–107].

3.1. Photoredox and energy transfer processes of complexes

Primary photoreactions that lead to net oxidation or reduction of complexes result from the charge-transfer excited states (CTES) promoted by a radial redistribution of an electron in the excited state. Again, the CT bands observed are not always pure CT in character and often are not separated from other types of transitions. Furthermore, initial CT excitation energy can be dissipated into other reaction pathways and establishing reaction patterns characteristic of different excited states is not always straightforward. The usual short lifetimes of primary photoredox products usually preclude transient measurements and investigation of this reaction by product analyses and quantum yield determination by using a conventional photostationary system are useful.

Among the various types of CT transitions, this section deals primarily with systems in which light absorption results in a transfer of electron density directly to a ligand, namely MLCT, a transfer of electronic charge away from the ligand toward a metal center, ligand-to-metal charge-transfer (LMCT), and charge-transfer to solvent, CTTS.

Some energy transfer processes are also discussed. A nonradiative energy transfer process results from simultaneous deactivation of the originally excited species to its ground state and the promotion of a second to a higher, electronically excited state. It is a powerful tool for obtaining information about excited states, mechanisms of photochemical reactions, and is exploited in molecular-scale electronic devices. It is of great importance in photosynthesis and potentially in artificial photosynthesis [108,109]. It also can be conveniently used to quench undesired photoreactions, increase yields of useful photoreactions and to extend the useful wavelength range used to produce excited states [20,23,108–110].

3.1.1. Photosolvated electron formation

Photoelectron formation from $[Fe(CN)_5L]^{3-}$ complexes has not received much attention in comparison with other cyanoferrate species [49,111–117] or transition metal cyanide complexes in general [118–120]. Except for the anomalous $[Fe(CN)_5NO]^{2-}$ ion [121], just few examples are reported to photoeject electrons [122–125].

We have been investigating this process in a series of $[Fe(CN)_5L]^{3-}$ complexes under different conditions and excitation energies using laser flash photolysis and transient absorption spectrum measurements in the picosecond to second time

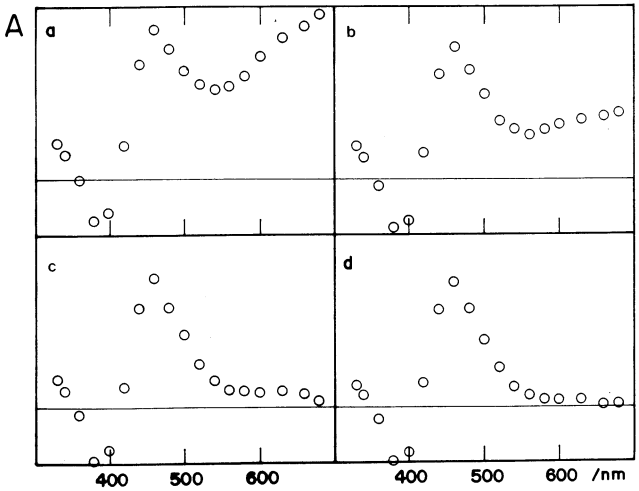


Fig. 5. Transient spectra recorded after laser flash irradiation with pulses of 308 nm. (a) 2.2; (b) 2.8; (c) 4.4; and (d) 7.2 μs delay. $[[Fe(CN)_5(en)]^{3-}] = 3.3 \times 10^{-3}$ M, $[en] = 1.0 \times 10^{-2}$ M.

domain using Nd:YAG (355 and 266 nm), excimer (308 nm), or N_2 (337 nm) lasers [126].

Irradiation of $[Fe(CN)_5CO]^{3-}$, $[Fe(CN)_5PPh_3]^{3-}$, or $[Fe(CN)_5(en)]^{3-}$ in aqueous solutions with laser pulse results in an immediate absorption peak around 700 nm followed by a rapid decay, as seen in Fig. 5. The transient absorption spectra, as well as the disappearance of this absorption after saturation of the sample with N_2O, lead to the assignment of this species as hydrated electron [126]. The quantum yields (Φ) determined as a function of irradiation wavelength, monitoring the absorbance at 720 nm and based on actinometry with $[Co(NH_3)_5Br]^{2+}$ are given in Table 5.

