# Supramolecular Photochemistry and Solar Cells

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## ABSTRACT

Supramolecular photochemistry as well as solar cells are fascinating topics of current interest in Inorganic Photochemistry and very active research fields which have attracted wide attention in last two decades. A brief outline of the investigations in these fields carried out in our Laboratory of Inorganic Photochemistry and Energy Conversion is given here with no attempt of an exhaustive coverage of the literature. The emphasis is placed on recent work and information on the above mentioned subjects. Three types of supramolecular systems have been the focus of this work: (i) cage-type coordination compounds; (ii) second-sphere coordination compounds, exemplified by ion-pair photochemistry of cobalt complexes and (iii) covalently-linked systems. In the latter, modulation of the photoluminescence and photochemistry of some rhenium complexes are discussed. Solar energy conversion and development of thin-layer photoelectrochemical solar cells based on sensitization of nanocrystalline semiconductor films by some ruthenium polypyridyl complexes are presented as an important application that resulted from specifically engineered artificial assemblies.

**Key words:** inorganic photochemistry, supramolecular photochemistry, solar cells, photoelectrochemical devices.

## 1. INTRODUCTION

The photophysical and photochemical behavior of several $d^6$ transition metals coordinated to $N$-heterocyclic ligands have been intensively investigated (Baba *et al.* 1998, Omberg *et al.* 1999, and references therein). A variety of applications based on fundamental investigation of photophysical and photochemical properties have emerged, such as luminescence-based sensors and displays, photoreactive polymers and dye-sensitization of semiconductors (Schanze & Schmehl 1997).

The development of more complex systems, especially within the framework of supramolecular chemistry, gives rise to the possibility of designing organized systems as components of molecular-level photochemical devices (Lehn 1995, 1988). Supramolecular systems are constituted of a number of discrete molecular components with definite individual properties, held together by chemical interactions. This organization is particularly interesting for the development of systems capable of performing useful functions, such as use of light for energy or information purposes (Balzani *et al.* 1998). These chemical systems have led to applications of inorganic photochemistry in areas such as biological chemistry, luminescence sensors, and advanced materials (Schanze & Schmehl 1997).

Molecular devices are 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, in analytical chemistry, and in the development of new materials and nanoscale electronic devices (Balzani 1987, Meyer 1989, Balzani & Scandola 1991, Lehn 1995, Meyer 1997, Schanze & Schmehl 1997, Kalyanasundaram & Grätzel 1998). In this aspect, caged metal ions, their ion-pairs and some covalently-linked systems studied by our group will be discussed here. Also, regenerative photoelectrochemical cells and some ruthenium complexes used as sensitizer for charge injection into nanocrystalline semiconductors will be presented to illustrate an application that has evolved from a fundamental investigation of inorganic photochemistry by use of a specifically designed assembly to conceive artificial molecular devices.

## 2. SUPRAMOLECULAR PHOTOCHEMISTRY

A particular type of perturbation can be introduced when a metal ion is encapsulated in a single, polydentate cage-type ligand. For instance, cobalt(III) sepulcrate, $[Co(sep)]^{3+}$ where sep = 1,3,6,8,10,13, 16,19-octaazabicyclo[6.6.6]eicosane, is considered a caged version of hexaamine cobalt(III), $[Co(NH_3)_6]^{3+}$, and presents a similar absorption spectrum, while its photochemical reactivity is quite different ($\Phi < 10^{-6}$) in comparison to the non-caged $[Co(NH_3)_6]^{3+}$ complex ($\Phi = 0.16$) (Balzani $et$ $al.$ 1986). Because of its characteristics, $[Co(sep)]^{3+}$ can be used as an electron transfer photosensitizer in ion-pair systems. When the photoreaction is carried out in the presence of colloidal platinum, the complex plays the role of a photosensitizer for the evolution of hydrogen from aqueous solutions with oxalate ions as sacrificial agent (Pina $et$ $al.$ 1985, Garcia $et$ $al.$ 1999 and references therein).

