

# Remote interfacial electron transfer processes on nanocrystalline TiO<sub>2</sub> sensitized with polynuclear complexes

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**ABSTRACT.** The kinetic study of interfacial electron transfer in sensitized nanocrystalline semiconductor is essential to the design of molecular devices performing specific light induced functions in a microheterogeneous environment. A series of molecular assemblies performing direct and remote charge injection to the semiconductor have been discussed in the context of artificial photosynthesis. A particular attention in this article has been paid to the factors that control the interfacial electron transfer processes in nanocrystalline TiO<sub>2</sub> films sensitized with mononuclear and polynuclear transition metal complexes.

## 1. GENERAL REMARKS ON SENSITIZATION OF SEMICONDUCTORS

The general principles of dye sensitization of wide-band-gap semiconductors were already well established in the 1970s [1, 2, 3, 4] and advancements in the application of such techniques to solar energy conversion have been initially very slow due to the poor light absorption showed by monolayer of dyes on electrodes of small surface roughness. A substantial increase in light energy to electrical energy conversion efficiencies, obtained with sensitized semiconductor electrodes, started with the development of high surface area nanocrystalline semiconductors [5] and of suitable molecular sensitizers [5, 6, 7, 8, 9, 10, 11].

The accepted model for dye sensitization in regenerative photoelectrochemical devices is shown in Figure 1

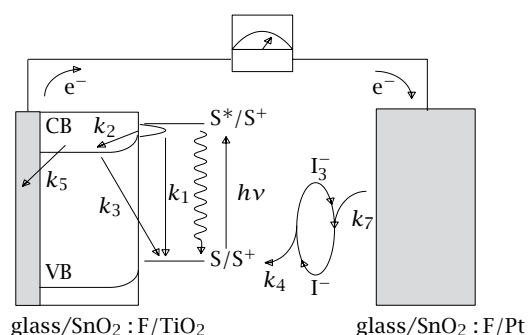


Figure 1. Schematic representation of the kinetic processes occurring in a regenerative photoelectrochemical cell.

[1, 2, 3, 4, 5, 8, 9, 10, 11]. The cell consists of a molecular sensitizer (S) anchored to the semiconductor surface, a solution containing a relay electrolyte (LiI, I<sub>2</sub>), and a counter electrode. Light excitation promotes the sensitizer to upper lying electronic excited-states that convert very rapidly and efficiently to the lowest-lying

electronic excited-state (S\*). The excited dye injects an electron into the conduction band of the semiconductor from a normal distribution of donor levels [10, 11] at a rate  $k_2$ , and becomes oxidized. The oxidized dye (S<sup>+</sup>) is then reduced by an electron donor (I<sup>-</sup>) acting as relay electrolyte, at a rate  $k_4$ . The electron flows ( $k_5$ ) through an external circuit to perform useful work. Reduction of the oxidized donor (I<sub>3</sub><sup>-</sup>) occurs at the counter electrode ( $k_7$ ) and the solar cell is therefore regenerative. Radiative decay and nonradiative decay ( $k_1$ ) of the excited dye molecule, and recombination of the photoinjected electron with the oxidized dye ( $k_3$ ), represent loss mechanisms. Additional loss mechanisms, such as recombination of the conduction band electrons with the oxidized electron donor, are represented by the rate constant  $k_6$  (not shown in Figure 1). Other loss mechanisms, as chemical reactions taking place from the oxidized or excited dye sensitizer, are not shown in Figure 1.

The meaningful parameters used to quantify on a macroscopic level the performance of a cell are the Incident Photon to Current conversion Efficiency (IPCE), the open circuit photovoltage ( $V_{oc}$ ), and the overall efficiency of the photovoltaic cell ( $\eta_{cell}$ ).

The wavelength dependent IPCE term can be expressed as a product of the quantum yield for charge injection ( $\Phi$ ), the efficiency of collecting electrons in the external circuit ( $\eta$ ), and the fraction of radiant power absorbed by the material or «light harvesting efficiency» (LHE), equation (1):

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \phi \eta. \quad (1)$$

While  $\Phi$  and  $\eta$ , can be rationalized on the basis of kinetic parameters, LHE depends on the active surface area of the semiconductor and on the cross section for light absorption of the molecular sensitizer. In practice the IPCE measurements are performed with monochro-

matic light and calculated according to equation (2)

$$\text{IPCE}(\lambda) = \frac{12.4 \cdot 10^3 (\text{V} \cdot \text{nm}) \times \text{photocurrent density} (\mu\text{A} \cdot \text{cm}^{-2})}{\text{wavelength} (\text{nm}) \times \text{photon flux} (\text{W} \cdot \text{m}^{-2})} \quad (2)$$

