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Review

Design of molecular dyes for application in photoelectrochemical and electrochromic devices based on nanocrystalline metal oxide semiconductors

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Dedicated to Professor Michael Grätzel in recognition of his achievements

Contents

Abstract

This review describes the work which has mainly been developed in our laboratory on photoelectrochemical solar cells and on electrochemical devices in which suitable dyes are used for light harvesting and interfacial electron transfer processes with nanocrystalline wide band-gap semiconductors. A summary of results obtained over the last ten years in the field of supramolecular photochemistry at semiconductor interfaces is presented. A particular attention is given to the design and characterization of coordination compounds that can be integrated into semiconductor devices and to the present status of research on this new generation of photovoltaic and electrochromic devices. These studies provide a general molecular approach for the controlled conversion of light into an electrical response and thus have potential applications in solar devices, displays, sensors, electrochromic, and other molecular photonic devices.

Keywords: Heterosupramolecular; Dye-sensitized; DSSC; Electrochromic; Mixed-valence

1. Introduction

In 2000, Green [1] described the current state of solar cell technology as well as an outline of developments expected

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over coming few decades and an idea of energy policy and programs in several countries. He also stated that large centralized solar photovoltaic power stations able to provide low cost electricity on a large scale would become increasingly attractive by the year 2020. In 2001, Yamaguchi [2] reported the status and prospects of photovoltaic technology in Japan as well as an overview of Japanese government PV programs. From the status of research, development and manufacturing reported in his work, it is possible to preview power generation systems based on advancements in the science and technology of photovoltaics being widely applied and contributing to the future lives of human beings as one of the major sources of clean energy. According to both of these reviews, photovoltaics should grow to maturity in the 21st century, since this technology is on the verge of a major transition from "first generation" silicon wafer-based technologies to a "second generation" thin film product or, further, towards a new material next-generation solar cell. Dye-sensitized solar cells (DSSCs) is one of the technologies cited, which is expected to attract investment in major manufacturing facilities that will sustain the downward pressure on cell prices.

In dye-sensitized solar cells, light absorption and charge carrier transport are separated and the charge separation takes place at the interface of a wide band-gap semiconductor following photoinduced electron injection from a dye adsorbed on it. The prospect of low production cost [2] associated with other attractive features of this photoelectrochemical device, such as its transparency, when desired, as well as its ability to perform energy conversion even in the shadow, make these solar cells a choice for affordable power generation plus a possibility of having power generating windows [3–8].

Other interesting applications, arising from the possibility of adsorbing a dye to high surface wide band-gap semiconductors, are bound to new types of electrochromic devices which appear to be promising for display applications. In past years, four major classes of materials have evolved for incorporation into electrochromic devices, namely, liquid crystals, molecular dyes, metal oxide films and conductive polymers. High surface area nanocrystalline TiO_2 electrodes have been recently proposed for supporting electroactive species which can be bound to the semiconductor surface by means of suitable anchoring units. Depending on the molecular design, high contrast electrochromic devices with sharp colors can be produced. In addition, short response times are obtained since all molecules bound to the semiconductor surface are in contact with the solution containing the counter ions, ensuring for a fast charge compensation during the redox process.

Over the last ten years, our group has been working in the field of supramolecular photochemistry at semiconductor interfaces. In particular, we have been interested in the design, synthesis and characterization of supramolecular coordination compounds, i.e. inorganic coordination compounds with suitable built-in light-induced and electron transfer functions, that can be integrated into semiconductor devices. These studies provide a general molecular approach for the controlled conversion of light into an electrical response and thus have potential applications in displays, sensors, electrochromic, and other molecular photonic devices.

This review chapter describes the work which has mainly been developed in our laboratory on photoelectrochemical solar cells and on electrochemical devices in which suitable dyes are used for light harvesting and interfacial electron transfer process with nanocrystalline wide-band gap semiconductors. The main attention will be given to the developments on liquid junction devices functionalized with metal complexes, the present status of research and development prospects of this new generation of photovoltaic and electrochromic devices.

2. Dye-sensitized solar cells (DSSC)

The research described here has been motivated by the development of photovoltaic cells based on sensitized nanocrystalline TiO_2 [9]. These studies have shown that although the basic photophysical properties of the molecular components are maintained upon immobilization of a molecular component on a semiconducting surface the interaction with the surface can greatly change the rate of the individual photophysical processes. For example, when bound to TiO_2, ruthenium polypyridyl complexes that are intrinsically photolabile in solution become photostable. This change in behavior is explained by the very fast sub-picosecond charge injection from the excited state of the surface bound compound into the conduction band of the semiconductor [10–13]. In addition to this fast injection, the back electron transfer process, involving conduction band electrons and the oxidized form of the sensitizer, is several orders of magnitude slower than the forward electron transfer reaction and as a result effective charge separation is observed [14]. This ability of the TiO_2 surface to assist in a long-lived charge separation has been one of the driving forces behind the work carried out in this area [15,16].

The inherent electronic nature of semiconductor metal oxides can directly interact with molecular excited states in a manner not energetically possible with insulators. More specifically, an excited sensitizer, S^*, may transfer an electron to the semiconductor forming a charge separated pair (Eqs. (1) and (2).

$$(TiO_2)\text{–}S + h\nu \rightarrow (TiO_2)\text{–}S^* \tag{1}$$

$$(TiO_2)\text{–}S^* \rightarrow (TiO_2\text{-}e^-)\text{–}S^+ \tag{2}$$

For artificial photosynthetic applications, the importance of this charge-separation process is that it provides a molecular basis for the conversion of photons into potential energy. If the interfacial charge-separation pair has a sufficiently long lifetime, it may undergo subsequent bimolecular redox processes forming useful chemical products. For these types of applications, it is desiderable to prevent the energy-wasting charge recombination process that yield ground-state products. A fundamental goal, therefore, is to form interfacial charge-separated states that have long lifetimes.

A particular advantage of interfacial charge-separated states at semiconductor materials is that the injected electrons can be collected as an electrical response. This forms the basis for new applications that exploit both electronic and optical properties of the sensitized materials such as charge storage, displays and optical switching.

To date, one of the most promising applications has been the direct conversion of light into electricity with sensitized nanocrystalline semiconductor films. Grätzel and co-workers developed polycrystalline nanostructured TiO_2 films with high surface area [9,17,18]. As a result, light absorption by molecular dyes spread through the three-dimensional array is more efficient, passing across hundreds of adsorbed dye layers. Investigation employing such polycrystalline TiO_2 electrodes resulted in astonishing results, setting a new step in photocurrent values.

In order to take advantage of nanometer-sized semiconductor clusters, one must provide an electron pathway for conduction between the particles. This has been achieved by sintering colloidal semiconductor oxides deposited on conductive glasses. The resulting material is a porous nanostructured film which retains many of the characteristics of colloidal solutions, but is in a more manageable form and may be produced in a transparent form. Furthermore, the Fermi level within each semiconductor particle can be controlled potentiostatically, a feature which is fundamental for the functioning of the electrochromic devices described in Section 3.

The discussion that follows is divided into three parts. The first describes studies of polynuclear compounds with a surface bound unit that can accept energy from covalently linked chromophoric groups and inject electrons into the semiconductor from their excited state. The second deals with supramolecular assemblies designed to promote intramolecular and interfacial electron transfer upon light absorption. In the third part studies on mononuclear inorganic and organic sensitizers recently developed by our research groups are summarized.

2.1. Antenna sensitizers

The requisites for the supramolecular antenna sensitizers are: (i) an efficient antenna effect, vectorially translating absorbed energy towards a molecular component; and (ii) the capability of the molecular component bound to the semiconductor surface to inject electrons into the semiconductor from its excited state. The idea of using sensitizer-antenna molecular devices in the sensitization of semiconductors stems from the low efficiency observed with multilayers of sensitizers deposited on electrode surfaces. The antenna effect is expected to be of relevance for applications requiring very thin porous films or planar semiconductor surfaces. The investigation of the feasibility of such an approach was carried out with the $[NC–Ru(bpy)_2–CN–Ru(dcbH_2)_2–NC–Ru(bpy)_2–CN]^{2+}$ trinuclear compound [19]. Efficient energy funneling from the peripheral chromophores to the central $–Ru(dcbH_2)_2$ unit was demonstrated by conventional photophysical experiments and by time-resolved resonance Raman spectroscopy [20]. Experiments carried out with this branched antenna sensitizer on TiO_2, resulted in significant photocurrents. Plots of the photocurrent efficiency versus the excitation wavelength were similar to the absorption spectrum, indicating that the efficiency with which absorbed light was converted to electrons in the external circuit was constant and did not depend on whether the incident light was absorbed by the central unit or by the terminal ones. Subsequent experiments on this complex anchored to nanocrystalline TiO_2 gave a global conversion efficiency of ca. 7% under simulated sunlight conditions with turnover numbers of at least five million without decomposition [9,21]. High photocurrent efficiencies were also observed with related compounds based on the same $[Ru(dcb)_2(CN)_2]$ core and lateral Ru(phen) antenna [22].

The charge injection process from photoexcited $[NC–Ru(bpy)_2–CN–Ru(dcbH_2)_2–NC–Ru(bpy)_2–CN]^{2+}$ to the TiO_2 semiconductor was investigated by monitoring the initial decay of the time resolved luminescence [23]. From the lifetime of the fast emission component (170 ps), an injection rate of $\sim 6 \times 10^9\ s^{-1}$ was estimated. Obviously the possibility of remote interfacial electron transfer from the MLCT states localized on the lateral $–Ru(bpy)_2$ units cannot be ruled out. Remote electron injection would have, however, to compete with intramolecular energy transfer processes which fall for this class of compounds in the picosecond time domain [24].