The complex $fac$-$[(Co(pic)_3]^{3+}$, where pic = 2-aminomethylpyridine, may be considered the simplest non-caged analogue of $[Co(sep)]^{3+}$, exhibiting similar redox and photochemical properties. In our work, we obtained the true quantum yield of

the photoprocess by investigating both the $fac$-$[(Co(pic)_3]^{3+}$ and $[Co(sep)]^{3+}$ ion-pair systems with $C_2O_4^{2-}$, determining the ion-pair association constant under the same conditions as the photochemical studies (Azzellini $et$ $al.$ 1996, Garcia $et$ $al.$ 1999). The study of the static as well as dynamic process has also been performed for the

$$[Co(sep)]^{3+} / C_2O_4^{2-}$$
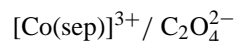
system. One of the important features of these processes is based on a photoredox water splitting cycle, where the complex can play the role of an electron mediator relay. A disadvantage is the use of sacrificial scavengers, for instance oxalate or EDTA, to avoid back reaction (Balzani 1987, Garcia $et$ $al.$ 1999).

A metal complex sensitized intraligand photochemistry and the use of the photoisomerizable properties of the $trans$-1,2-bis(4-pyridyl)ethylene, $t$-bpe, were exploited to investigate photoresponsive structural change and modulation of the photoluminescence of $fac$-$[Re(CO)_3(phen)(t$-bpe$)]^+$, where phen = 1,10-phenanthroline (Itokazu & Murakami Iha 1999). Upon coordination, the quantum yields for the isomerization were higher than compared to the free ligand, even at 365-nm irradiation, which is ineffective for photolysis of the ligand itself. Also an increasing luminescence centered at 570 nm is observed at room temperature as the $cis$-isomer is formed and makes this photoassisted isomerization of the ligand an interesting feature in the design of photochemical molecular devices with an attractive characteristic for photoswitches.

On the other hand, when the complex forms a binuclear species with the $[Fe(CN)_5]^{3-}$ moiety, a new $Fe^{II} \rightarrow t$-bpe MLCT low energy transition ($\lambda_{max} = 600$ nm) appears. No isomerization process can be detected in photochemical experiments performed with methanolic solutions of

$$[Re(CO)_3(phen)(t\text{-bpe})Fe(CN)_5]^{2-}$$
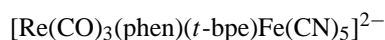
due to an effective deactivation pathway to MLCT states quenching the photoisomerization process (Itokazu $et$ $al.$ 1997). Such systems, where the excitation causes the $trans$-$cis$ isomerization, are also

employed to control coordination ability by light (Balzani *et al.* 1998).

Covalently-linked systems involving cyanoferrate(II) complexes and $[Cr(bpy)_2(BL)]^{3+}$, where bpy = 2,2'-bipyridine, BL = the bidentate bridging ligand 2,2'-bipyrimidine (bpm) or 2,3-bis(2'-pyridyl)pyrazine (dpp), were also investigated. The iron chromophore presents intense bands in the visible region and unreactive MLCT states toward photosubstitution reactions, appropriate for antenna fragments, while the monomeric $[Cr(bpy)_2(dpp)]^{3+}$ and $[Cr(bpy)_2(bpm)]^{3+}$ species present at 77 K a sharp $^2E \rightarrow {}^4A_2$ emission around 715 nm (Lima *et al.* 1993), which characterizes good luminophores. In general, light absorption by the chromophore is followed by emission from the luminophore, the so called photonic molecular wire (Petersen *et al.* 1991).

The lack of emission for both $[(CN)_4Fe(bpm)Cr(bpy)_2]^+$ and $[(CN)_4Fe(dpp)Cr(bpy)_2]^+$ bimetallic species upon excitation of the intense MLCT band in the visible region indicated intermediate or possibly even strongly coupled metal centers (Lima *et al.* 1993).

These investigations show that supramolecular photochemistry involving covalently-linked systems can be exploited as a base for the building blocks to perform a specific function. 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. The preparation and characterization of these compounds having desired photophysical and photochemical characteristics is one of the most important areas of research in this field.

