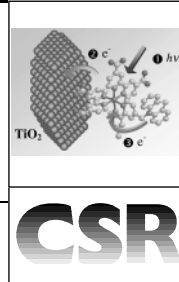


Molecular and supramolecular sensitization of nanocrystalline wide band-gap semiconductors with mononuclear and polynuclear metal complexes



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Some strategies for the design of mononuclear sensitizers and of artificial supramolecular systems useful in the sensitization of wide band-gap semiconductors, and featuring functions such as photoinduced charge separation and the antenna effect for their use in sensitization of semiconductors are reviewed. Such functions depend on the choice of specific molecular components which may control the kinetics of the interfacial and intercomponent electron transfer processes. Examples of molecular devices, which may prevent interfacial charge recombination in sensitized semiconductor cells, and examples of polynuclear complexes, supporting efficient intramolecular energy transfer to sensitizer units, are discussed.

1 Introduction

The use of solid-state materials for conversion of solar energy into electricity is a topic of much interest to scientists. Colloids and nanocrystalline films of several semiconductor systems have been employed in the direct conversion of solar energy

into chemical or electrical energy.^{1,2} In the 1950s the improvements in silicon purity and solid-state junctions created a revolution in the development of solar cells. Silicon solar cell efficiencies improved by an order of magnitude in the 1950s onwards to reach 24% in 1995.³ In the 1990s a major photoelectrochemical solar cell development was obtained with the introduction of thin film dye sensitized solar cells devised by Grätzel.⁴ For the first time a solar energy device operating on a molecular level showed the stability and the efficiency required for potential practical applications.⁴⁻⁶

Although the general principles of dye sensitization of wide band-gap semiconductors were already well established in the 1970s,⁷ progress in the application of such techniques to light energy conversion has been initially very slow due to the limited light absorption shown by monolayers of dyes on electrodes of low surface roughness. Substantial advances in conversion efficiencies, obtained with sensitized semiconductor electrodes, started with the development of high surface area nanocrystalline semiconductors⁴ and of suitable molecular sensitizers.^{4-6,8}

Most of the nanocrystalline semiconductors studied up to now have been metal oxides or chalcogenides, such as TiO₂,

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ZnO, SnO₂, Nb₂O₅, WO₃, SrTiO₃, Ta₂O₅ or CdS. Films based on these materials constitute a network of mesoscopic particles which are in close contact with each other and allow for efficient electronic migration. Because of their high roughness factor and relatively good conductivity, these materials are ideal candidates for a number of interesting applications such as photoelectrochemical solar cells, sensors, electro- and photochromic materials, and photocatalytic devices.⁹ Wide band-gap n-type semiconductors such as TiO₂ and ZnO are materials that do not undergo decomposition upon irradiation or heating and are therefore generally utilized in dye sensitized photoelectrochemical solar cells.^{2,10} The development of these materials and of efficient molecular sensitizers has caused a sharp acceleration in the field, and active research on several aspects of this technology is now being performed in many laboratories.

Over the last ten years, our group has been working in the field of supramolecular photochemistry. In particular, we have been interested in the design, synthesis and characterization of inorganic photochemical molecular devices, *i.e.* supramolecular systems based on inorganic building blocks with suitable built-in light-induced functions.¹⁰

The aim of this contribution is to use representative experimental results, mainly taken from the work of our group, to exemplify a supramolecular approach to the sensitization of semiconductors. At first the article deals with some background material on sensitization of wide band-gap semiconductors and factors affecting conversion efficiencies in photoelectrochemical cells. In following sections, it discusses experimental results concerning mononuclear and polynuclear complexes as molecular sensitizers, and polynuclear complexes as supramolecular charge-separating sensitizers. The nature of this review precludes a full bibliographic survey; hence the context of such studies and additional literature are best obtained from the reference cited.