The light harvesting efficiency can be related to the dye molar extinction coefficient ( $\epsilon(\lambda)$ ,  $1 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ;  $\lambda$  = wavelength) and to the surface coverage ( $\Gamma$ ,  $\text{mol} \cdot \text{cm}^{-2}$ ) by equation (3)

$$\text{LHE}(\lambda) = 1 - 10^{-[1000\epsilon(\lambda)\Gamma]} \quad (3)$$

An LHE factor of unity is ideal for a solar energy device as all the incident radiant power is collected. The development of high surface area nanocrystalline  $\text{TiO}_2$  has produced an enhancement of LHE [8].

In the absence of photodecomposition reactions, the quantum yield for electron injection from the excited sensitizer to the semiconductor is given by equation (4)

$$\Phi = k_2 / (k_1 + k_2) = k_2 \tau, \quad (4)$$

where  $k_1$  is the radiative and nonradiative rate constant of the excited dye molecule ( $k_1 = k_{\text{r}} + k_{\text{nr}}$ ),  $k_2$  is the rate constant for the charge injection process and  $\tau$  represents the excited-state lifetime of the dye sensitizer anchored to the surface of the semiconductor.

Charge injection from the excited dye will be activated if the donor energy is positive with respect to the conduction band-edge. Electron injection will be, on the contrary, activationless if the donor level has an energy equal to, or more negative than, the conduction band-edge. For an activationless charge injection process, it is generally accepted that electron transfer from the excited sensitizer to the conduction band is irreversible due to extremely fast thermalization processes to the conduction band edge.

The fraction of injected charges, which percolate through the  $\text{TiO}_2$  membrane and reach the back contact of the photoanode, is represented by the factor  $\eta$ , equation 5

$$\eta = \frac{k_4[I^-]}{k_3[e^-] + k_4[I^-]} \quad \text{or} \quad \eta = 1 - \frac{k_3[e^-]}{k_3[e^-] + k_4[I^-]} \quad (5)$$

The  $\eta$  term can be evaluated from equation 5 by time resolved transient absorption measurements on  $\text{TiO}_2$  films, by monitoring the decay of the spectral features of the nascent oxidized sensitizer in absence ( $k_3$ ) or presence ( $k_4$ ) of iodide [12].

The maximum open-circuit photovoltage, attainable in the dye sensitized solar cell, is the difference between the Fermi level of the solid under illumination and the Nernst potential of the redox couple in the electrolyte. However, for these devices this limitation has not been realized and  $V_{\text{oc}}$  is in general much smaller. It appears that  $V_{\text{oc}}$  is kinetically limited and for an n-type semiconductor in a regenerative cell the diode equation (6) can be applied [13].

$$V_{\text{oc}} = \left( \frac{kT}{e} \right) \ln \left( \frac{I_{\text{inj}}}{n \sum_i k_i [A_i]} \right), \quad (6)$$

where  $I_{\text{inj}}$  is the electron injection flux,  $n$  is the concentration of electrons in  $\text{TiO}_2$ , and the summation is for all electron transfer rates to acceptors  $A_i$ . One successful strategy for increasing  $V_{\text{oc}}$  has been to add pyridine derivatives to the electrolyte [9]. Pyridine is thought to adsorb on the  $\text{TiO}_2$  surface and to inhibit recombination of injected electrons with  $\text{I}_3^-$  ( $k_6$ ). An alternative approach involve the use of supramolecular systems containing a sensitizer unit covalently bound to a suitable electron donor unit that allows to translate the positive charge from the oxidized form of the sensitizer.

The overall efficiency of the photovoltaic cell,  $\eta_{\text{cell}}$  is given by equation (7)

$$\eta_{\text{cell}} = \frac{i_{\text{ph}} \times V_{\text{oc}} \times ff}{I_s}, \quad (7)$$

where  $i_{\text{ph}}$  is the integrated photocurrent density,  $ff$  the cell fill factor, and  $I_s$  the intensity of the incident light. The integrated photocurrent density represents the overlap between the solar emission and the monochromatic current yield [14]. The maximum overall efficiencies reported so far are in the 7–11% range, depending on the fill factor of the cells. Under optimal current collection geometry, minimizing ohmic losses due to the resistance of the conductive glass, and under reduced solar irradiance, fill factors of 0.8 have been obtained [15].