The data in Table 5 reveal that the LF transition energy for each complex ($\lambda_{max} = 303$, 360 and 395 nm for CO, phosphine and ethylenediamine derivatives, respectively) plays an important role in the electron ejection process. The wavelength dependence of the quantum yields and its magnitude can be associated with the energy of the d–d band. When the ligand field state is at lower energy, there is

Table 5
Solvated electron formation versus irradiation wavelengths for $[Fe(CN)_5L]^{3-}$

λ_{irr} (nm)	$\Phi_{[Fe(CN)_5CO]^{3-}}$	$\Phi_{[Fe(CN)_5PPh3]^{3-}}$	$\Phi_{[Fe(CN)_5(en)]^{3-}}$
354	n.d.[a]	n.d.	n.d.
337	n.d.	<0.003	0.010 ± 0.005
308	0.012 ± 0.002	0.012 ± 0.002	0.10 ± 0.01
266	0.043 ± 0.004	0.15 ± 0.02	0.52 ± 0.05

[a] n.d., non detectable.

less possibility of the relaxation process to a LF level, increasing the efficiency of the CT process. An attempt to correlate the photoelectron ejection yields with the redox potentials of the complexes does not result in a straightforward relationship.

3.1.2. Photochemical and photophysical properties

Complexes of the type *fac*-[Re(CO)$_3$(LL′)X], where LL′ = one bidentate or two monodentate azines and X = halide or neutral monodentate ligands, have been the subject of numerous studies focusing both thermal and photochemical reactivities [127–149]. This is, in part, due to the promising application of such compounds as catalysts and as photosensitizers. Upon excitation on selected wavelengths, these complexes feature the lowest excited states involving increased electron density on the LL′ ligand, like the one-electron reduced molecule, resulting in a species having greater reducing power than the ground state. Simultaneously, the excited species has decreased its electron density in the lowest occupied orbital like the one-electron oxidized molecule, which results in enhanced oxidizing power of the excited state in comparison to the ground state. That is, the excited state is both a better reductant and a better oxidant. Furthermore, the photochemical and photophysical properties of these complexes have provided important information about the nature of low-lying excited states.

We have been investigating structural, thermal, photophysical and photochemical properties of some *fac*-[Re(CO)$_3$L$_2$X] compounds, where L = isoquinoline, quinoline, 4-cyanopyridine, 2,3-bis(2-pyridyl)-1,3,5-triazine, *trans*-1,2-bis(4-pyridyl)-ethylene, L$_2$ = phenanthroline or bipyridine derivatives, among others and X = chloride or monodentate ligands. Few azine ligands L, such as 4-cyanopyridine or quinoline, were found to be more labile in these compounds than in other related Re(I) complexes [150,151] and conveniently used to prepare mixed-ligand complexes. The complexes with L = quinoline and isoquinoline (isq) were prepared and characterized by X-ray crystallography and various spectroscopies [151]. Their photochemical and photophysical properties were investigated under steady and laser flash irradiations and compared with those of homologous rhenium complexes. Room temperature luminescence was strongly related to the MLCT excited states and the emission spectra and lifetimes of emission were consistent with large contributions from the radiative relaxation of the Re → azine state to the luminescence. By contrast, their 77 K emission spectra and the lifetime of the long-lived emission compared very well with those reported for the phosphorescence of the protonated ligands, indicating that the radiative relaxation of the intraligand excited states dominated the process [152].

The decay of the emission at 77 K was described by a double exponential with lifetime τ_1 and τ_2, respectively, 10 ns and 340 μs for the isoquinoline complex, and 16 ns and 250 μs for the quinoline one. The diphasic decay of the luminescence at 77 K was explained by conversion of the ^{3}CT state to the emissive $^3\pi\pi^*$ state in competition with radiative and radiationless relaxations to the ground state.