2 Sensitization of wide band-gap semiconductors

Dye sensitization, *i.e.* charge injection from an electronically excited adsorbed dye, is a well established technique that allows photoelectrochemical and photocatalytic processes on wide band-gap semiconductors using sub band-gap excitation. The energy gradient initially stored in the interfacial charge separated pair TiO₂(e⁻)/D⁺ can be utilized to drive chemical reactions as well as to convert visible light into electricity.^{9,10}

An accepted model for dye sensitization in regenerative photoelectrochemical cells is shown in Fig. 1. The cell consists

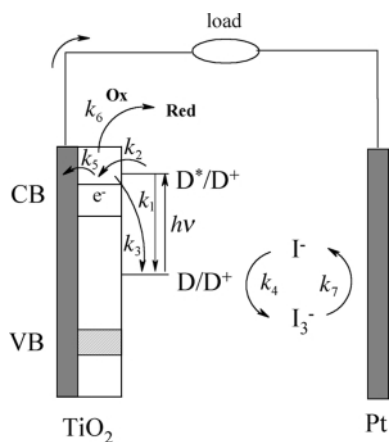


Fig. 1 Schematic representation of the elementary steps involved in a regenerative photoelectrochemical cell for light conversion based on dye sensitization of semiconductors.

of a molecular sensitizer anchored to the semiconductor surface, a solution containing a relay electrolyte, 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. The excited dye injects an electron into the conduction band of the semiconductor from a normal distribution of donor levels at a rate k_2 , and becomes oxidized. The oxidized dye is then reduced by an electron donor (I⁻) 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 (I₃⁻) occurs at the counter electrode (k_7) and the solar cell is therefore regenerative. Radiative decay, 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 . Other loss mechanisms, such as chemical reactions taking place from the oxidized or excited dye sensitizer, are not shown in Fig. 1.

The performance of the cell can be quantified on a macroscopic level with parameters such as incident photon to current efficiency (IPCE), open circuit photovoltage (V_{oc}), and the overall efficiency of the photovoltaic cell, η_{cell} .

2.1 Incident photon to current efficiency (IPCE)

The parameter measuring directly how efficiently incident photons are converted into electrons is the incident photon to current conversion efficiency (IPCE).^{4,6,8} The wavelength dependent IPCE term can be expressed as a product of the quantum yield for charge injection (Φ), the efficiency of collecting electrons in the external circuit (η), and the fraction of radiant power absorbed by the material or 'light harvesting efficiency' (LHE), eqn. (1).

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

While Φ and η 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.¹⁰ In practice the IPCE measurements are performed with monochromatic light and calculated according eqn. (2).

$$\text{IPCE}(\lambda)\% = \frac{1.24 \cdot 10^3 (\text{V nm}) \times \text{photocurrent density } (\mu\text{A cm}^{-2})}{\text{wavelength (nm)} \times \text{photon flux } (\text{W m}^{-2})} \quad (2)$$

2.2 Open circuit photovoltage (V_{oc})

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_{oc} is in general much smaller. It appears that V_{oc} is kinetically limited and for an n-type semiconductor in a regenerative cell the diode eqn. (3) can be applied,¹¹

$$V_{oc} = \left(\frac{kT}{e} \right) \ln \left(\frac{I_{inj}}{n \sum_i k_i [A_i]} \right) \quad (3)$$

where I_{inj} is the electron injection flux, n is the concentration of electrons in TiO₂, and the summation is for all electron transfer rates to acceptors A_i . One successful strategy for increasing V_{oc} has been to add pyridine derivatives to the electrolyte.⁶ Pyridine is thought to adsorb on the TiO₂ surface and to inhibit

recombination of injected electrons with I_3^- (k_6). An alternative approach, which will be discussed in section 4, involves the use of supramolecular systems containing a sensitizer unit covalently bound to a suitable electron donor unit that allows translation of the positive charge from the oxidized form of the sensitizer.

2.3 Overall efficiency of the photovoltaic cell (η_{cell})

The overall efficiency of the photovoltaic cell, η_{cell} , is given by eqn. (4),

$$\eta_{\text{cell}} = \frac{i_{\text{ph}} \times V_{\text{oc}} \times \text{ff}}{I_s} \quad (4)$$

where i_{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.² 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.¹²

3 Molecular sensitizers

Photosensitization of TiO_2 with transition metal complexes, chlorophyll derivatives, and related natural porphyrins has been reported.¹⁰ Besides these studies, a different approach involving coupling of two semiconductor particles with different energy levels, such as CdS-ZnO and CdSe-TiO_2 , has been proposed by Kamat.¹³

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.