2.2. Charge separation in heterotriads

In addition to interfacial electron transfer, heterosupramolecular systems have been designed to support intramolecular electron transfer functions.

Two simple supramolecular dyad systems, containing a chromophoric component called a sensitizer (S) and a covalently linked acceptor (A) or donor (D) component bound to a semiconductor are shown in Fig. 1.

When anchored to a semiconductor surface that can act as an electron acceptor, these dyads may be referred to as "heterotriads". The heterotriads shown are designed to perform efficiently the steps indicated by (1) and (2) in Fig. 1. The goal is to quantitatively photocreate an interfacial charge-separated pair with an electron in the semiconductor and a "hole" localized on a molecular unit away from the semiconductor surface. The rate constant for electron–hole recombination may be inhibited relative to that observed with a simple molecular sensitizer by achieving long-lived charge separation. In the heterotriad shown in Fig. 1a, interfacial excited state electron transfer is expected to be

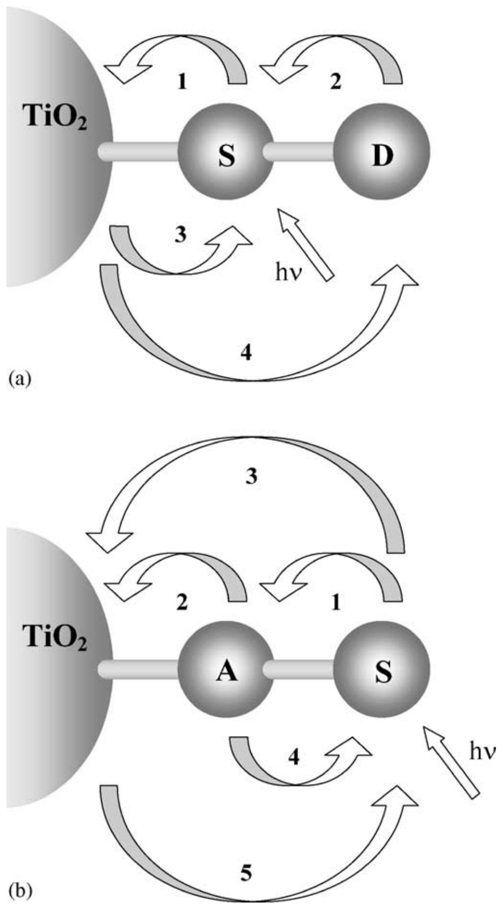


Fig. 1. Stepwise photoinduced electron transfer processes in TiO_2–sensitizer–donor (a) and TiO_2–acceptor–sensitizer (b) heterotriads.

quantitative and ultrafast, so the key to the overall efficiency is likely to be determined by the kinetic competition between the secondary electron transfer (step 2) and the primary charge recombination process (step 3). In the second example, on the other hand, the relative kinetics for intramolecular and interfacial electron transfer is expected to control the overall efficiency (steps 4 and 2, respectively).

The first dyad synthesized to perform the function shown in Fig. 1a is $[Ru(dcbH_2)_2(4\text{-}CH_3,4'\text{-}CH_2\text{-}PTZ\text{-}2,2'\text{-bipyridine})]^{2+}$, where PTZ is the electron donor phenothiazine [15,16]. The resulting heterotriad with TiO_2 is shown schematically in Fig. 2.

Irradiation of the dyad with visible light results in the creation of a MLCT excited state, which is quenched by electron transfer from the PTZ group in fluid solution. The reductive excited state quenching is moderately exergonic (<0.25 eV) and has a rate constant of $2.5 \times 10^8\ s^{-1}$ in methanol, as estimated from the lifetime of the residual *Ru(II) emission. The corresponding charge recombination step is faster than the forward one so that no appreciable transient accumulation of the electron transfer product is observed.

When the dyad system is attached to TiO_2, MLCT excitation results in a new charge separated state with an electron in TiO_2 and an oxidized PTZ group, abbreviated as $TiO_2(e^-)$–Ru–PTZ^+. Recombination of the electron in TiO_2 with the oxidized PTZ to yield the ground state occurs with a rate constant of $3.6 \times 10^3\ s^{-1}$. Excitation of a model compound that does not contain the PTZ donor, $[Ru(dmb)(dcbH_2)_2]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine), under identical conditions gave rise to the immediate formation of a charge separated state, $TiO_2(e^-)$–Ru(III), whose recombination kinetics can be analyzed by a distribution model, with an average rate constant of $3.9 \times 10^6\ s^{-1}$. Therefore, translating the “hole” from the Ru center to the pendant PTZ moiety inhibits recombination rates by about three orders of magnitude [16].

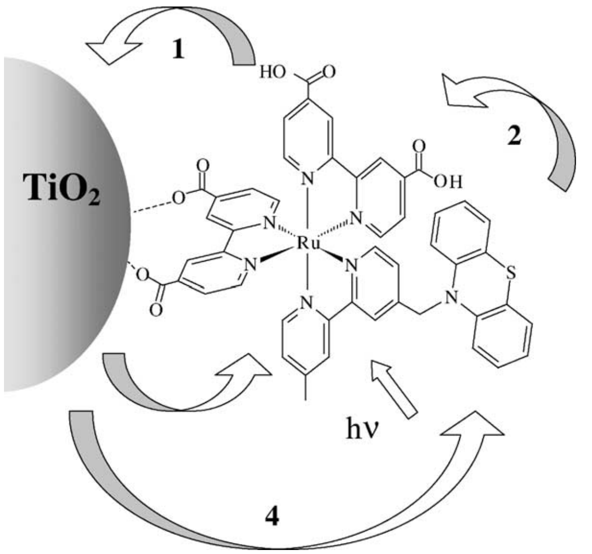


Fig. 2. Interfacial and intramolecular electron transfer processes in $[Ru(dcbH_2)_2(4\text{-}CH_3,4'\text{-}CH_2\text{-}PTZ,\text{-}2,2'\text{-bipyridine})]^{2+}$ anchored on TiO_2.

Grätzel and co-workers have reported an interesting study of heterotriads of this type and have emphasized their potential application in photochromic devices [25]. The authors found long-lived charge-separation, like that described for the TiO_2–Ru(II)–PTZ system, in some cases, but not in others.

The binuclear compound $[Ru(dcbH_2)_2(Cl)\text{–}BPA\text{–}Os(bpy)_2Cl]^{2+}$, where BPA is 1,2-bis(4-pyridyl)ethane and bpy is 2,2′-bipyridine, shown in Fig. 3 was employed to study processes similar to those shown in Fig. 1a [26].

A key difference between this binuclear compound and the Ru(II)–PTZ dyads is that the Os(II) donor is a chromophore that absorbs visible light. The Ru–Os binuclear compound binds to TiO_2 thin films with about 1/2 the surface coverage of a model compound, $[Ru(dcbH_2)_2(Cl)(py)]^+$, where py is pyridine. This suggests that the binuclear complex lies on the nanocrystalline TiO_2 surface in a more or less extended conformation.

Transient absorbance difference spectra measured following 532 nm laser excitation, where both Ru(II) and Os(II) chromophores absorb, revealed a typical bleaching of the spin-forbidden MLCT transition localized on the Os(II) group. Spectral and kinetic analysis of the transient signals

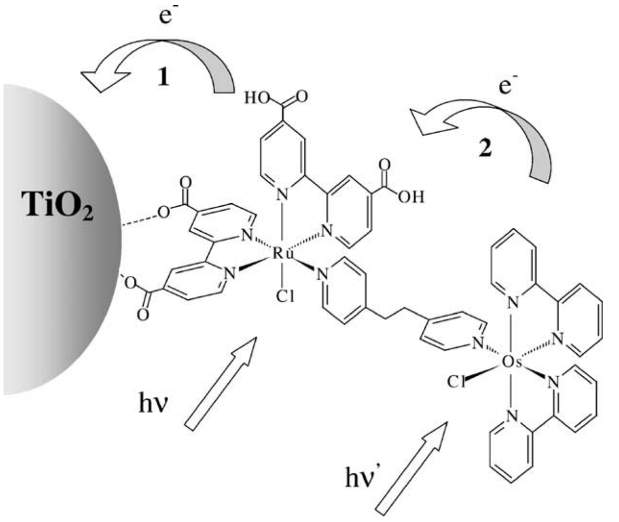


Fig. 3. Interfacial and intramolecular electron transfer processes in $[Ru(dcbH_2)_2(Cl)\text{-}BPA\text{-}Os(bpy)_2Cl]^{2+}$ anchored on TiO_2.

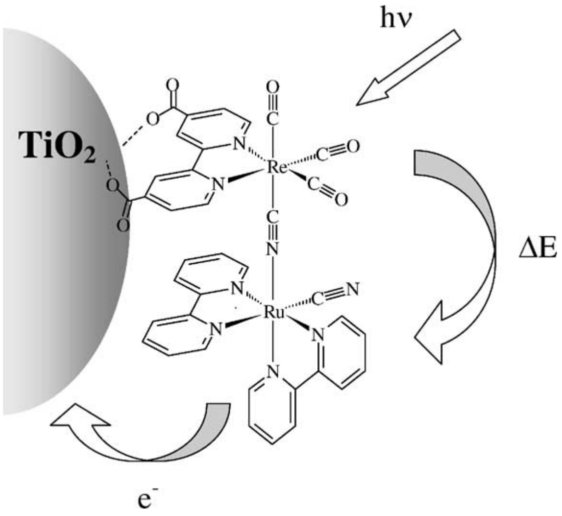


Fig. 5. Intramolecular energy transfer and remote charge injection in the binuclear complex $[Re(dcbH_2)(CO)_3(CN)Ru(bpy)_2(CN)]^+$ anchored on TiO_2.