The transient absorption decay within several microseconds in flash photolyses at wavelengths between 330 and 360 nm left almost no residual absorption, which could be assigned to the photoproducts. On the other hand, the primary photoreac-

Table 6
Quantum yields for formation of $[CuL']^+$ from interception of a biradical intermediate and emission lifetime (τ) of *fac*-$[Re(CO)_3(isq)_2Cl]$[a] at 308 nm laser pulse flash photolyses in the presence of $[CuL']^{2+}$

$[Cu(L')]^{2+}$ (10^{-5} M)	Φ	τ (μs)
		0.95 ± 0.07
1.0	0.024 ± 0.003	0.92 ± 0.03
2.0	0.022 ± 0.002	0.91 ± 0.04
4.0	0.020 ± 0.002	0.81 ± 0.04
5.0	0.023 ± 0.002	0.80 ± 0.03
6.0	0.021 ± 0.002	0.80 ± 0.05
8.0	0.021 ± 0.002	0.76 ± 0.04
30.0	0.026 ± 0.003	0.51 ± 0.04

[a] [*fac*-$[Re(CO)_3(isq)_2Cl]$] $= 1.0 \times 10^{-4}$ M.

tions of *fac*-$[Re(CO)_3(isq)_2Cl]$ in acetonitrile at wavelengths where the population of intraligand states is optically important, $\lambda_{ex} \leq 308$ nm, were found to generate a biradical intermediate, as represented in Eq. (4).

$$fac\text{-}[Re(CO)_3(isq)_2Cl] \xrightarrow[\lambda \leq 308\ nm]{h\nu} fac\text{-}[Re(CO)_3(isq^{\bullet +})(isq^{\bullet -})Cl] \quad (4)$$

The nature of the intermediate was investigated via flash irradiation of the complex solution in the 1.0×10^{-5} to 30.0×10^{-5} M concentration range in $[CuL']^{2+}$, where L′ is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene [142,153]. Time-resolved measurements of the absorbance and luminescence intensity revealed the formation of $[CuL']^+$, $\lambda_{max} \approx 745$ nm, represented by Eq. (5), with a parallel quenching of the emission, as can be observed in Table 6.

$$fac\text{-}[Re(CO)_3(isq^{\bullet +})(isq^{\bullet -})Cl] + [CuL']^{2+}$$
$$\rightarrow fac\text{-}[Re(CO)_3(isq)(isq^{\bullet +})Cl] + [CuL']^{+} \quad (5)$$

The trapping of the biradical intermediate by $[CuL']^{2+}$ proved to be very fast for the quinoline and isoquinoline complexes with an additional complication associated with diffusional effects.

3.2. Photoredox and energy transfer processes of supramolecular systems

Supramolecular systems are constituted of a number of discrete molecular components with definite individual properties, held together by chemical interactions. As the development of chemistry evolved from the molecular level to more complex supramolecular systems, research in supramolecular photochemistry has also attracted great interest. Supramolecular systems brought the concept of molecular devices, assemblies of molecular components designed to achieve specific functions, such as photoinduced electron and energy transfer in solar energy conversion, electron collection, remote photosensitization, antenna effect, photoswitching of electric signals, light-energy up conversion, photoinduced structural changes in switch on/off applications (photoisomerizable systems), molecular wires and sensors [20,23,38,154–157].

3.2.1. Ion-pair photochemistry

The formation of ion-pairs between $[Co(sep)]^{3+}$, where sep is 1,3,6,8,10,13,16,19-octaazabicyclo[6,6,6]eicosane, and some anions can give rise to supramolecular charge-transfer interactions [158,159]. When the anion is a reducing species such as $C_2O_4^{2-}$, a second-sphere charge-transfer band (SSCT) appears in the near-UV or visible spectral region [23,158–166]. The spectroscopic transition in the 200–400 nm region can not be explained as the sum of the components forming the ion-pairs, but rather is the result of an ion-pair charge-transfer transition, IPCT.

This kind of contact ion-pair is considered the simplest case of a supermolecule. Since the reactants are already assembled, more informative kinetic and thermodynamic parameters can be evaluated compared to intermolecular ones [23,160].

Examples of IPCT compounds based on metal complexes are still rare, but the interest in these systems has increased, since they are distinguished by interesting photochemical and photocatalytical behavior [23,158–160].

The excitation at the IPCT band leads to very efficient photoredox reactions in low-energy regions, where each component itself does not show photoredox reactivity. In the past several years special attention has been given to the photochemistry of cage type complexes which do not undergo ligand replacement upon one-electron reduction [161–167]. For instance, irradiation of the $[Co(sep)]^{3+}/C_2O_4^{2-}$ IPCT band induces an electron transfer to the complex and oxidation of oxalate ions to carbon dioxide [162,165]. When the photoreaction is carried out in the presence of colloidal platinum, $[Co(sep)]^{3+}$ plays the role of a photosensitizer for the evolution of hydrogen from aqueous solutions with oxalate ions as sacrificial agents.