## 2. MONONUCLEAR MLCT SENSITIZERS

In order to be useful in a photoregenerative cell, the molecular sensitizer should fulfil several requirements, including:

- The ability to adsorb firmly on the semiconductor.
- Efficient light absorption in the visible region.
- An excited-state redox potential negative enough for electron injection into the conduction band.
- A ground-state redox potential as positive as possible, compatible with b) and c).
- Small reorganizational energy for excited- and ground-state redox processes, so as to minimize free energy losses in primary and secondary electron transfer steps.

The most successful sensitizers, used so far, are based on polypyridine complexes of  $d^6$  metal ions, such as Ru(II), Os(II), and Re(I). The absorption spectra of these complexes are dominated by intense metal-to-ligand charge transfer (MLCT) absorption bands in the visible region. Excitation into these bands populate MLCT excited-states that are mainly singlet in character. This process is then followed by fast ( $k > 10^{12} \text{ s}^{-1}$ ) and quantitative intersystem crossing to lower-lying, mainly triplet in character, MLCT excited-states [16].

The energies of these states can be varied systematically by changing the substituents at the chromophoric ligands. Electron-withdrawing substituents tend to decrease the energy of the  $\pi^*$  orbitals of the polypyridine ligand, while the opposite effect is observed with electron donating substituents. The electronic effects are also partially transmitted to the metal centres [17].

Energy tuning of MLCT states can also be obtained by changing the non-chromophoric ligands. For bis-chelate complexes of the type *cis*-[Ru<sup>II</sup>(bpy)<sub>2</sub>(X)<sub>2</sub>], as well as for the analogous Os<sup>II</sup> complexes, MLCT absorption bands shift to higher energy changing X from  $\pi$  donating ligands to  $\pi$  accepting ligands. The main effect, in this case, is a direct perturbation of the electronic density at the metal centre [17].

In order to obtain maximum conversion of visible photons into electrons, it is important that the absorption spectrum of the dye sensitizer has significant overlap with the spectrum of the solar radiation. Additionally, charge injection to the semiconductor and electron transfer processes between the oxidized dye and the relay must compete favourably with excited-state relaxation processes and with chemical reactions taking place from the excited dye and its ground-state oxidized form. These requisites have all been met by using ruthenium polypyridine complexes. The presence of carboxylic acid functions on the bpy ligand allows a stable linkage with TiO<sub>2</sub> and promotes a strong electronic coupling between the  $\pi^*$  orbitals of the bipyridine ligand and the conduction band of the semiconductor, as evidenced by long term stability, in anhydrous solvents, of the surface adsorbed dyes [18] and the very high charge injection rates observed for different MLCT sensitizers [19, 20, 21, 22, 23]. The high coupling is thought to be mediated by  $\pi$  electrons in the bridging group leading to increased delocalization of the  $\pi^*$  levels of the bipyridine ligand.

In the series of complexes of the type *cis*-[Ru(dcbH<sub>2</sub>)<sub>2</sub>(X)<sub>2</sub>] (dcbH<sub>2</sub> = 4,4'-dicarboxy-2,2'-bipyridine; X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NCS<sup>-</sup> and CN<sup>-</sup>), MLCT absorption and emission maxima were found to shift towards longer wavelength by decreasing the ligand field strength of the ligand X, with  $E_{1/2}$  Ru<sup>(III)/(II)</sup> decreasing in the expected order, CN > NCS > halides. These complexes were generally found to act as efficient sensitizers for nanocrystalline TiO<sub>2</sub>. In particular, the performances of the NCS complex in photoelectrochemical solar cells were found to be outstanding and unmatched by any other sensitizer [9, 11]. The complex showed a photoaction spectrum dominating almost the entire visible region, with IPCE of the order of 90% between 500–600 nm. Short-circuit photocurrents exceeding 17 mA/cm<sup>2</sup> in simulated A.M. 1.5 sunlight and open-circuit photovoltages of the order of 0.7 V, were obtained by using iodide as redox electrolyte. For the first time a photoelectrochemical device was found to give an overall conversion efficiency of 10% [9].

In an attempt to extend the spectral sensitivity of mononuclear dyes towards the red, new *cis*-[Ru(5,5'-

dcbH<sub>2</sub>)<sub>2</sub>(X)<sub>2</sub>] complexes based on the ligand 5,5'-dicarboxy-2,2'-bipyridine (X = Cl<sup>-</sup>, NCS<sup>-</sup>, CN<sup>-</sup>) were synthesized [11]. The change of the carboxylic function position from 4,4' to 5,5' causes a lowering of the energy of the  $\pi^*$  accepting orbitals. A sustained conversion of light to electricity was demonstrated for [Ru(5,5'-dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>] achieving the goal of extending the photoelectrochemical cell responsivity to longer wavelengths.