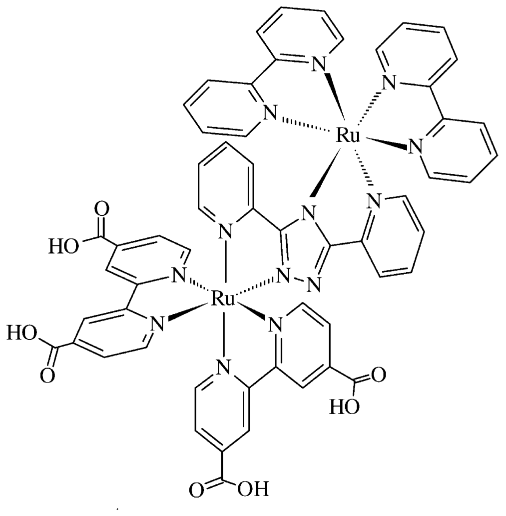
were consistent with the formation of the charge separated state $TiO_2(e^-)$–Ru(II)–Os(III). This state can be formed through charge injection from the excited Ru chromophore followed by intramolecular Os(II) → Ru(III) electron transfer, or via remote electron transfer from the MLCT excited state localized on the $Os^{II}(bpy)_2$ unit. Comparative actinometry revealed that the desired intramolecular electron transfer processes occurs efficiently at 532 or 417 nm light excitation. The lifetime of the $TiO_2(e^-)$–Ru(II)–Os(III) was not significantly different than that of model compounds, presumably because of the semiconductor-dyad orientation.

Two additional binuclear ruthenium and osmium containing polypyridyl complexes (**1**, **2**) (Fig. 4), based on the bridging ligand 3,5-bis-(pyridin-2-yl)-1,2,4-triazole (Hbpt) and immobilized on nanocrystalline TiO_2 surfaces, have been studied [27].

An important difference between the bpt-based compounds and that shown in Fig. 3 is that the bpt bridge is very rigid and do not allow rotation around the linker. Upon immobilization of these binuclear compounds onto a solid substrate no osmium-based emission was observed for the TiO_2–Ru–Os triad studied. Only one final product, $TiO_2(e^-)$–Ru(II)–Os(III) is obtained upon irradiation of TiO_2–Ru–Os.

A supramolecular approach with controlled orientation of the component units on the semiconductor surfaces was reported (Fig. 5).

The binuclear compound is based on a *fac*-$[Re^I(dcbH_2)(CO)_3]$ surface anchoring unit and a $–Ru(II)(bpy)_2$ chro-



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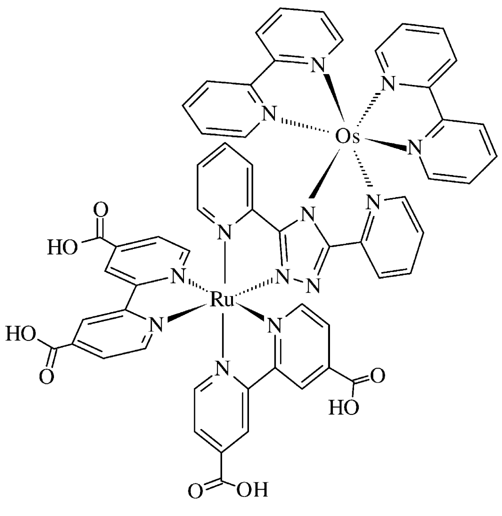

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Fig. 4. Ru–Ru and Ru–Os binuclear complexes containing the bridging ligand 3,5-bis-(pyridin-2-yl)-1,2,4-triazole.

mophore linked through an ambidentate cyanide ligand [28]. Due to the facial geometry of the surface-bound Re-group, the –Ru(bpy)$_2$ unit is forced to be proximate to the semiconductor surface.

Visible light excitation of TiO_2 photoanodes, loaded with [Re(dcbH$_2$)(CO)$_3$(CN)Ru(bpy)$_2$(CN)]$^+$ or its linkage isomer, in a regenerative solar cell resulted in efficient light-to-electrical energy conversion. Plots of the photocurrent efficiency versus excitation wavelength demonstrated that the Ru–polypyridine group absorbs the visible light and converts it efficiently into electrical current. The transient absorption difference spectra for these sensitizers on TiO_2 showed a broad bleach in the region from 400 to 600 nm, expected for the TiO_2(e$^-$)–Re(I)–Ru(III) state. The prompt formation of this state indicates that either remote electron injection into TiO_2, or intraligand (bpy$^-$ → dcb) electron hopping from Ru(III)(bpy$^-$) to Re(I)(dcb) occurs within the laser pulse ($k > 5 \times 10^8$). This demonstrates a rapid and efficient injection process from a chromophoric group, which is not directly coupled to the semiconductor surface. In fact, the solar energy conversion efficiencies obtained with TiO_2–Re(I)–Ru(II) in regenerative photoelectrochemical cells were the same to those measured for *cis*-[Ru(dcb)$_2$(CN)$_2$]. The study showed that covalent linkage of the sensitizer to the semiconductor surface through chromophoric ligands is not strictly necessary for achieving efficient interfacial electron transfer.

Examples of heterotriads shown in Fig. 1b were also considered. Two Ru(II)–Rh(III) polypyridine dyads, containing carboxylic acids groups at the Rh(III) unit, [Rh(dcb)$_2$–(BL)–Ru(dmp)$_2$] and [Rh(dcb)$_2$–(BL)–Ru(bpy)$_2$], where BL is 1,2-bis[4-(4′-methyl-2,2′-bipyridyl)]ethane) and dmp is 4,7-dimethyl-1,10-phenanthroline, were prepared and studied [29]. In both dyads, the Ru unit was designed to play the role of the chromophoric donor and the Rh unit that of the acceptor.

The Rh–Ru dyads anchored to TiO_2 gave rise to maximum IPCE values of ∼40–50% with iodide electron donors in acetonitrile. The photoinduced electron transfer in the heterosupramolecular systems TiO_2–Rh–Ru(dmb)$_2$ and TiO_2–Rh–Ru(bpy)$_2$ can be summarized as follows. Upon light excitation of the Ru(II) unit, 1/3 of the surface bound dyads undergo direct electron injection from the excited state of the Ru chromophore, TiO_2–Rh(III)-Ru(II)* → TiO_2(e$^-$)–Rh(III)–Ru(III), with a rate constant $>10^8\,s^{-1}$. The dyads that undergo this remote injection process probably have different surface orientations or accidental contacts in small cavities within the nanocrystalline TiO_2 film. The remaining dyads display stepwise charge injection processes:

$$\mathrm{TiO_2{-}Rh(III){-}Ru(II)^* \rightarrow TiO_2{-}Rh(II){-}Ru(III)}$$
$$\mathrm{\rightarrow TiO_2(e^-){-}Rh(III){-}Ru(III)}$$

The first process has rates and efficiencies comparable to those for the free dyads in fluid solution. The second step is 40% efficient, because of primary charge recombination between the reduced Rh unit and the oxidized Ru, TiO_2–Rh(II)–Ru(III) → TiO_2–Rh(III)–Ru(II). When the recombination of the injected electrons and oxidized Ru(III) sites was studied, a remarkable slowing down was observed relative to a simple mononuclear sensitizer, TiO_2–Ru(dcb)$_2$dmb^{2+}. The most important aspect of these studies was to demonstrate a ‘stepwise’ interfacial electron transfer process, like that shown in Fig. 1b.

2.3. Mononuclear metal complexes

Many different compounds have been investigated for semiconductor sensitization, such as chlorophyll derivatives [30–34], porphyrins [30,35,36], phthalocyanines [37–44], platinum complexes [45–47], coumarin 343 [48,49], carboxylated derivatives of anthracene [50,51], polymeric films [52], coupled semiconductors with lower energy band-gaps [40,53–57], among others [4,58–67]. An interesting new class of complexes, having the hydroxamic acid, dobH$_2$ = 4,4′-(CONHOH)$_2$-2,2′-bipyridine, as an anchoring group to be attached on the mesoporous nanostructured surface of the semiconductor oxide, has been reported recently [68]. Fruit extracts have also been used as natural sensitizers in photoelectrochemical solar cells [69–76]. However, the best solar to electric power conversion efficiency has been achieved by ruthenium(II) polypyridyl complexes with carboxylated ligands, which are often employed as TiO_2 sensitizers in such cells. These species present intense visible metal-to-ligand charge transfer bands. The carboxylic groups enable the necessary electronic coupling between the sensitizer and TiO_2 surface, although a direct covalent attachment between them is not a requirement for efficient electron transfer [28,77]. Following visible light excitation, dye species are electronically excited resulting in an efficient electron transfer into the semiconductor [77,78–84], among this family of compounds, outstanding results have been achieved with thiocyanate derivatives [78,84,85–89].

Photoelectrochemical solar cells based on these dyes have shown solar-to-electricity conversion efficiencies that have been, in part, rationalized on the basis of their redox, spectroscopic and excited state properties. It has been shown in particular that a rational design, which takes into account the properties of the different molecular components, allows to increase the spectral sensitivity and the light harvesting efficiency of the dye. In addition, when charge injection processes to the semiconductor and electron transfer processes involving the oxidized sensitizer can effectively compete with ground state relaxation and chemical reactivity, dye molecules with short-lived excited states or showing photochemical reactivity or a chemical process coupled with a redox one, can be successfully used in the dye-sensitized solar cells [90].

Polypyridine complexes of d^6 metal ions, such as Ru(II), Os(II), and Re(I) show intense MLCT bands in the visible region, which correspond to states where one electronic charge has been transferred from the metal center to an antibonding ligand orbital [91]. These states are of potential interest for promoting charge injection processes to the d band of wide band-gap semiconductors such as TiO_2, SnO_2 and ZnO.