It should be noticed that the photoregenerative device described in the previous section (see Fig. 1) has the peculiarity of operating with molecular sensitizers having short lived excited-states, and with sensitizers showing photochemical instability or irreversible ground-state redox behaviour. This peculiarity is satisfied when charge injection processes to the semiconductor are very fast and competitive with deactivation or chemical reactivity of the excited sensitizer. A fast reduction of the sensitizer oxidized form can be obtained by increasing the concentration of iodide in the electrolytic solution.

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) showing intense metal to ligand charge transfer transitions in the visible region, leading to MLCT states. 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 π^* orbitals of the polypyridine ligand, while the opposite effect is observed with electron donating substituents) as well as by changing the non-chromophoric ligands. For bis-chelate complexes of the type $\text{cis-[Ru}^{\text{II}}(\text{bpy})_2(\text{X})_2]$, as well as for the analogous Os^{II} complexes, MLCT absorption bands shift to higher energy changing X from π donating ligands to π

accepting ligands. The main effect, in this case, is a direct perturbation of the electronic density at the metal centre.¹⁰

In the series of complexes of the type $\text{cis-[Ru}(\text{dcbH}_2)_2(\text{X})_2]$ ($\text{dcbH}_2 = 4,4'$ -dicarboxy-2,2'-bipyridine; $\text{X} = \text{Cl}^-$, Br^- , I^- , NCS^- and CN^-), MLCT absorption and emission maxima were found to shift towards longer wavelength by decreasing the ligand field strength of the ligand X, with $E_3 \text{Ru}^{\text{III/II}}$ decreasing in the expected order, $\text{CN}^- > \text{NCS}^- > \text{halides}$. These complexes were generally found to act as efficient sensitizers for nanocrystalline TiO_2 . In particular, the performances of the NCS complex in photoelectrochemical solar cells were found to be outstanding and unmatched by any other sensitizer.^{6,8} The complex showed a photoaction spectrum (IPCE vs. λ) dominating almost the entire visible region, with IPCE of the order of 90% between 500–600 nm. Short-circuit photocurrents exceeding 17 mA cm^{-2} 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%.⁶ These performances, in part expected for the high reducing ability of the $^3\text{MLCT}$ state (*ca.* -1 eV vs. SCE) and the positive ground-state oxidation potential ($+0.85 \text{ eV vs. SCE}$), contrast with the lower IPCE observed for other sensitizers having comparable ground and excited-state properties.¹⁴ This fact suggests that a peculiar molecular level property of the $\text{cis-[Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$ complex affects one of the key processes of the cell mechanism. This view is consistent with the results of photoelectron spectroscopy and INDO/S calculations, indicating that the d_π Ru orbitals interact strongly with the π orbitals of NCS, resulting in MO orbitals of mixed nature.¹⁵ In particular, the calculations show that the sulfur 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 $\text{TiO}_2/\text{Ru}^{\text{III}}\text{NCS}$ and I^- . This would lead to an increase in the rate constant of the reductive process (k_4 in Fig. 1), and as a consequence in IPCE.¹⁶

In an attempt to extend the spectral sensitivity of mononuclear dyes towards the red, new $\text{cis-[Ru}(5,5'\text{-dcbH}_2)_2(\text{X})_2]$ complexes based on the ligand 5,5'-dicarboxy-2,2'-bipyridine ($\text{X} = \text{Cl}^-$, NCS^- , CN^-) were synthesized.⁸ The change of the carboxylic function position from 4,4' to 5,5' causes a lowering of the energy of the π^* accepting orbitals. The absorption spectra of these species, which are dominated in the visible by $d_\pi\text{-}\pi^*(5,5'\text{-dcbH}_2)$ transitions, are thus red shifted with respect to those of the corresponding $[\text{Ru}(\text{dcbH}_2)_2(\text{X})_2]$ complexes, pointing towards a possible improvement in the photoelectrochemical performances of these dyes due to an increased spectral matching with the solar spectrum. To better understand the effects of this change, the electrochemical, spectroscopic and photoelectrochemical properties of these complexes were compared to those of the analogous species based on the dcbH_2 ligand. As expected, no differences were found in the $\text{Ru}^{\text{II/III}}$ oxidation potential for the corresponding species, suggesting that no significant perturbation of the d_π orbital energy of the metal occurs upon changes in the substituent position at the chromophoric ligand. On the contrary, a substantial decrease in the reduction potential of the chromophoric ligand was observed for the complex $[\text{Ru}(5,5'\text{-dcbH}_2)(\text{NCS})_2]$ with respect to $[\text{Ru}(4,4'\text{-dcbH}_2)(\text{NCS})_2]$, in agreement with the lower π^* energy for the former dye. The absorption spectra of the $[\text{Ru}(5,5'\text{-dcbH}_2)_2(\text{X})_2]$ complexes in DMF showed MLCT bands remarkably red shifted with respect to the corresponding $[\text{Ru}(4,4'\text{-dcbH}_2)_2(\text{X})_2]$ species. A sustained conversion of light to electricity was demonstrated with this new family of molecular devices achieving the goal of extending the photoelectrochemical cell responsivity to longer wavelengths.