As a complementary strategy to polypyridyl substitution, several attempts have been made to find suitable ancillary ligands for complexes of the type *cis*-[Ru(dcbH<sub>2</sub>)<sub>2</sub>X<sub>2</sub>] in order to have better mononuclear ruthenium sensitizers. The complexes *cis*-[Ru(dcbH<sub>2</sub>)<sub>2</sub>(isq)<sub>2</sub>] (isq = isoquinoline) [24], *cis*-[Ru(dcbH<sub>2</sub>)<sub>2</sub>(ppy)<sub>2</sub>] and *cis*-[Ru(dcbH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(ppy)] [25] (ppy = 4-phenylpyridine) have shown good photoelectrochemical properties, despite their photochemical instability in solution, with IPCE values ranging from 40% for the isoquinoline and bis(4-phenylpyridine) complexes to 50% for [Ru(dcbH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(ppy)]. In another study, dithiocarbamate ligands [26] were considered to be good candidates to extend the spectral sensitivity of mononuclear Ru sensitizers towards red. New violet dyes of general formula [Ru(dcbH)(dcbH<sub>2</sub>)(L)], where L is diethyldithiocarbamate, dibenzylidithiocarbamate or pyrrolidinedithiocarbamate, have been synthesized, characterized and tested on TiO<sub>2</sub> based photoelectrochemical regenerative cells using [Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>] as a reference compound. These dyes showed intense  $d_{\pi} - \pi^*$  MLCT transitions in the visible with the lower energy band slightly red shifted with respect to the thiocyanate complex. Contrary to what observed for [Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>], the cyclic voltammetry of the dithiocarbamate complexes gave reversible waves both in the protonated and anionic forms testifying a greater stability of the oxidized species towards ligand loss or substitution, as expected from the chelating nature of these ancillary ligands. The photoelectrochemical behaviour of regenerative cells with LiI 0.5 M/I<sub>2</sub> 0.05 M in acetonitrile gave IPCE values for the violet dyes consistently lower than the reference complex, being, on the average, around 50%. In order to rationalize this different behaviour, the kinetics of the primary processes of charge injection ( $k_2$ ) and recombination ( $k_3$  and  $k_4$ ) was explored by nanosecond transient absorption spectroscopy. Absorption difference spectra recorded after 532 nm excitation of the complexes bound to TiO<sub>2</sub> in argon saturated 1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN solutions, showed mainly the bleaching and recovery of the MLCT absorption of the dyes. In all cases the formation of the oxidized sensitizer occurred within the instrument response function ( $k_2 > 10^8$  s<sup>-1</sup>) and the recombination rate ( $k_3$ ) was found to be approximately the same for the dithiocarbamate complexes and the reference compound. The kinetics of reduction of the oxidized sensitizer by iodide ions ( $k_4$ ) was examined with the same technique at different I<sup>-</sup> concentrations. Stern-Volmer analysis

of the integrated area under the absorption transients gave  $K_{SV} = 100\text{M}^{-1}$  for  $[\text{Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$  and  $K_{SV} = 30\text{M}^{-1}$  for the three dithiocarbamate sensitizers. The slower reduction rate of the oxidized dithiocarbamate species by  $\text{I}^-$  is thought to be consistent with the observed trend in IPCE values by virtue of a reduced charge collection efficiency  $\eta$  equation (5).

Since one of the problems encountered with the carboxy polypyridine class of sensitizers is the slow desorption from the semiconductor surface in the presence of water, the search for new anchoring group is advisable. Along this line of research, we have recently prepared complexes based on the derivatization of 2,2'-bipyridine with a phenylboronic functionality [27]. The photoaction spectra of  $\text{TiO}_2$  electrodes sensitized with the  $[\text{Ru}(4\text{-phenylboronic-2,2'-bipyridine})_2(\text{CN})_2]$  complex showed IPCE values comparable to those observed for  $[\text{Ru}(\text{dcbH}_2)_2(\text{CN})_2]$  [10, 11], indicating that the new type of linkage does not reduce the electron injection yield.