The energies of the MLCT states can be modified systematically by changing the substituents at the chromophoric ligands (electron-withdrawing substituents tend to decrease the π^* orbital energy of the polypyridine ligand, while the opposite effect is observed with electron donating substituents) as well as by changing the ancillary ligands. For bis-chelate complexes of the type *cis*-$[Ru^{II}(bpy)_2(L)_2]$, as well as for the analogous Os^{II} complexes, MLCT absorption bands shift to higher energy changing L from π donating ligands to the π accepting ones. The main effect, in this case, is a direct perturbation of the electronic density at the metal center.

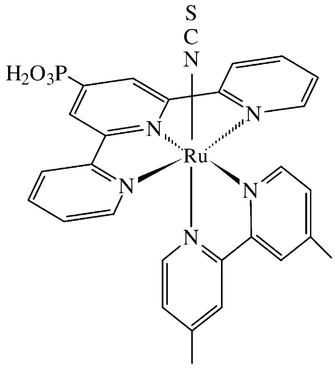
The proper selection of the ancillary ligands L and L′ in *cis*-$[(dcbH_2)_2RuLL']$ provides the suitable control of the energetic and redox properties of the species. Different compounds with appropriate characteristics can be molecularly engineered enabling the design of efficient sensitizers of TiO_2 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 spectral response to the visible light [85,92–97]. L and L′ can also be occupied by other chromophoric oligomers, resulting in antenna systems with enhanced light harvesting properties as the polynuclear sensitizers discussed in Section 2.1.

In the series of complexes *cis*-$[Ru(dcbH_2)_2(L)_2]$ ($L = Cl^-$, Br^-, I^-, NCS^- and CN^-), MLCT absorption and emission maxima shift towards longer wavelength by decreasing the ligand field strength of the ancillary ligands, with $E_{1/2}$ for $Ru^{(III)/(II)}$ decreasing in the expected order, CN > NCS > halides. These complexes are generally found to act as efficient sensitizers for nanocrystalline TiO_2 [78]. The NCS complex, commonly known as N3, shows a photoaction spectrum dominating almost the entire visible region, with IPCE of 90% between 500 and 600 nm. Short circuit photocurrents exceeding 16 mA/cm^2 in simulated AM 1.5 sunlight and open circuit photovoltages around 0.7 V, were obtained by using iodide as redox mediator. This is in part expected for the high reducing ability of its ^{3}MLCT state (ca. −1 eV versus SCE) and its positive ground-state oxidation potential (+0.86 V versus SCE), and contrasts with the lower IPCE observed for other sensitizers having comparable ground and excited state properties. This fact suggests that a peculiar molecular level property of the *cis*-$[Ru(dcbH_2)_2(NCS)_2]$ complex affects one of the key processes responsible of the functioning of the solar cell device. This view is consistent with the results of photoelectron spectroscopy and INDO/S calculations indicating that the dπ Ru orbitals interact strongly with the π^* orbitals of NCS, resulting in MO of mixed nature [90,98,99]. In particular, calculations show that the sulphur 3p orbitals give a considerable contribution to the outermost orbitals of the complex. Hole delocalization across the NCS ligands can, thus, be responsible for an increased electronic matrix element for the electron transfer reaction involving $TiO_2/Ru^{III}NCS$ and I^-, leading to an increase of the electron transfer rate constant [100].

Several attempts have been made to find suitable ancillary ligands for complexes of the type *cis*-$[Ru(dcbH_2)_2LL_2]$ in order to have better mononuclear ruthenium sensitizers [95–97,101]. Violet dyes of general formula $[Ru(dcbH)(dcbH_2)(L)]$, where L is diethyldithiocarbamate, dibenzyldithiocarbamate or pyrrolidinedithiocarbamate and dcbH is the monoprotonated 4,4′-dicarboxy-2,2′-bipyridine, were synthesized, characterized and tested on TiO_2-based photoelectrochemical regenerative cells using $[Ru(dcbH_2)_2(NCS)_2]$ as a reference compound [102]. These dyes show intense dπ–π^* MLCT transitions in the visible with the lower energy band slightly red shifted with respect to the thiocyanate complex. On the contrary to what has been observed for $[Ru(dcbH_2)_2(NCS)_2]$, cyclic voltammograms of the dithiocarbamate complexes give reversible waves both in the protonated and anionic forms. Photoelectrochemical measurements of regenerative cells with LiI 0.5 M/I_2 0.05 M in acetonitrile give IPCE values for the violet dyes consistently lower than the reference complex, being, on the average, around 50%. The slower reduction rate of the oxidized dithiocarbamate species by I^- is considered responsible for the observed trend on the IPCE values.

The outstanding photoelectrochemical performances given by N3 have been surpassed by an analogous species based on the terpyridine ligand [79]. TiO_2 electrodes covered with the complex $[Ru(H_3tcterpy)(NCS)_3]^-$, where H_3tcterpy is 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine, displayed very efficient panchromatic sensitization covering the whole visible spectrum and extending the spectral response to the near IR region with maximum IPCE values comparable to those obtained with the N3 complex. Good performances were also observed for ruthenium complexes coordinated with unsymmetrical terpyridinyl ligands carrying vicinal carboxylic acids [103]. The photoaction spectra on TiO_2 of the two sensitizers, [4′-*p*-tolyl-2,2′-6′,2″-terpyridine][2,2′-6′,2″-terpyridine-3′,4′-dicarboxylic acid])ruthenium(II) and bis-[2,2′-6′,2″-terpyridine-3′, 4′-dicarboxylic acid]ruthenium(II) show photoconversion efficiencies, corrected for glass absorption, exceeding 80%.

An increased stability has also been observed for ruthenium dyes based on phosphonated bipyridine with respect to analogous species containing the $dcbH_2$ ligand [104]. Phosphonic acid is a potentially valuable anchoring group because it forms particularly stable covalent bonds with many transition metals and particularly with zirconium(IV), titanium(IV) and tin(IV) [105,106]. As such, molecules functionnalized by phosphonic acids can also be very useful for other applications such as electrochromic devices [107,108], functional electrodes for molecular sensing [109–111], electrocatalysis [112,113] and molecular electronics [114–118],



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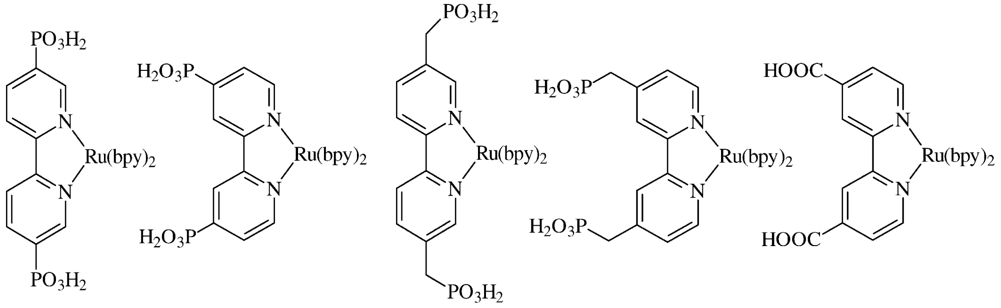


4 **5** **6** **7** **8**

Fig. 6. Ru complexes containing the phosphonic acid substituted ligand. Complex (**8**) is assumed as a reference.

where the stable immobilization of a molecular species on a surface plays a crucial role.

The first sensitizer bearing phosphonic acid anchoring group was a ruthenium terpyridine complex (**3**) (Fig. 6) reported by Grätzel and co-workers in 1995 [119,120]. We focused our attention on ruthenium complexes containing phosphonated substituted bipyridine [104]. Initially, a series of ruthenium tris-bipyridine complexes consisting of a bipyridine functionalized by two phosphonic acid groups and a $Ru(bpy)_2$ core (bpy = 2,2′-bipyridine) were prepared and investigated (Fig. 6).

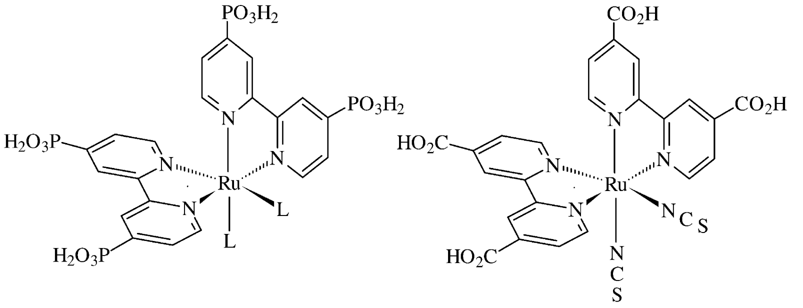
The four complexes **4–7** were prepared in order to probe the influence of two parameters on their photoelectrochemical properties. The influence of the position of the phosphonic acid group (4,4′ versus 5,5′), and the presence of an intervening methylene spacer between the bpy ligand and the phosphonic acid group ($–CH_2PO_3H_2$ versus $–PO_3H_2$) were investigated. The photoelectrochemical performances on transparent TiO_2 films showed that when the phosphonate groups are directly attached to bipyridine ring, the change in position from 4,4′ to 5,5′ cause a decrease of the IPCE. This fact is in line with what observed with the analogous complexes derivatized by carboxylic acid groups [85,121]. The introduction of a methylene spacer also lowers the IPCE most probably due to a reduced electronic coupling between excited dye and the d band of the semiconductor. Transient absorbance measurements, undertaken to quantify the injection yield of complexes **4–7**, were supportive of this interpretation.

The series of complexes of general formula RuL_2X_2 (L = 4,4′-bis-phosphonic acid-2,2′-bipyridine and X = *Cl*, CN, NCS) were also prepared and characterized (**9–11**) (Fig. 7) [122].

This study was motivated by the fact that the complex $[Ru(4,4'dcbH_2)_2(NCS)_2]$ (**12**) (Fig. 7) is known to be an efficient sensitizer and by the fact that phosphonic acid substituents are expected to increase the stability of the linkage with TiO_2.