Another strategy found in the literature to improve the light harvesting efficiency and sensitivity at longer wavelengths of

mononuclear sensitizers, is the introduction of phenyl groups in the chromophoric ligands.¹⁷ Kohle *et al.* reported the synthesis and properties of several Ru(II) complexes with 4,4'-dicarboxy-2,2'-bipyridine (dcbH₂) as anchoring ligand and containing 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (dmbip) or 2,6-bis(1-methylbenzimidazol-2-yl)-4-phenylpyridine (ph-dmbip), (Fig. 2), and monodentate ligands (X⁻ = Cl⁻, I⁻, NCS⁻, NCS²⁻, CN⁻).

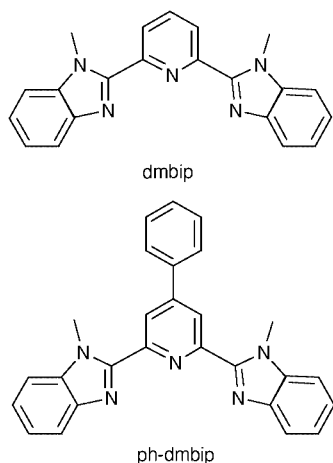


Fig. 2 Structural formulae of the ligands 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (dmbip) and 2,6-bis(1-methylbenzimidazol-2-yl)-4-phenylpyridine (ph-dmbip).

The introduction of phenyl groups in suitable positions of polypyridine ligands was known to determine an increase in the absorption coefficients of MLCT transitions. Moreover, a heavy atom ancillary ligand such as I⁻ was thought to increase the spin-orbit coupling constant of the complex leading to an enhancement of the spin-forbidden, low energy, singlet-triplet MLCT transitions. All the complexes were found to be less efficient sensitizers when compared to *cis*-[Ru(dcbH₂)₂(NCS)₂]. In particular, the halide complexes Na[Ru(dmbip)(dcbH)₂X] (X = Cl⁻, I⁻) gave a strongly reduced IPCE with respect to the corresponding thiocyanate dye. The thiocyanate group is a weaker σ donor compared to halide ions and determines a lower destabilization of the Ru(d_π) orbitals. This could increase the driving force for the reductive quenching of the oxidized dye by I⁻ ions (*k*₄) in the cell. However, the small difference observed in the oxidation potentials of the thiocyanate and iodo complexes did not explain the remarkable difference in IPCE. An interesting observation was the chemical and photochemical lability of the metal-halide bond in the presence of water. The aquo complex was found to inject electrons into TiO₂ more efficiently than the halide one. Despite the higher extinction coefficient and the similarity of ground-state redox properties, the phenylated complex [Ru(ph-dmbip)(dcbH)(NCS)] exhibited a lower IPCE with respect to [Ru(dmbip)(dcbH)(NCS)]. The observed IPCE was, however, quite high (60% at 520 nm).

As a complementary strategy to polypyridyl substitution, several attempts have been made to find suitable ancillary ligands for complexes of the type *cis*-[Ru(dcbH₂)₂X₂] in order to have better mononuclear ruthenium sensitizers. The complexes *cis*-[Ru(dcbH₂)₂(isq)₂] (isq = isoquinoline),¹⁸ *cis*-[Ru(dcbH₂)₂(ppy)₂] and *cis*-[Ru(dcbH₂)₂(H₂O)(ppy)]¹⁹ (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(dcbH₂)₂(H₂O)(ppy)]. In another study, dithiocarbamate ligands¹⁴ 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)(dcbH₂)(L)], where L