Another different approach, recently explored [28], is based on the electropolymerization of molecular assemblies containing the ligand 4-methyl-4'-vinyl-2,2'-bipyridine (vbpy). Mononuclear as well as polynuclear metal complexes such as  $[\text{Ru}(\text{vbpy})_3]^{2+}$  and  $[(\text{bpy})_2(\text{CN})\text{Ru}(\text{NC})\text{Ru}(\text{vbpy})_2(\text{NC})\text{Ru}(\text{CN})(\text{bpy})_2)]^{2+}$  form very stable and uniform films on  $\text{TiO}_2$  particles upon electrochemical reduction of  $\pi^*(\text{vbpy})$  followed by radical polymerization. Electropolymerized species can be advantageously used as overlayer structures to enhance the stability of previously adsorbed sensitizers. Considering that the electronic coupling between the polymerized sensitizer and the semiconductor is not comparable to that of chemically adsorbed species, the IPCE values were found lower with respect to those given by analogous complexes based on the dcb ligand. The reduction of IPCE in overlaid structures is ascribed also to excited state quenching due to trap sites formation in the polymer network.

### 3. SUPRAMOLECULAR SENSITIZERS

Studies on sensitization of nanocrystalline  $\text{TiO}_2$  with supramolecular species may provide fundamental insights into interfacial electron transfer processes that would not be gained with simple molecular compounds. A supramolecular species possesses in general the following attributes: (i) the intrinsic properties of the molecular components are not significantly perturbed, and (ii) the properties of the supramolecular system are not simply the superposition of the properties of the molecular components, but there is a supramolecular function. Upon substitution of one of the molecular components by a condensed phase, *i.e.* a nanocrystalline semiconductor, a heterosupramolecular system is formed. Two simple supramolecular dyad systems, containing a chromophoric molecular component (photosensitizers, P), covalently linked acceptor (A) or donor (D) components on a semiconductor surface, are schematized in Figure 2.

Since one of the components is a condensed phase, this system can be considered as a "heterotriad". In order to give the heterosupramolecular systems the functions as depicted in Figure 2, several nontrivial problems must be solved. Apart from various important issues related to molecular architecture (choice of the appropriate molecular components so that each step is thermodynamically allowed, assembling of the components *via* suitable connectors in the right sequence, binding of the supramolecular system to the semiconductor surface in the appropriate orientation, *etc.*), delicate problems of kinetic nature must be addressed. As a matter of fact, the kinetics of each of the electron transfer steps must be optimized, so as to bring to 100% efficient charge separation. In particular, the key to the problem is likely to be the competition between the secondary electron transfer step (2 in Figure 2a) and the primary charge recombination process (4 in Figure 2a).

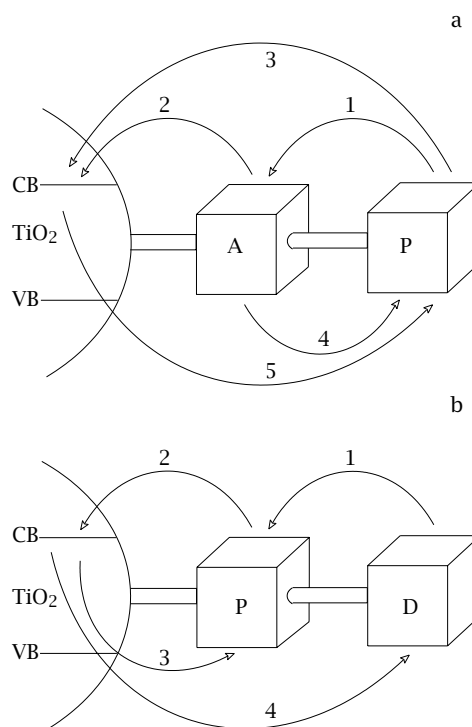


Figure 2. Intramolecular and interfacial electron transfer processes in dyads adsorbed on a semiconductor.

It is evident that a good deal of control on the factors (driving force, reorganizational barriers, electronic factors), that govern electron transfer rates, must be reached before a successful supramolecular device of this kind is developed. Both systems in Figure 2 are designed to translate the electron hole away from the surface and reduce the rate of electron-hole recombination ( $k_3$  in Figure 1), and thus increase the overall cell efficiency. In principle, an extension from dyads to larger systems can be envisioned keeping in mind that each additional charge separation step will reduce the driving force which can be stored in the interfacial charge separated state.

#### 4. CHROMOPHORE-ELECTRON DONOR SYSTEM

The vectorial translation of the electron-hole, away from the surface, can be accomplished by using a system of the type sketched in Figure 2b. The dyad system, Ru-PTZ, which was prepared to model this function, is shown in Figure 3. The chromophoric unit is represented by the Ru(II) moiety (with two dcbH and one dmb ligands), while the covalently bound phenothiazine (PTZ) acts as the electron donor [29, 30].