Due to this interesting electron transfer sensitizer property, several photochemical studies have been focused on the $[Co(sep)]^{3+}$/anion system [158–169]. One of the main aims is the determination of the true quantum yield of the photoprocess, since light is absorbed both by the ion-pair and the complex itself. Although a few studies have been reported, none has determined the ion-pair association constant under the same condition, ionic strength, pH and temperature, as in the photochemical studies.

In our work we performed careful experiments with the $[Co(sep)]^{3+}/C_2O_4^{2-}$ system at different oxalate ion concentrations, at a constant ionic strength, determining the apparent quantum yields [170]. The true quantum yield was determined using the ion-pair association constant, K_{IP}, and its molar absorptivity, ε_{IP}, measured under the same controlled conditions employed for the photochemical experiments. The association of the oxalate ions with $[Co(sep)]^{3+}$ was also investigated at 0.40 M (KCl) ionic strength, pH 6.00 and 25.0°C, and the existence of only 1:1 ion-pairs in this system was determined under the same condition. The apparent quantum yields for the photochemical reduction of the complex varied from 0.05 to 0.28 in the 0.010–0.10 M range in $C_2O_4^{2-}$. The true quantum yield, Φ_t, for the photochemical electron transfer process was calculated by using the fraction of the excitation light absorbed by the ion-pair, which was obtained by using the association constant and the molar absorptivity of the $[Co(sep)]^{3+}/C_2O_4^{2-}$ ion-pairs, 4.7 M^{-1} and 3.4×10^2 M^{-1} cm^{-1}, respectively, at 313 nm. Fig. 6 shows the apparent quantum yield variation as well as the corrected one.

The photochemical reactivity of the *fac*-$[Co(pic)_3]^{3+}$ ion, where pic is 2-aminomethylpyridine, and ion-pairs with some anions, such as oxalate, edta, citrate and iodide, was also investigated at 313 nm photolysis. The complex is quite inert in neutral and acidic solution, and does not react photochemically by itself. Although the *fac*-$[Co(pic)_3]^{3+}$ ion has a simpler structure than $[Co(sep)]^{3+}$, it has singular characteristics, such as a ligand reactivity in basic solution [171,172] inertness as the Co(II) complex [173–175] and a very interesting photoreactivity after forming ion-pairs [174–176].

The photolysis at its IPCT band led to spectral changes due to the reduction of the complex and the oxidation of the anion. Oxygen bubbling into irradiated solutions, at appropriate pHs, regenerated the starting complex. When the photoreaction was carried out in the presence of oxygen, no net reaction of *fac*-$[Co(pic)_3]^{3+}$ ion could be detected since the photochemically generated *fac*-$[Co(pic)_3]^{2+}$ ion was oxidized reversibly by O_2.

The apparent quantum yields for the photochemical process 2*fac*-$[Co(pic)_3]^{3+}/C_2O_4^{2-} \rightarrow$ 2*fac*-$[Co(pic)_3]^{2+} + 2CO_2$ were determined by analyzing the disappearance of the *fac*-$[Co(pic)_3]^{3+}$ ion and the formation of CO_2, at ionic strength 0.35 M (KCl) and 25°C. The true quantum yield at the irradiation wavelength, $\Phi_t = 0.58$, was calculated using the fraction of the excitation light absorbed by the ion-pairs [177]. A photodecarboxylation reaction mechanism was proposed. The study showed that *fac*-$[Co(pic)_3]^{3+}$, analogously to $[Co(sep)]^{3+}$ [170], plays the role of a photosensitizer in an electron-transfer reaction.

3.2.2. Photochemistry and photophysics of covalently-linked systems

Supramolecular photochemistry involving the covalently-linked systems is also of major importance to the field with expressive applications which have already been mentioned in Section 3.2. In polynuclear complexes the metal-based components are linked together by bridging ligands, which determine the structure of the system and control the electronic communication between the metal-based components [20,23,38,157,178].