The electronic spectra of these new complexes are shown in Fig. 8.

The usual π–π^* transition located around 300 nm and the two metal to ligand charge transfer transitions (MLCT) at ca. 360 and 520 nm can be observed. One finding of this study was that the red sensitivity of the $[Ru(4,4'dcbH_2)_2(NCS)_2]$ complex is due to ligand-to-ligand (π^* NCS → π^* bpy) transitions. The absorption spectrum of the phosphonated complex is however blue shifted with respect to the carboxylated species. This fact was rationalized by molecular orbital calculations made by density functional theory (DFT). Density functional molecular orbitals calculations made on these complexes indicated that phosphonic acid substituents destabilize the LUMO orbitals with respect to carboxylic acids. This difference is due to the fact that the sp^3 hybridization of the phosphorous atom in $–PO_3H_2$ does not



9: L = Cl⁻
10: L = CN⁻
11: L = NCS⁻

12

Fig. 7. Complexes of general formula [Ru(4,4′(PO_3H_2)$_2$-bpy)(L)$_2$] along with the analogous reference compound with the carboxylated bpy ligand.

favor the interactions with the bpy core as it happens with the sp^2 hybridized carbon of –CO_2H in which co-planarity with the carbonyl and the pyridine ring can be reached.

Photoelectrochemical performances of the new complexes were evaluated in TiO_2 sandwich cell using I^-/I_3^- as electron mediator in acetonitrile. Incident photon to current efficiency plotted as a function of the excitation wavelength are shown in Fig. 9.

The best sensitizer within the series is the [Ru(4,4′-(PO_3H_2)$_2$-bpy)$_2$(NCS)$_2$] complex which contains the NCS^- ligand. However, this complex displays a ca. 30% lower overall efficiency than that of the carboxylated analogue due to the blue shifted absorption spectrum, which cause a decrease of the light harvesting efficiency above 650 nm.

Impressive results have also been reported by the Lewis's group on Os(II) complexes based on the $dcbH_2$ chromophoric ligand [14,123,124]. Replacement of the ruthenium metal center with osmium extends the light absorption and spectral response of nanocrystalline TiO_2 photoelectrodes to higher wavelength values without reducing photoelectrochemical energy conversion performances. These studies points to the possibility of further improving the performances of sensitized solar cells through the use of charge transfer sensitizers where metal centers with high

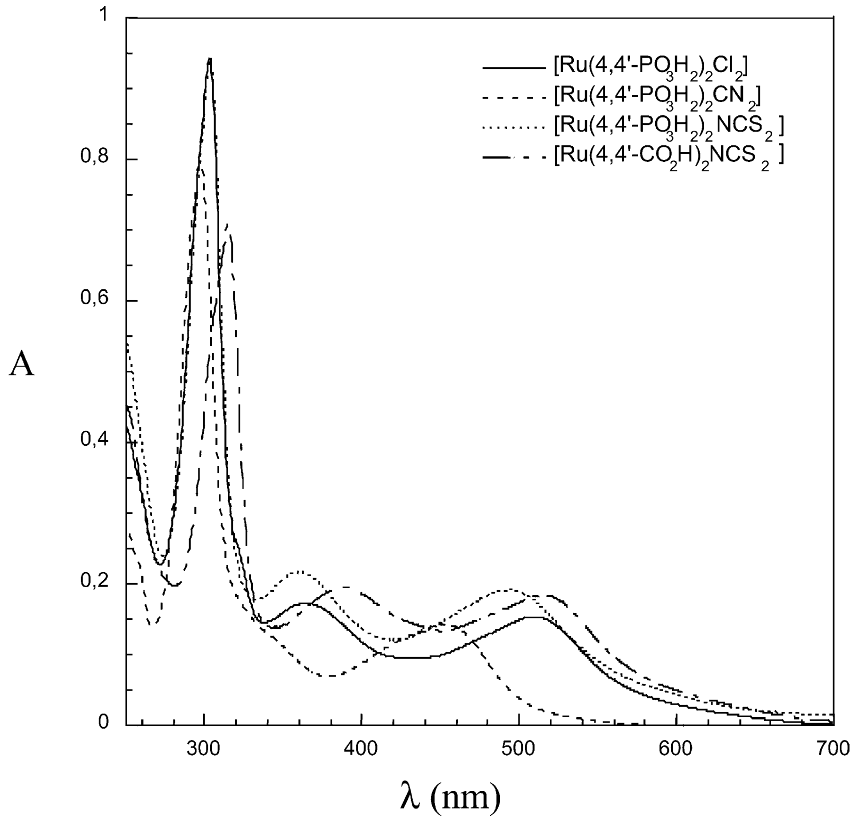


Fig. 8. UV-Vis absorption spectra of the complexes (**9**–**12**) recorded in sulfuric acid solution (0.1 N).

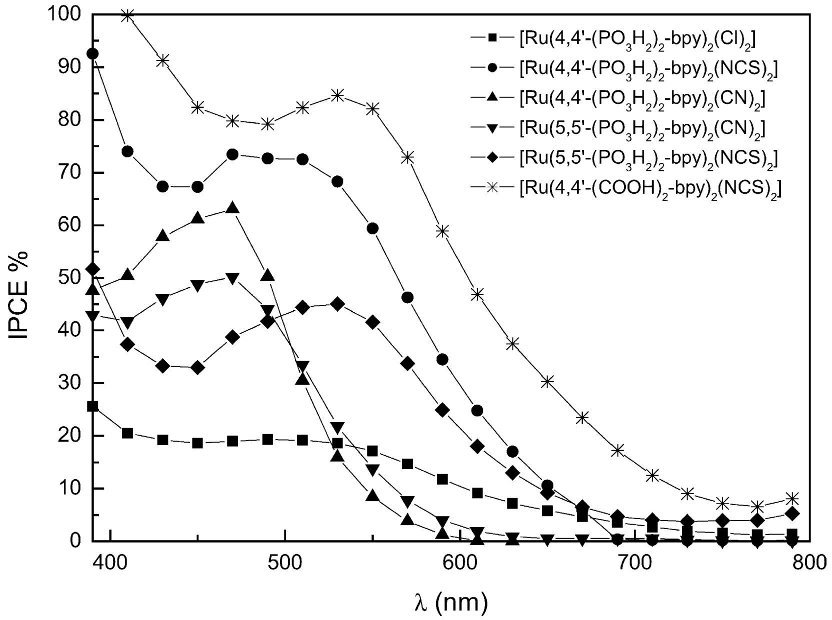


Fig. 9. Photoaction spectra of the complexes (**9**–**11**) recorded in a TiO_2 sandwich cell in comparison with (**12**).

spin–orbit coupling constants are present. 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.

Based on these principles the complex ion $[Os^{II}(H_3tcterpy)(CN)_3]^-$ (H_3tcterpy = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine) was recently prepared by an easy methodology and characterized. The UV-Vis absorption in CH_3OH shows a series of MLCT bands with distinct maxima spanning the whole visible spectrum and a remarkably intense band ($\varepsilon \approx 1500\,M^{-1}\,cm^{-1}$) at 811 nm associated to a spin-forbidden singlet–triplet MLCT transition allowed by spin–orbit coupling (Fig. 10).

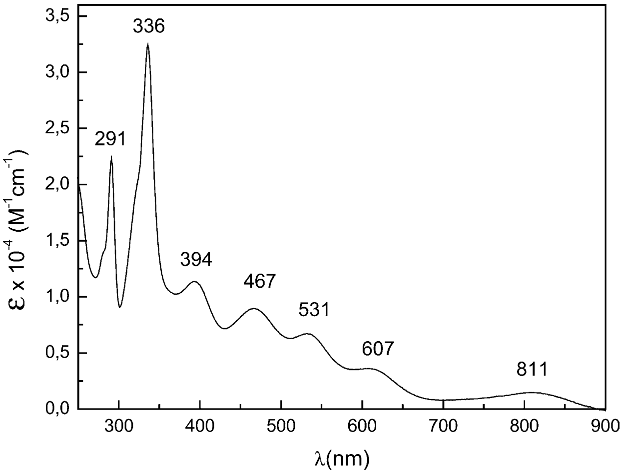


Fig. 10. UV-Vis spectrum of $[Os^{II}(H_3tcterpy)(CN)_3]^-$ in CH_3OH.

Cyclic voltammetry of the complex in CH_3OH showed a reversible $Os^{II} \rightarrow Os^{III}$ oxidation process with $E_{1/2} = 663\,mV$. Controlled shifting of MLCT absorption and Os oxidation potential was accomplished by simply changing the degree of protonation of the carboxylic groups. The behavior of the complex as sensitizer in DSSCs was tested giving satisfactory IPCE values and showing contribution to the photoaction spectrum from the singlet–triplet MLCT transition. The photochemical stability was checked in CH_3OH and CH_3CN and found to be superior to that of $[Ru^{II}(Htcterpy)(NCS)_3]^{3-}$. It can be concluded that the $[Os^{II}(H_3tcterpy)(CN)_3]^-$ complex can be chosen as a model for the development of new osmium-based sensitizers where spin forbidden transitions could play a fundamental role in extending the spectral response in the NIR region for photoelectrochemical applications.