Irradiation with visible light in solution results in the population of the Ru(III)(dcbH<sup>-</sup>)<sup>3</sup>MLCT excited-state, which is followed by reductive quenching of the excited-state by the PTZ moiety. The reductive quenching of the excited-state (Figure 4) is moderately exergonic (by *ca.* 0.25 eV) and has a rate constant of *ca.*  $2.5 \times 10^8 \text{ s}^{-1}$  in methanol, as measured from the lifetime of the residual \*Ru(II) emission.

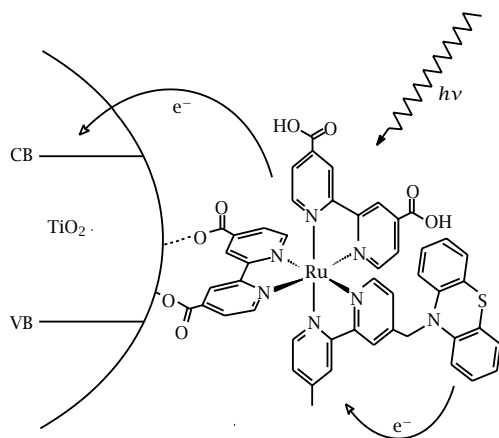


Figure 3. Structural formula of the Ru-PTZ chromophore-electron donor system and related kinetic processes on TiO<sub>2</sub>.

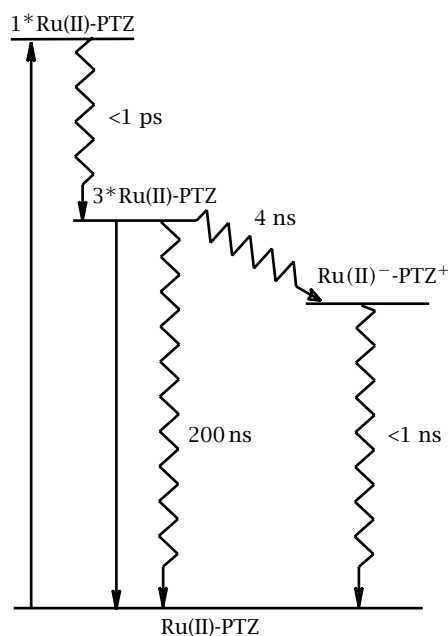


Figure 4. Excited state electron transfer processes in the Ru-PTZ chromophore-electron donor system.

The corresponding charge recombination step, presumably faster than the forward one, leads the system back to the ground-state without appreciable transient accumulation of the electron transfer product.

When the dyad system is attached to TiO<sub>2</sub>, excitation of the Ru chromophore can result in a new charge separated state, TiO<sub>2</sub>(e<sup>-</sup>)-Ru-PTZ<sup>+</sup>. In principle there are two possible pathways available to reach this charge separation. In pathway 1 (Figure 5), charge injection is followed by the charge shift to the donor, while in

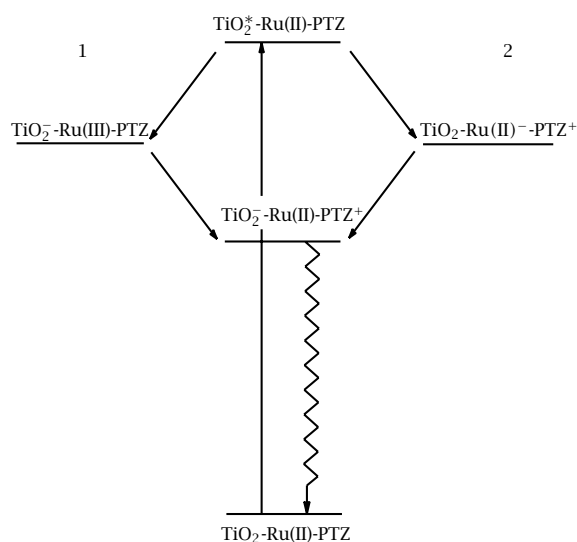


Figure 5. Possible intramolecular and interfacial electron transfer processes in the TiO<sub>2</sub>-Ru-PTZ system.

pathway 2, reductive quenching by the PTZ moiety is followed by charge injection.