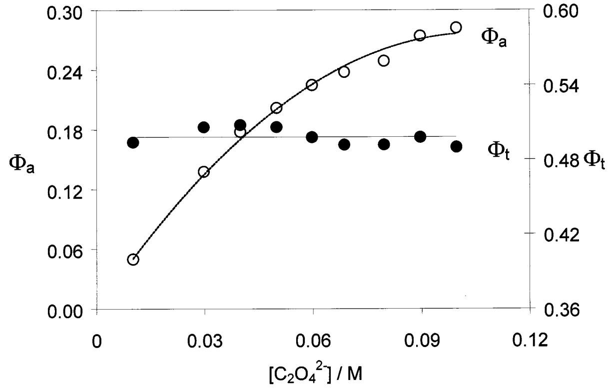


Fig. 6. Apparent quantum yields (Φ_a) and true quantum yields (Φ_t) vs. oxalate concentration for the photoreduction of $[Co(sep)]^{3+}$. $I = 4.0$, pH 6.0, $T = 298$ K.

Intramolecular energy transfer in polynuclear metal complexes has been the subject of many reviews, some of them with particular attention to systems with Ru(II) complexes interconnected by cyanide [178–186] or polypyridyl ligands [181,186,187].

Several covalently-linked systems have been prepared in collaboration with other research groups and the investigation about their photochemical and photophysical properties has been carried out [96,141,188–190]. One example is the pentanuclear species, represented by the general formula

$$[(\mathrm{phen})(\mathrm{CO})_3\mathrm{Re}(\mathrm{CN})[\mathrm{Ru}(\mathrm{bpy})_2(\mathrm{CN})]_n\mathrm{Ru}(\mathrm{bpy})_2(\mathrm{CN})]^{(n+1)+} \quad (n = 0\text{–}3)$$

in which every $\mathrm{Ru^{II}}$ center is linked to two cyanides, oriented with the N-end pointing towards the terminal Ru(II) center [141]. These polynuclear complexes present a directional energy migration and are of great importance for the design of photochemical molecular devices involving spectral sensitization, antenna effects and remote photosensitization [23,156].

Energy transfer processes in other Re based polynuclear complexes have been investigated by analyzing quenching of photoisomerization in the binuclear $[\mathrm{Re(CO)_3(phen)}(t\text{-bpe})\mathrm{Fe(CN)_5}]^{2-}$ complex mentioned in Section 2.3. The process is explained by an effective deactivation channel to the new $\mathrm{Fe^{II}}(t\text{-bpe})$ MLCT states [94].

Covalently-linked systems involving cyanoferrate(II) complexes and $[\mathrm{Cr(bpy)_2(BL)}]^{3+}$, where BL is the bidentate bridging ligand 2,2′-bipyrimidine (bpm) or 2,3-bis(2′-pyridyl)pyrazine (dpp), have also been investigated. The iron chromophore presents some interesting features, such as intense bands in the visible region and unreactive MLCT states toward photosubstitution reactions, appropriate for antenna fragment [191–193]. The monomeric $[\mathrm{Cr(bpy)_2(dpp)}]^{3+}$ and $[\mathrm{Cr(bpy)_2(bpm)}]^{3+}$ species present at 77 K a sharp emission band located around 715 nm, assigned to the $^2\mathrm{E} \rightarrow {}^4\mathrm{A}_2$ transition [188,189], that characterizes them as good luminophores. In general, light absorption by the chromophore is followed by emission from the luminophore, the so called photonic molecular wire [193–198].

After establishing some important patterns of the photochemical behavior of cyanoferrate(II) complexes described previously, we have extended our investigations on the photochemistry of bimetallic compounds with $[\mathrm{(CN)_4Fe(bpm)Cr(bpy)_2}]^{+}$ and $[\mathrm{(CN)_4Fe(dpp)Cr(bpy)_2}]^{+}$. The lack of emission for both bimetallic species upon excitation on the intense MLCT band in the visible region indicated intermediate or possibly even strong coupled metal centers [188–190].

4. Solar cells

4.1. Photosensitization of wide band-gap semiconductors

The conversion of solar energy into electricity has been a very active research field. Historically, chemically-based systems such as photogalvanic and photoelectrochemical cells have been developed as an alternative for the solid-state silicon-based cells [108,199–204].

In photogalvanic cells, species dissolved in an electrolyte solution absorb light directly, generating photochemically active species, which in turn are capable of undergoing electron transfer, ultimately producing electricity or converting low-energy starting materials into high-energy products. An example is the $[Ru(bpy)_3]^{2+}$ system for water splitting. Although simple and elegant, with efficient visible light absorption, such homogeneous systems have low efficiencies due to rapid recombination of the photoredox products in solution [201,205–212].