2.4. Porphyrin sensitizers

With respect to metal polypyridine complexes, organic dyes have been less investigated for sensitization of wide band gap semiconductors. Apart from the coumarin derivative recently published by Arakawa and co-workers [125,126], organic dyes such as porphyrins [35,36,127–133], phthalocyanines [37–39,41–43,134,135], perylene bis-amides [64,136,137], xanthenes [65,138,139] and polyenes [140] show low photon to electron conversion efficiencies. The understanding of the factors that determine these low performances could lead to the development of new efficient dyes, cheaper to manufacture with respect to transition metal complexes. Towards this end, we have synthesized a series of porphyrin derivatives and studied their spectro-electrochemical properties [141]. The porphyrin

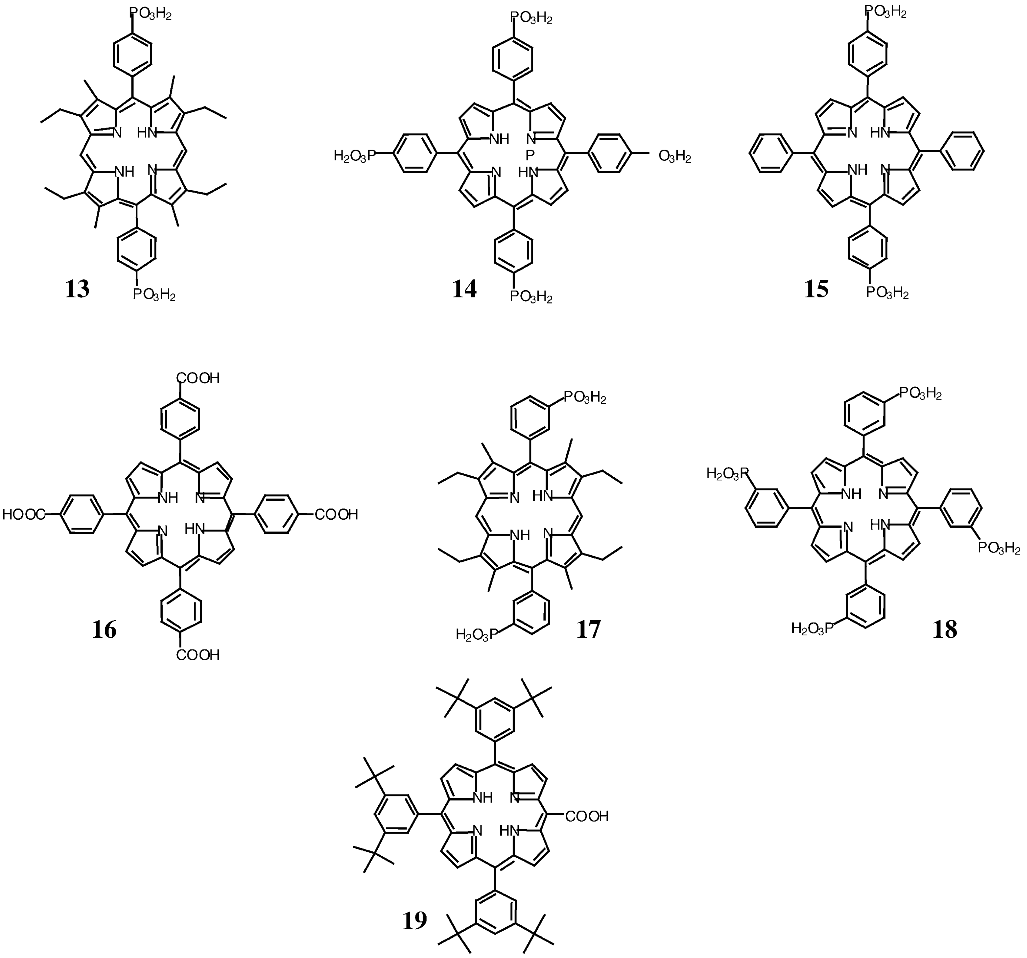


Fig. 11. Functionalized porphyrin sensitizers.

dyes are substituted by phosphonic acid or carboxylic acid groups that are attached on different positions (**13–19**) (Fig. 11).

The structural variations of the porphyrin were chosen in order to probe the influence of the driving force for electron injection (octaalkyl porphyrin versus tetraarylporphyrin) and of the electronic coupling between the porphyrin and TiO_2 (anchoring groups attached on different positions on the porphyrin unit).

The photoaction spectra of the porphyrin, measured in regenerative TiO_2 sandwich cells show in general very low performance Fig. 12.

Comparison of the fluorescence spectra of the porphyrin on TiO_2 and ZrO_2 electrodes indicate that the singlet porphyrin excited state was far from being completely quenched. The intense fluorescence signal of all porphyrins on TiO_2 was consistent with a low charge injection yield. This was either attributed to the endoergonicity of the electron injection process as well as to weak electronic coupling between the dye and TiO_2. Porphyrins in which the anchoring groups are positioned on the meso aryl substituent of the porphyrin, are weakly coupled to the semiconductor phase, because meso aryl substituents are known to orient perpendicularly to the porphyrin macrocycle, suppressing thus the electronic conjugation [142]. The third factor which was considered to contribute to the low performances observed was the presence of excited state self-quenching due to dye aggregation.

3. Electrochromic devices

Classically speaking, electrochromic materials are chemical species whose color can be interchanged electrochemically due to the generation of a different electronic absorption band in the visible region [143]. In more general sense, the terminology does not only include visible color changes, but also electrochemically induced changes in the near infrared, thermal infrared and microwave regions. This broader definition is reasonable considering the more recent progress toward a multispectral energy modulation of radiation by absorbance and reflection.

The appeal of electrochromic materials is at least twofold. From a fundamental point of view, the field encompasses a wide range of systems and presents a challenge to the chemists' understanding of their redox operation

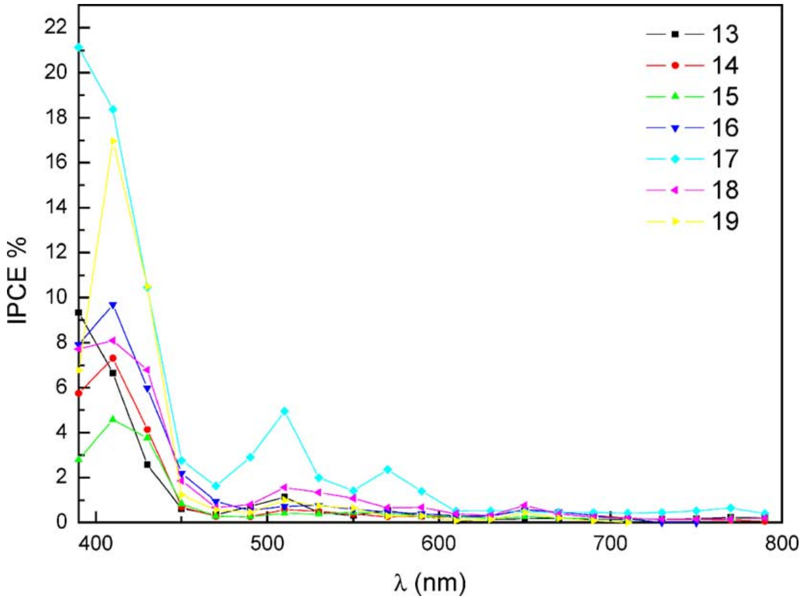


Fig. 12. Photoaction spectra of porphyrin sensitizers (**13**–**19**) in sandwich type cells.

and the accompanying physicochemical structure changes [143,144]. From a commercial standpoint, even though only very few devices have been successfully brought to the market, electrochromic devices hold much promise and several areas of interest have been proposed and are currently under investigation [145].

Among the electrochromic products currently under development are switchable windows and mirrors, electromagnetic shutters, slow display technologies, earth-tone chameleon materials, protective eyewear, controllable light-reflective or light-transmissive devices for optical information and storage, controllable aircraft canopies, and glare reduction systems for offices [145]. Car rear-view mirrors have already achieved commercial success. They act as safety devices by preventing mirror reflected glare which causes an ‘after image’ to stay on the eye’s retina. Prototypes of window glass that is almost infinitely variable in its degree of tinting have been demonstrated and are very close to commercialization. Those smart windows offer control of thermal conditions within a building for energy conservation at low projected cost [146].

From these desired applications, several key elements and properties of the electrochromic materials can be derived, their respective importance depending on their use. Among them are a high contrast ratio (sharp colors), high coloration efficiency (adsorbance change/charge injected per unit area), long cycle life, low response time, and good write–erase efficiency (percentage of originally formed coloration that may be subsequently electrobleached) [3].

Not surprisingly, the research field of electrochromic compounds is very broad and includes inorganic, organic and polymeric, as well as several hybrid materials [143,147,148]. We describe here our work on electrochromic devices based on nanocrystalline TiO_2 and SnO_2 transparent films functionalized with transition metal complexes.

Previous studies have shown that substituted viologens containing $–PO_3H_2$ or –COOH functions were suitable species for application in electrochromic devices that try to combine the advantages of metal oxide films with those based on redox chromophores [149–152]. A monolayer of diphosphonoethyl substituted viologen is hereby chemisorbed onto a nanostructured TiO_2 film on an ITO electrode. Since the redox potential of the viologen lies above the conduction band edge of TiO_2 at the liquid–solid interface, electrons can be transferred reversibly from the conduction band to the molecule and the semi-conductor becomes conducting for the adsorbed species Upon application of a negative potential of about -1 V, the viologen molecules are reduced and the electrode turns deeply blue at a rapid rate [153]. The high coloration can be explained by the surface roughness of the nanostructured film that effectively stacks the redox chromophores, leading to 100–1000 fold amplification compared to a flat monolayer [152]. Due to the direct linking of the redox chromophore to the electrode surface, the rate of the reduction is not limited to the diffusion rate of solution phase chromophores. Furthermore, the accumulated negative charge on the electrode is easily compensated by ions adsorbed at the surface of the nanostructured film, making the color switch independent of the slow ion intercalation characteristic of pure metal oxide systems. The system is self-erasing due to the reaction of a redox promoter, such as Ferrocene, with the reduced viologen. Modification of the substituents on the viologen has lead to the accessibility of other colors, such as green and pink in similar systems [154].