A laser flash photolysis study of the heterotriad showed that visible light excitation results in the Ru-based MLCT excited-state which rapidly injects an electron into the semiconductor. The injection process is then followed by electron transfer from PTZ to the oxidized Ru centre ( $-\Delta G$  *ca.* 0.36 eV), resulting in the charge separated state TiO<sub>2</sub>(e<sup>-</sup>)-Ru(II)-PTZ<sup>+</sup>. The recombination of this state to the ground-state occurs with a rate of  $3.6 \times 10^3 \text{ s}^{-1}$ . Excitation of the model compound [Ru(dmb)(dcbH)<sub>2</sub>], gives rise to the formation of the charge separated state TiO<sub>2</sub>(e<sup>-</sup>)-Ru(III), whose recombination kinetics is complex and can be analysed by a distribution model, with an average rate constant  $k_3 = 3.9 \times 10^6 \text{ s}^{-1}$ . Translating the hole from the Ru centre to the pendant PTZ moiety produces a delay in recombination rates ( $k_3$ ) by three order of magnitude [29, 30].

The dyad and model molecules were also tested in regenerative solar cells, with iodide as an electron donor. While the observed IPCE was of the order of 45% for both systems, the open circuit photovoltage was observed to be higher for the dyad by 100 mV. The effect was more pronounced in the absence of iodide with  $V_{oc}$  180 mV larger over 5 decades of irradiation. Applying the measured interfacial electron transfer rates to the

diode equation equation (6) gave the predicted increase of  $V_{oc}$  of 200 mV, which was in agreement with the obtained value (180 mV) [29, 30]. It is therefore encouraging that an increase of the lifetime of the interfacial charge separated state  $TiO_2(e^-)-Ru(II)-PTZ^+$  has a direct influence on the overall efficiency of the cell.

## 5. REMOTE CHARGE INJECTION PROCESSES

As discussed before, the binding to the semiconductor surface is an important factor for solar cells, in terms of stability and electronic coupling. Ligands with linkage groups containing  $(CH_2)_n$  spacers were used in molecular dyes [31]. Surprisingly, the reduced electronic coupling between the excited sensitizer and the conduction band of  $TiO_2$  did not affect the performance of the solar cell. This suggested that intimate linkage between the chromophoric unit and the semiconductor surface is not a strict requirement for the design of a molecular sensitizer, and that remote charge injection processes can be profitably used to achieve efficient dye sensitization.

A supramolecular approach for designing a molecular sensitizer, which can control the orientation of the component units on the semiconductor surface, is shown in Figure 6. The binuclear compound is based on the  $-Re(I)(dcbH_2)_2$  and  $-Ru(II)(bpy)_2$  moieties, undergoing ultra-fast and efficient photoinduced  $Re^* \rightarrow Ru$  energy transfer [32]. Due to the facial geometry of the surface-bound Re-moiety, the  $-Ru(bpy)_2$  unit is forced to be close to the surface.

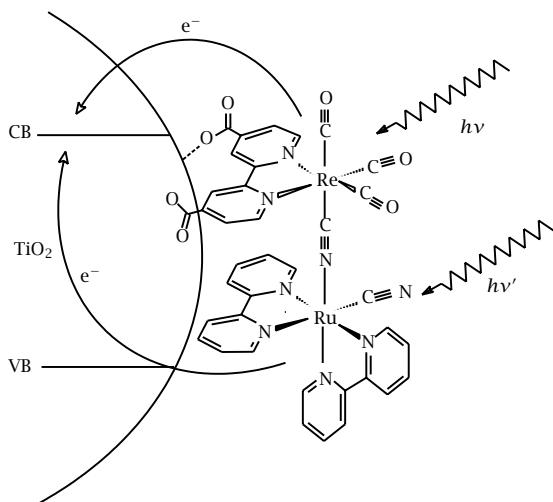


Figure 6. Structural formula of the Re-Ru binuclear complex and related kinetic processes on  $TiO_2$ .

Visible excitation of  $TiO_2$  photoanodes, loaded with the binuclear sensitizer, resulted in an efficient photon-to-current conversion. The photoaction spectrum showed that the Ru-polypyridine moiety absorbs most of the visible light with uncorrected maximum IPCE values of the order of 70%. The transient absorption difference spectra for the sensitizers bound to  $TiO_2$  showed a broad bleach in the region from 400 to

600 nm, typical for the  $TiO_2(e^-)/Re(I)-Ru(III)$  state. The formation of this state is promptly observed after the laser pulse. This indicates that either remote electron injection into  $TiO_2$ , or intraligand ( $bpy^{*+} dcbH_2$ ) electron hopping from Ru(III) ( $bpy^{*+}$ ) to Re(I) ( $dcbH_2$ ), occurs within the laser pulse ( $k > 5 \times 10^7$ ). In conclusion, a rapid and efficient injection process is observed from a chromophoric group which is not directly coupled to the semiconductor surface. These data indicate that direct covalent attachment is not strictly necessary for designing efficient molecular sensitizers.