This limitation was overcome with semiconductor-based photoelectrochemical cells, in which the light-absorbing species was a solid wide band-gap oxide semiconductor in contact with a solution containing an appropriate redox relay. The semiconductor/liquid electrolyte interface separates the photoproduced oxidative and reductive equivalents, inhibiting back electron transfer. However, practical applications of such heterogeneous systems for the conversion of visible light into energy were unlikely, due to the wide band-gap of the photostable semiconductors employed, which required high-energy light to create electron-hole pairs [201,209,212–217]. Dye sensitization was of limited utility because of sub-monolayer coverage and low absorptivities.

Spectral sensitization of nanocrystalline films of wide band-gap semiconductors by attached dyes has provided a successful solution to extending the range of activity of the cells to low-energy light with effective results [26,157,218–221]. In this approach, attached dyes, rather than the semiconductor itself, are the absorbing species, thus separating the light-absorption and charge-separation processes. Following light absorption, the excited dye promotes electron injection into the semiconductor conduction band, keeping the electron-hole pair separated by the semiconductor-sensitizer interface. The oxidized sensitizer is regenerated by the reduced form of a redox mediator couple, the oxidized form of which, in turn, migrates toward the counter-electrode to be reduced, concluding the redox cycle. The system operates as a regenerative electrochemical cell, in which visible light is efficiently converted into electricity without any permanent chemical change. Electron injection into the semiconductor's conduction band from an excited sensitizer allows population of the band with light of energy lower than the semiconductor band-gap, providing a good match with the solar spectrum in ideal cases for practical applications. The maximum output voltage which can be achieved corresponds to the difference between the redox potential of the mediator couple and the Fermi level of the semiconductor [222,223].

The most efficient solar cells are based on dye sensitization of titanium dioxide, TiO_2. Among many semiconductors, *n*-type nanocrystalline TiO_2 presents the appropriate properties to perform energy conversion in such cells. It is stable, inexpensive, easily processed, and has appropriate energetics [224–227]. Many different sensitizers have been investigated for this purpose, such as chlorophyll derivatives [228–232], porphyrins [229,233], phthalocyanines [234–238], carboxylated derivatives of anthracene [239,240], polymeric films [241], and even other coupled semiconductors with lower energy band-gaps [225,237,242–246], among others [247–250]. However, the best solar to electric power conversion efficiency has been achieved by Ru(II) polypyridyl compounds with carboxylic acid groups, with special attention paid to $Ru(dcbH_2)_2LL'$ derivatives, where L and $L' = H_2O$, X^-, CN^-, SCN^-, etc. and $dcbH_2 = 4,4'\text{-}(CO_2H)_2\text{–}2,2'$-bipyridine [157,218,251–255]. Among this family of compounds, outstanding results have been achieved with thiocyanate derivatives [251,253,256].

Based on the properties previously described for the Re(I) complexes containing isoquinoline, isq, and 4-phenylpyridine, ppy, [150,151] we prepared a series of sensitizers, including *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$, *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$ and *cis*-$[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ [257–261]. These compounds have broad absorption spectra with intense MLCT bands overlapping the solar spectrum, combined with suitable photoelectrochemical properties and high stability in the Ru^{III} oxidized state. 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 states (CTES) of the sensitizer and the wavefunction of the semiconductor conduction band. As a consequence, dye excitation with visible light results in the very fast electron transfer through the carboxylic groups to the semiconductor described in the literature [26,157,223,251]. Fig. 7 illustrates the electron injection into the semiconductor from these molecular sensitizers with some ancillary ligands employed in our studies.

4.2. Thin-layer solar cells

Photosensitization of wide band-gap semiconductors to visible light has been studied for 30 years [262], but initially it had a slow progress. In the last decade, with the development of nanocrystalline TiO_2 films with high effective surface areas, this approach has advanced remarkably [255,263,264]. In a porous film, consisting of TiO_2 particles of nanometer dimensions, the effective surface area is increased by ca. 1000 times, resulting in effective light absorption. As a result of this advance, the development of low-cost efficient solar cells became possible [255].