In order to obtain a chromophoric window with an extended memory, the reaction of the redox promoter with the viologen chromophore must be avoided [153]. This can be achieved by substituting the redox promoter with a second electrochromophoric compound which has an appropriate oxidation potential and which is deposited on the surface of the anode. For example, a modified phenothiazine has been chemisorbed on a Sb:SnO_2 electrode in combination with the described viologen TiO_2 electrode. Upon applying an external potential biasing the TiO_2 electrode 1.2 V negative of the SnO_2:Sb electrode, the viologen is reduced, while the phenothiazine is oxidized to their respective radical cations [153]. The net result is a fast color change from transparent to blue–red. The steady state current is low assuring the preservation of the color in the absence of the external potential. A high stability both under electrochromic cycling and under prolonged coloration was achieved [152,153].

3.1. Mixed-valence complexes

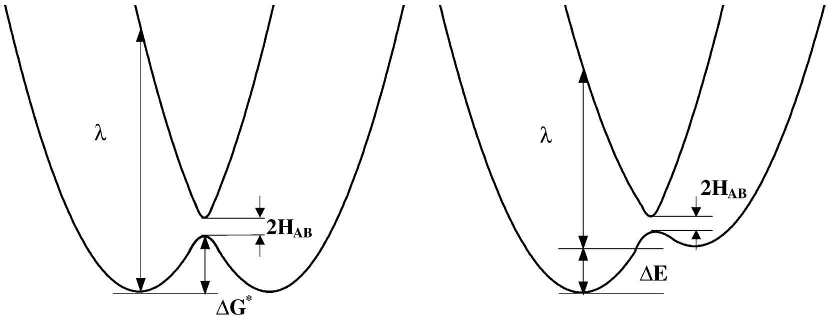
Mixed-valence compounds have been the subjects of intense experimental investigation [155,156]. Relying on a systematic review of experimental results, Hush [157,158] has developed a theoretical model linking the physical properties of the mixed-valence compounds with the subject of electron transfer reactions in solution. His model predicts that mixed-valence compounds should display a so called intervalence transfer, IT (or metal-to-metal charge transfer) band only if moderately coupled and that the properties of this transition are closely linked to the kinetic and thermodynamic factors governing the corresponding thermal electron transfer process. In particular, the absorption energy is related to the energetic barrier of the thermal electron transfer. The theory also allows calculation of the degree of electronic coupling (H_{AB}) between the metal centers from the position and band intensity of the observed IT band. The correlation of these properties can be illustrated in a diagram plotting potential energy versus nuclear configuration for a symmetrical mixed-valence complex (Fig. 13a).

Based on the strength of the electronic coupling between the metals, Robin and Day [159] have developed a system in which mixed-valence compounds are broadly distinguished in three classes. Compounds classified in II are anticipated to show the IT band, with its position related to the activation energy of adiabatic thermal electron transfer ($E_{op} = \lambda = 4\,\Delta G^*$) [155]. The situation in unsymmetrical complexes can be similarly explained if the energy difference between the two states is taken into account ($E_{op} = \lambda + \Delta E$) (Fig. 13b).

As shown, optical electron-transfer transitions in polynuclear complexes are certainly not a new phenomenon and have been studied very broadly and thoroughly [160–163]. However, most of the examples are strictly solution-based and the attachment to an electrode has not been addressed. The general principle that we have followed in the molecular design of the polynuclear species is based on the introduction of a metal containing moiety which can be directly bound to the surface of the semiconductor and can be interconverted between two oxidation states at a potential close to 0 V versus SCE. This should allow the maximization of the electronic coupling with the semiconductor and promote color changes by applying a small potential difference between the electrodes, a very important feature in regard to low energy consumption. Following this idea a series of binuclear complexes (**20**–**22**) of the type shown in Fig. 14, have been prepared and tested [164].

All these species display a distinct metal-to-metal $Ru^{II} \rightarrow Ru^{III}$ charge transfer band in the one electron oxidized form rendering them green (**20**) or blue (**21**, **22**) in color. Upon reduction, the intervalence band is quenched and the color of the complex is now governed by the dπ–π* (Ru → py) MLCT band resulting in a color change to red. The absorption spectra measured following the reduction and oxidation of the $[(HOOCpy)CH_4C_5Ru^{III}(NH_3)_4(NC)Ru^{II}(bpy)]^{3+}$ complex in aqueous solution (Fig. 15a) and on transparent TiO_2 films (Fig. 15b) clearly show a distinct color change in a narrow potential range (−0.5 to +0.5 V versus SCE), with switching times in the order of milliseconds.

Stability tests performed in sandwich type cells containing the dyes adsorbed on SnO_2/Sb electrodes, demonstrated a high stability, with optical density changes lower than 2%



(a) $\mathbf{E_{op}} = \lambda$ (b) $\mathbf{E_{op}} = \lambda + \Delta E$

Fig. 13. Optical intervalence transfer in symmetric (a) and unsymmetric (b) mixed-valence compounds. Correlation between spectroscopic and thermodynamic parameters.

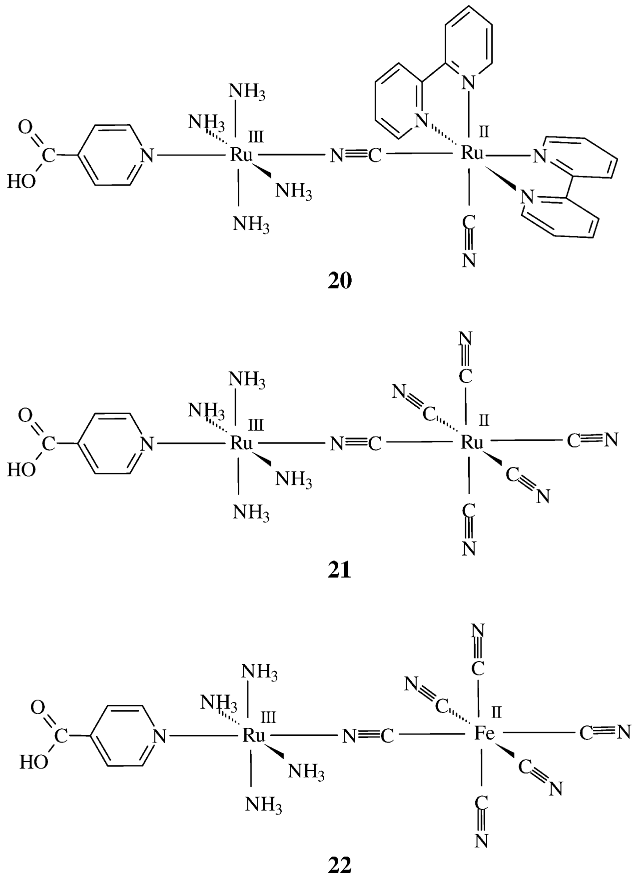


Fig. 14. Mixed-valence binuclear complexes.

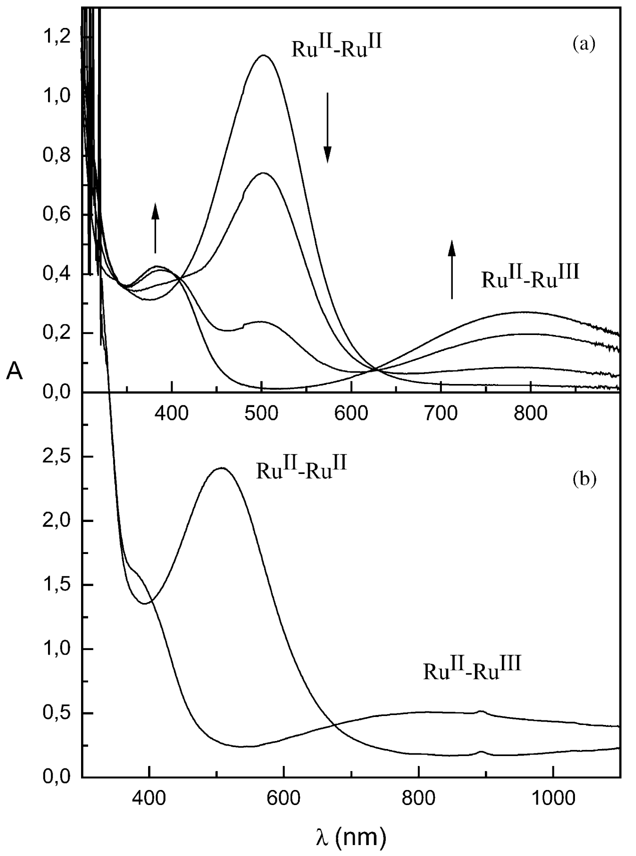


Fig. 15. UV-Vis spectral variations observed upon reduction and oxidation of the $[(HOOCpy)CH_4C_5Ru^{III}(NH_3)4(NC)Ru^{II}(bpy)]^{3+}$ complex in aqueous solution (a) and on transparent TiO_2 films (b).

after cycling the electrochromic device 20,000 times between −0.5 and +0.5 V.

Owing to the presence of the amine and cyanide ligands, known to give rise to specific donor–acceptor interaction with solvents [165–169] an interesting solvatochromic behavior is observed for these species. For complex (**20**) the spectral changes are dominated by amine interactions with the solvents as shown by the linear correlation of solvent donor number [170,171] with the IT band maxima and with the half-wave potential of the ruthenium amine moiety.

3.2. Ru–dioxolene complexes

In our ongoing effort [172] to develop electrochromic devices [143,145,147,173] we have synthesized a series of $Ru(bpy)_2$–dioxolene complexes (**23**–**26**) (Fig. 16) and investigated their spectroelectrochemical behavior in solution.