The occurrence of remote interfacial electron transfer processes has been further confirmed by studying the photophysics of the binuclear complex  $[Ru(dcbH_2)_2(Cl)-BPA-Os(bpy)_2Cl]^{2+}$  (BPA = 1,2-bis(4-pyridyl)ethane) on transparent  $TiO_2$  films [33]. At monolayer coverages the binuclear complex gives rise to 1/2 molecular adsorption with respect to the model complex  $[Ru(dcbH_2)_2(Cl)(py)]^+$ , indicating that the binuclear complex lies on the nanocrystals of  $TiO_2$  in a more or less extended conformation, as shown in Figure 7.

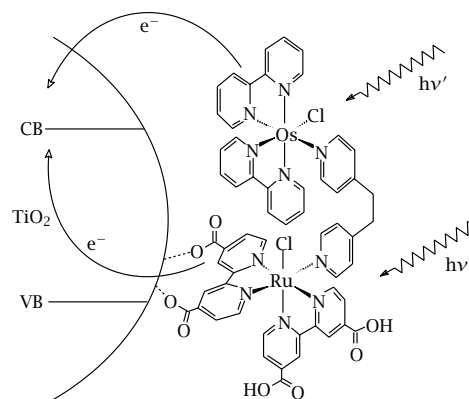


Figure 7. Structural formula of the Ru-BPA-Os binuclear complex and related kinetic processes on  $TiO_2$ .

Transient absorbance difference spectra following 532 nm laser excitation, where both Ru and Os chromophores absorb, reveal the typical bleaching of the spin-forbidden MLCT transition localized on the Os(II) moiety. Spectral and kinetic analysis of the transient signals are consistent with the formation of the charge separated state  $TiO_2(e^-)-Ru(II)-Os(III)$ . This state can either be formed through charge injection from the excited Ru chromophore followed by intramolecular Os(II)  $\rightarrow$  Ru(III) electron transfer, or *via* remote electron transfer from the  $^3MLCT$  excited-state localized on the Os(II) ( $bpy$ )<sub>2</sub> unit (Figure 8).

The occurrence of the latter process is confirmed by time resolved experiments in which selective laser excitation of the Os chromophore (at 683 nm) was obtained.

## 6. CONCLUSIONS

Some strategies for the design of mononuclear sensitizers and of artificial supramolecular systems, featuring functions such as photoinduced charge separation

and antenna effect for their use in sensitization of semiconductors, have been discussed. These functions depend on the choice of specific molecular components which may control the kinetics of the interfacial and intercomponent processes. On the basis of the knowledge gained in this field, molecular devices with predetermined built-in functions can now be rationally designed and synthesized. Studies on model systems suggest the possibility to prevent interfacial charge recombination in sensitized semiconductor cells, by taking

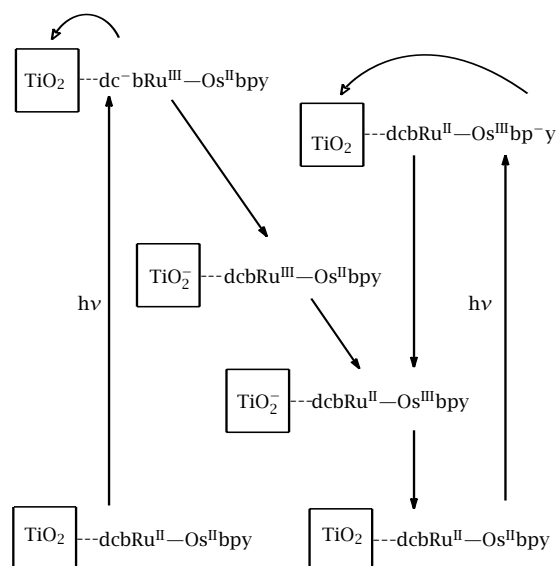


Figure 8. Possible intramolecular and interfacial electron transfer processes in the  $\text{TiO}_2$ -Ru-BPA-Os system.

advantage of photoinduced charge separation within the photosensitizer; they additionally indicate that intramolecular energy transfer processes in polynuclear complexes can be used to improve the overall cross-section for light absorption of a sensitizer.

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