As one of these promising devices, we have been developing thin-layer, transparent sandwich-type solar cells, the components of which are depicted in Fig. 8. The cell consists of a TCO, for instance a fluorine doped SnO_2 conducting glass, with the TiO_2 film sensitized by a complex, as a photoanode, I_2/LiI solution, as the redox relay and a transparent Pt film on TCO glass as a counter electrode.

Investigations of thin films have been carried out in a cooperative effort between our laboratory and an Industry group. Thin-layer TiO_2 film deposition techniques, such as spin-coating and painting, have been compared, which has provided a way to control physical properties such as film thickness and homogeneity [265]. The Industry–University collaboration has been an unique experience, providing students at both the undergraduate and graduate levels with the multi-disciplinary environment to become qualified professionals for many areas of modern science and technology in applied research.

The effectiveness for the sensitization of nanocrystalline TiO_2 films was determined employing several dyes described in Section 4.1 [257–261]. When employed

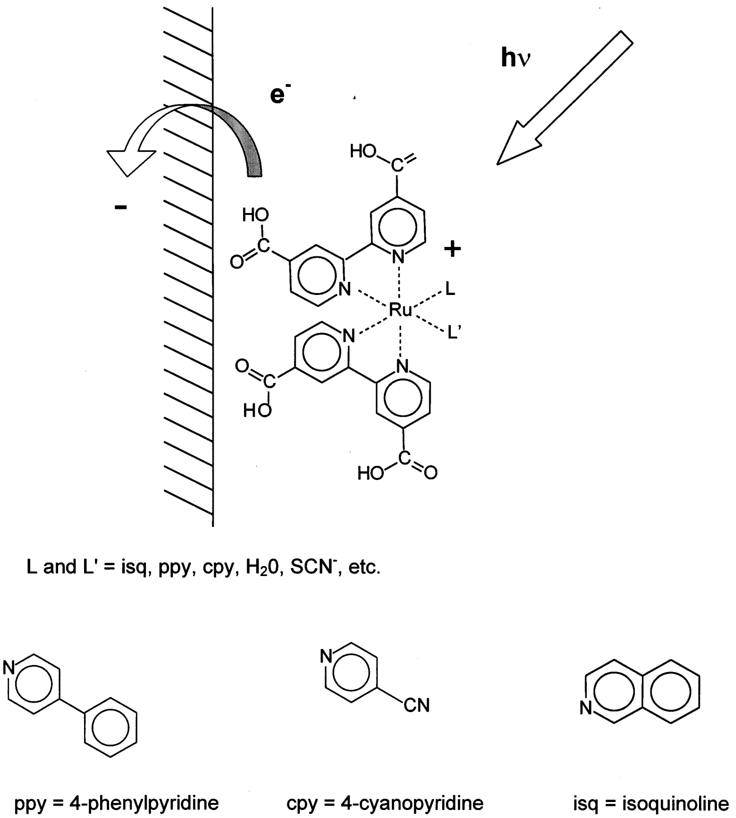


Fig. 7. Schematic representation of interfacial electron transfer following light absorption for the $Ru(dcbH_2)_2LL'$ derivative with some ancillary ligands.

in the regenerative thin-layer sandwich-type solar cells described here, the dyes provide enhanced spectral response of TiO_2 to visible light. The photocurrent action spectra obtained for the cell with dye coated *n*-type TiO_2 electrodes resulted in incident photon-to-current efficiency (IPCE) values up to 50% until 550 nm, as shown in Fig. 9. The complexes possess good light harvesting properties and act as efficient CT sensitizers for nanocrystalline TiO_2 in solar cells, converting visible light into electricity effectively [259,261]. The values confirm that the dyes adsorb efficiently to nanoporous TiO_2 with large internal surface area, and are comparable with those obtained by other ruthenium(II) polypyridyl-based sensitizers studied previously [252,253,264].