In addition, we have prepared the analogous compounds (**27**–**30**) (Fig. 16), where 2,2′-bipyridine-4,4′-dicarboxylic acid ligands have replaced the bpy ligands functioning as anchors to a nanocrystalline inorganic semiconductor surface, such as Sb-doped SnO_2. We have selected dioxolene ligands that represent large classes of dyes in order to have access to a pool of similar compounds allowing us to fine-tune the

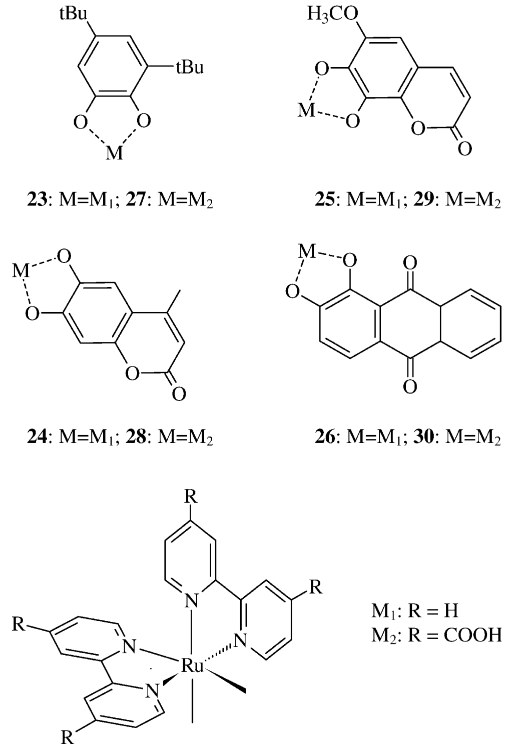


Fig. 16. Ru complexes with dioxolene ligands.

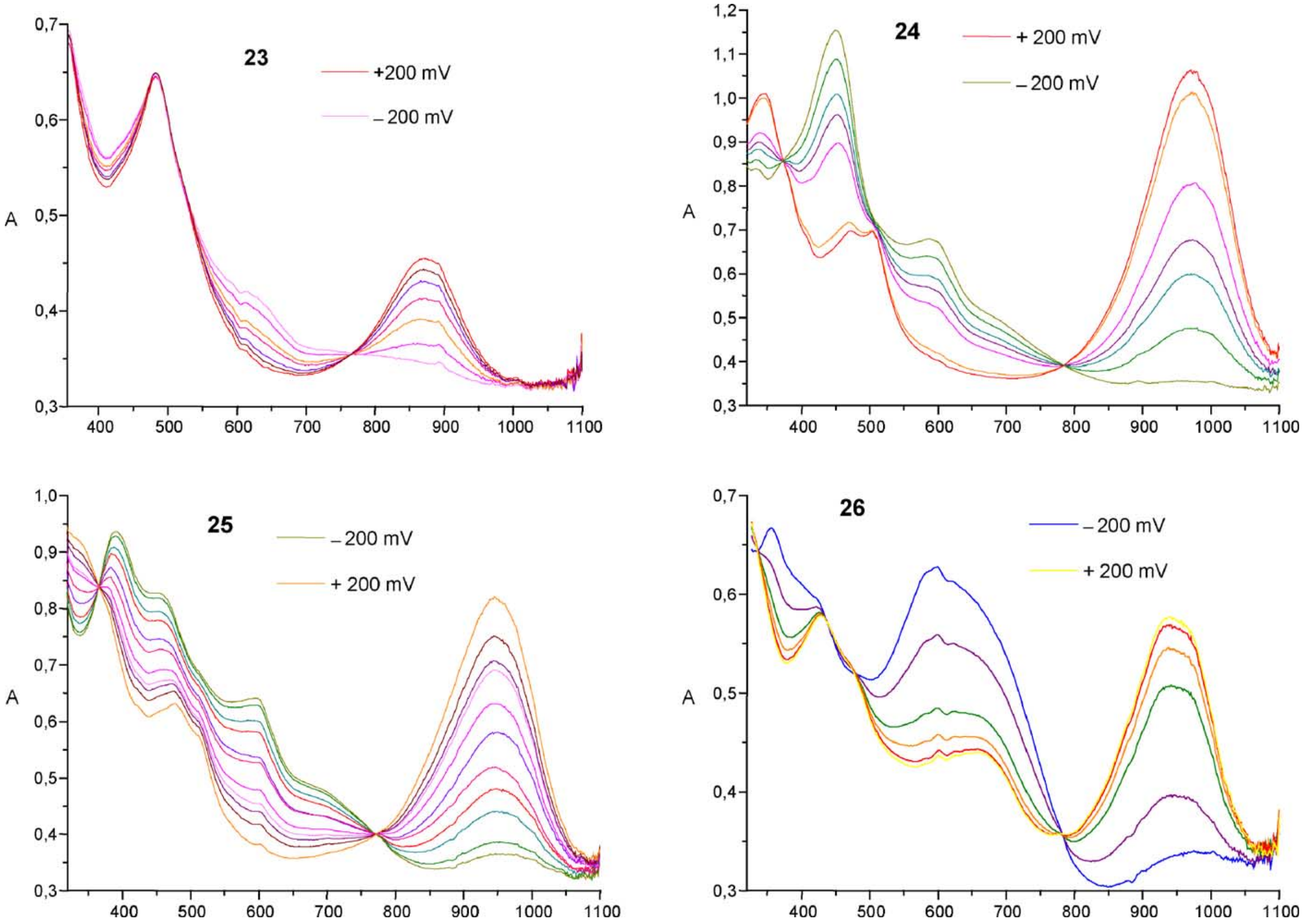


Fig. 17. UV-Vis spectral changes observed upon electrochemical reduction and oxidation of complexes (**23**–**26**) in acetonitrile (argon purged) containing tetrabutylammonium hexafluorophosphate 0.1 M. Potential values are referred to a quasi-reference Ag electrode.

properties of the complexes by simple replacement of the ligand.

As reference point, [Ru(bpy)$_2$(di-*t*-butyl-cat)] (**23**) was chosen since its electrochromic behavior in the NIR has been documented [174]. The other ligands used were alizarin, 7,8-dihydroxy-6-methoxy-coumarin, and 6,7-dihydroxy-4-methyl-coumarin.

The spectroelectrochemical properties have been characterized in an OTTLE cell using acetonitrile as the solvent and Bu_4NPF_6 as the base electrolyte (Fig. 17).

All species display the expected $Ru(d\pi) \rightarrow sq(\pi^*)$ MLCT band that can be activated and deactivated reversibly by simply switching between a positive and negative bias very close to 0 V versus SCE. The spectroelectrochemical measurements show several isosbestic points in all cases, demonstrating that the processes occur in one step and are completely reversible. It is worth noticing that the maximum of the NIR band is a function of the dioxolene ligand and ranges from 880 to about 974 nm, showing appreciable variation both between ligand families and among them as demonstrated by the coumarin dyes. We therefore expect to be able to fine-tune the absorption peak over a wide range in the NIR region. In addition to the distinct activation and deactivation of the band in the NIR, there are noticeable changes in the visible region of the spectrum, as well. Especially, the alizarin complex shows a sharp color change from blue to yellow upon oxidation. In principle, color changes should be adjustable through changes of the substituents on the core dioxolene ligand. The analogous dcb containing complexes can be anchored to the surface of an nanocrystalline inorganic semiconductor, such as Sb-doped SnO_2 [175]. For example, compound (**30**) adsorbs well onto the surface from an acetonitrile solution and the MLCT band in the NIR ($\lambda_{max} = 956$ nm) can be reversibly switched by applying a potential between +500 and −50 mV (Fig. 18). We are currently optimizing the conditions of the films in order to employ the species in electrochromic devices.

It can be concluded that this type of polynuclear system in general possesses a high degree of flexibility thanks to the possibility of tuning their spectroscopic properties through changes of metal centers, of coordinated or bridging ligands and solvent. In addition, the availability of a fast screening protocol to test suitable ligand/metal combinations for modifying their properties should be of considerable utility.

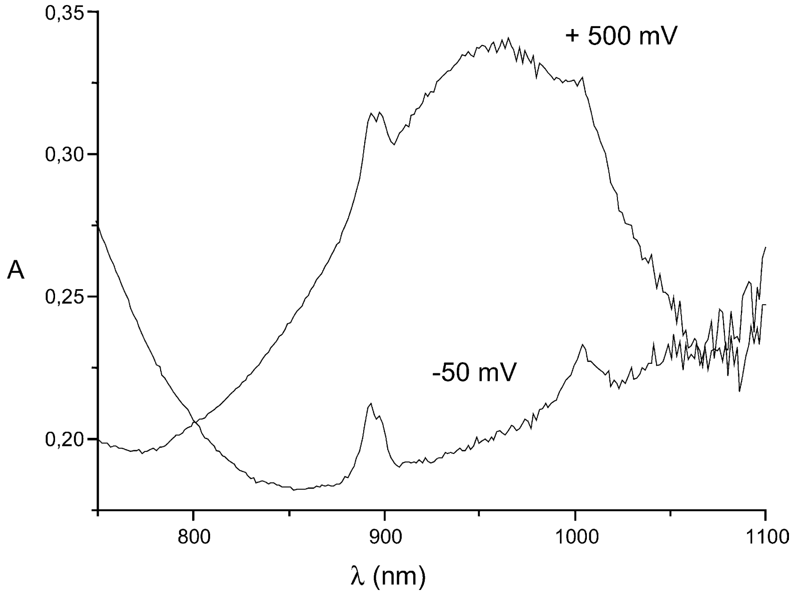


Fig. 18. Spectral variations in the NIR region observed upon electrochemical reduction and oxidation of complex (**30**), adsorbed on a Sb-doped SnO_2 nanocrystalline film, in the presence of tetrabutylammonium hexafluorophosphate 0.1 M. Potential values are referred to a quasi-reference.

Acknowledgements

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