### 3. SOLAR CELLS

Chemically-based systems such as photogalvanic and photoelectrochemical cells have been developed as an alternative to solid-state silicon-based cells for the conversion of solar energy into electricity (Connolly 1981, Grätzel 1983 and references therein).

The use of coordination compounds as light absorbers, for instance $[Ru(bpy)_3]^{2+}$ was one of the first approaches to convert low-energy starting materials into high-energy products, such as $H_2O$ into $H_2$ and $O_2$, in homogeneous cells. Although ingenious, the drawback was the low efficiencies (light-to-electrical conversion efficiency $< 0.5\%$) due to the fast recombination of the photoproducts in the solution (Connolly 1981). The answer seemed to be the use of photoelectrochemical cells, in which a semiconductor electrode was the light absorber with the band bending separating the reduction and oxidation sites. However, these cells displayed low efficiency conversion of visible light into redox energy, and were limited to the band-gap of the semiconductors employed (Connolly 1981, Wrighton 1983). The use of photostable wide band-gap semiconductors would require high-energy light to create electron-hole pairs and dye sensitization was of limited utility because of sub-monolayer coverage and low absorptivities, although it presented advantages over direct band to band excitation as in conventional solar cells due to the reduction of electron-hole recombination.

The development of mesoporous membrane type film with large surface areas prepared from nanosized colloidal semiconductor dispersion caused a remarkable growth in the field (Brown Jr. *et al.* 1999). Dye sensitization of nanostructured wide band-gap semiconductors has led to an extension of their photoresponse into the visible region and to efficient conversion of solar energy into electricity in photoelectrochemical devices (O'Reagan & Grätzel 1991). Similarly to chlorophyll molecules, adsorbed dyes act as light absorbing antenna to mimic the photosynthetic process by promoting photoinduced charge separation in an organized molecular structure on the nanometric scale.

In this approach, attached dyes, rather than the semiconductor itself, are the absorbing species and upon excitation inject electrons into the semiconductor conduction band which are then collected at a conducting surface, keeping the electron-hole pair separated and generating photocurrent. As a result of this advance, the development of low-cost efficient photochemical solar cells became possible (O'Reagan & Grätzel 1991, Ball 1997).
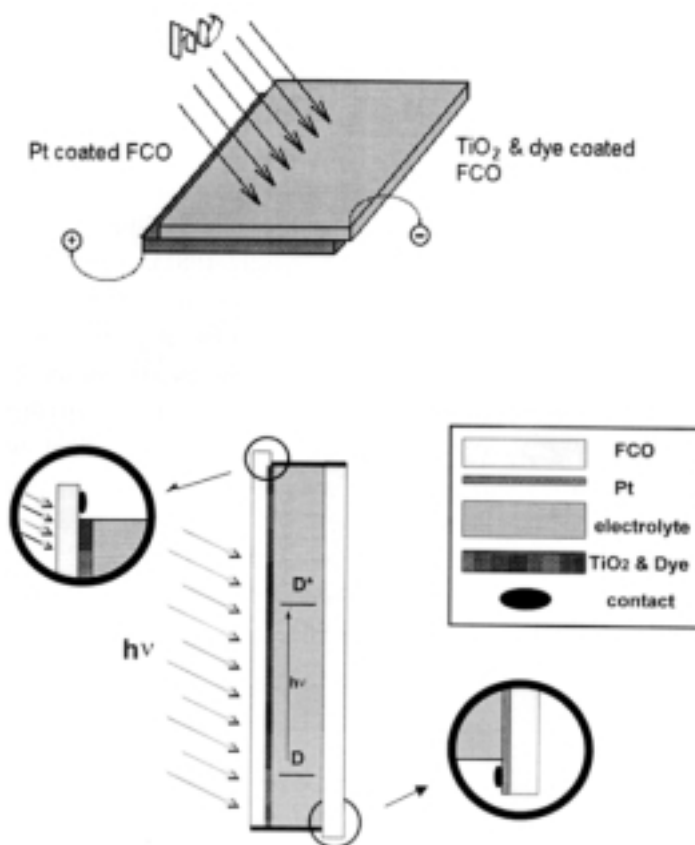
As one of these promising devices, we have