It is noteworthy that the IPCE values obtained for the mono-coordinated derivative, *cis*-$[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ are superior to those obtained for the bis-coordinated one, *cis*-$[(dcbH_2)_2Ru(ppy)_2]^{2+}$. This species with two different ancillary ligands presents a broader spectral response at longer wavelengths, when compared to the bis-coordinated ppy derivative, showing that the number and the

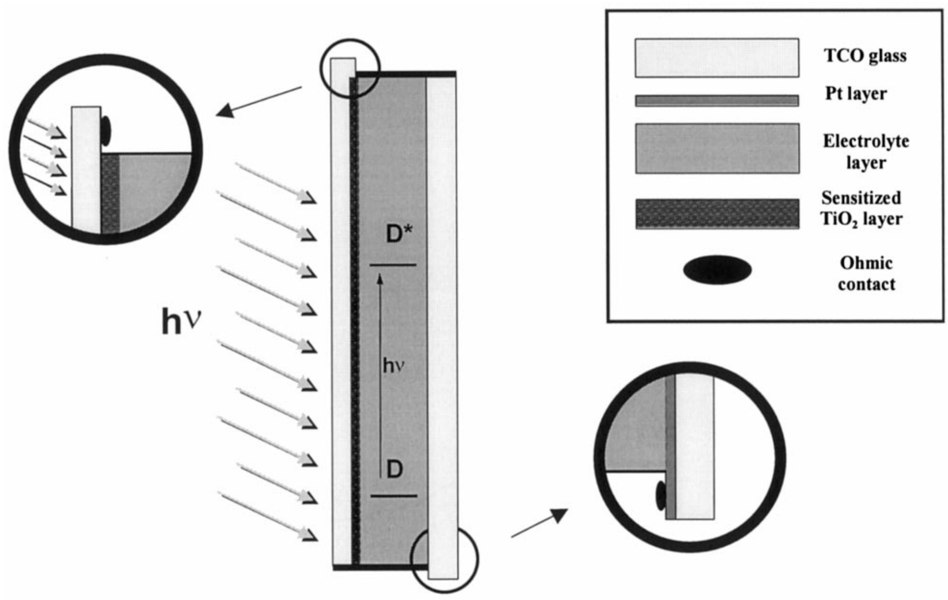


Fig. 8. Thin-layer transparent sandwich-type solar cell and its components.

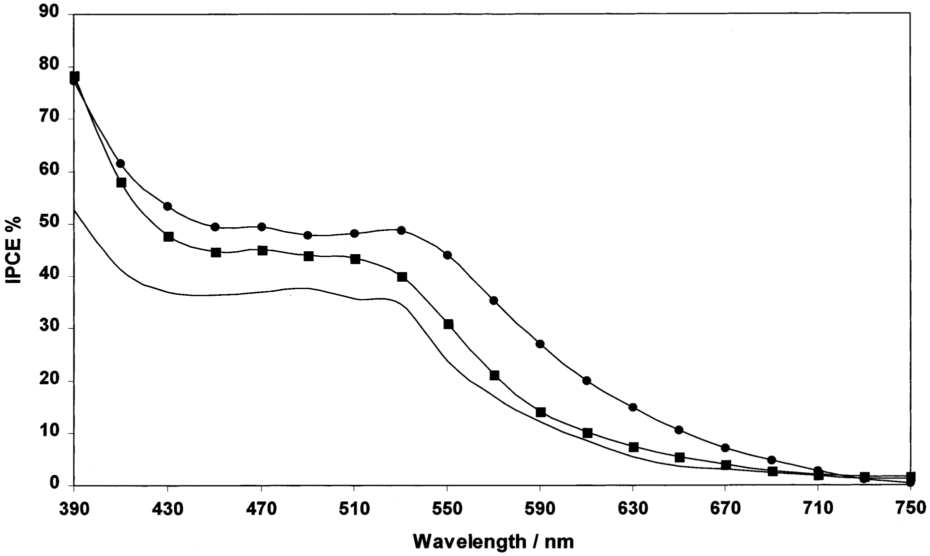


Fig. 9. Photocurrent action spectra obtained for nanocrystalline TiO_2 films coated with *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$ (—), $[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ (–■–) or $[(dcbH_2)_2Ru(ppy)(H_2O)](ClO_4)_2$ (–●–) as sensitizers in a thin-layer sandwich-type solar cell.

type of azine ligands coordinated to the non-attached side of the $(dcbH_2)_2RuLL'$ dye can be controlled, and plays an important role in tuning the overall properties of the system [261].

Acknowledgements

The authors are grateful to Professor Thomas J. Meyer for the incentive and valuable comments and suggestions, as well as for the thorough review of this manuscript. We also thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, and the Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP, for financial support of the reported researches.

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