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

been developing thin-layer, transparent sandwich-type solar cells (Murakami Iha *et al.* 1998, Garcia *et al.* 1998a,b 1999). The cell, as in Figure 1, consists of a fluorine doped $SnO_2$ conducting glass, FCO, with the $n$-$TiO_2$ film sensitized by a complex, as a photoanode, and a transparent Pt film on a conducting glass, as a counter electrode, arranged in a sandwich configuration with $LiI/I_2$ solution, as the redox relay, filling the inter-electrode space.

A series of sensitizers, $cis$-[(dcbH$_2$)$_2$RuLL’] derivatives, where L and L’ = H$_2$O, X$^-$, 4-phenylpyridine, isoquinoline, 4-cyanopyridine etc., and dcbH$_2$ = 4,4’-(CO$_2$H)$_2$-2,2’-bipyridine, were specially engineered and synthesized to promote electron injection after light excitation (Garcia *et al.* 1998a,b 1999). These compounds have good sensitizing properties due to broad absorption spectra with intense MLCT bands overlapping the solar

spectrum, combined with suitable redox 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, which results in the very fast electron transfer.

The oxidized dye (D$^+$) is quickly regenerated by the redox mediator couple $I_2/I_3^-$ present in the filling electrolyte which, in turn, is regenerated at the counter-electrode, concluding the redox cycle. The reduction of $I_2$ is catalyzed by small amounts of Pt deposited on the counter electrode. 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 conduction band of semiconductors 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 theoretical maximum output voltage that can be achieved corresponds to the difference between the redox potential of the mediator couple and the Fermi level (conduction band) of the semiconductor under illumination (Kalyanasundaram & Grätzel 1993, 1998). Several parameters such as spectral and redox properties of the dye, efficiency of charge injection and structural properties of the semiconductor electrode to collect and direct electrons through the external circuit determine the photocurrent values.

Under a special program promoted by our University for development of strategic fields of research, so called CIUPE, development of solar cells and investigations of thin films have been carried out in a cooperative effort between our laboratory and other research groups, including the participation of a company. Thin-layer $TiO_2$ film deposition techniques, such as spin-coating and painting, have been compared and provided a way to control physical properties, such as film thickness and homogeneity (Garcia & Murakami Iha 1999). Also, the Industry-University collaboration has been a 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 (Garcia *et al.* 1997). A layer of $TiO_2$ film deposited on a FTO is porous with a high surface area and after heating to reduce the film resistivity acts as a sponge to take up the sensitizer.

The effectiveness for the sensitization of nanocrystalline $TiO_2$ films was determined employing several dyes prepared in our Laboratory of Inorganic Photochemistry and Solar Energy Conversion at the IQ-USP, demonstrating the feasibility of operating photoelectrochemical solar cells. Time-resolved transient absorption experiments are in progress to monitor the photochemical changes and kinetics.

These novel sensitizers provided an enhanced spectral response of $TiO_2$ to visible light and effi-

cient charge separation in the regenerative thin-layer sandwich-type solar cells described here. Quantitative evaluation of the thin-layer, transparent sandwich-type solar cell performance can be given by measurements of the incident photon-to-current conversion efficiency (IPCE) for monochromatic radiation and can be considered as the effective quantum yield for the device. The photocurrent action spectra obtained for cells with dye coated *n*-type $TiO_2$ electrodes resulted in respectable IPCE values up to 50% until 550 nm (Garcia *et al.* 1999). Therefore, these complexes present good light harvesting properties and act as efficient charge-transfer sensitizers for nanocrystalline $TiO_2$ in solar cells, converting effectively visible light into electricity. The values confirm that the dyes adsorb efficiently to nanoporous $TiO_2$ with very high surface roughness, and are comparable or higher to those obtained by other ruthenium(II) polypyridyl-based sensitizers (Hagfeldt & Grätzel 1995, Meyer 1997).

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