is diethyl dithiocarbamate, dibenzyl dithiocarbamate or pyrrolidine dithiocarbamate, have been synthesized, characterized and tested on TiO₂-based photoelectrochemical regenerative cells using [Ru(dcbH₂)₂(NCS)₂] as a reference compound. These dyes showed intense d_π-π* MLCT transitions in the visible with the lower energy band slightly red shifted with respect to the thiocyanate complex. Contrary to what was observed for [Ru(dcbH₂)₂(NCS)₂], the cyclic voltammetry of the dithiocarbamate complexes gave reversible waves both in the protonated and anionic forms testifying to 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/I₂ 0.05 M in acetonitrile gave IPCE values for the violet dyes consistently lower than the reference complex, being, on 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) were explored by nanosecond transient absorption spectroscopy. Absorption difference spectra recorded after 532 nm excitation of the complexes bound to TiO₂ in argon saturated 1 M LiClO₄-CH₃CN 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 > 10⁸ s⁻¹) 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⁻ concentrations. Stern-Volmer analysis of the integrated area under the absorption transients gave *K*_{SV} = 100 M⁻¹ for [Ru(dcbH₂)₂(NCS)₂] and *K*_{SV} = 30 M⁻¹ for the three dithiocarbamate sensitizers. The slower reduction rate of the oxidized dithiocarbamate species by I⁻ is thought to be consistent with the observed trend in IPCE values by virtue of a reduced charge collection efficiency η.¹⁶

A third possible way to design molecular sensitizers for photoelectrochemical applications is to extend the flexibility of MLCT and redox tuning of the complex properties by using mixed chromophoric ligands with well optimized π* energies, together with an appropriate choice of non chromophoric ancillary ligands. Examples found in the literature are complexes of the type [Ru(dmbip)(dcbH)X], [Ru(dmbip)(dcbiqH)X] and [Ru(dhbip)(dcbH)X] where dmbip = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine, dhbip = 2,6-bis(1-hexadecylbenzimidazol-2-yl)pyridine, dcbH₂ = 4,4'-dicarboxy-2,2'-bipyridine, dcbiqH₂ = 4,4'-dicarboxy-2,2'-biquinoline (Fig. 3) and X = Cl⁻, NCS⁻, CN⁻ or H₂O.²⁰

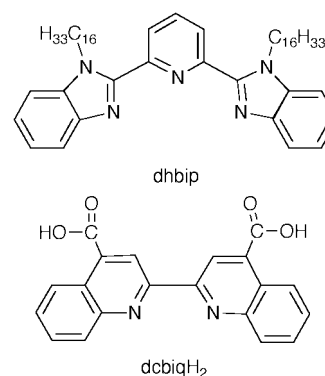


Fig. 3 Structural formulae of the ligands 2,6-bis(1-hexadecylbenzimidazol-2-yl)pyridine (dhbip) and 4,4'-dicarboxy-2,2'-biquinoline (dcbiqH₂).

The planar tridentate dmbip ligand behaves both as a strong σ donor (benzimidazole unit) and π-acceptor (pyridine rings) offering the choice of changing the substituents on the imidazole nitrogen to accomplish a fine tuning of ground- and

excited-state properties, as required. The low energy MLCT band is red shifted from 500 to 580 nm on changing the acceptor ligand from dcb to dcbiq. Resonance Raman spectroscopy experiments carried out on these compounds have identified the lowest energy MLCT state on the ligands bearing the carboxylic functionality (dcb or dcbiq). The cyclic voltammograms showed that the reductions are localized on the same ligands. Since these ligands are directly coupled to the semiconductor, a very efficient interfacial electron transfer is ensured. The photoelectrochemical properties measured by the IPCE efficiency appear to increase with increasing the excited-state reducing power, being maximum for $[\text{Ru}(\text{dmbip})(\text{dcb})(\text{H}_2\text{O})]$ (IPCE = 85%; $E[\text{Ru}(\text{III})/\text{Ru}^*] = -0.85$ V) and minimum for $[\text{Ru}(\text{dmbip})(\text{dcbiqH})(\text{NCS})]$ (IPCE \leq 10%; $E[\text{Ru}(\text{III})/\text{Ru}^*] = -0.23$ V). This and other evidence clearly demonstrates that the excited-state oxidation potential plays an important role in the electron transfer process.

The development of general synthetic procedures for the preparation of molecular sensitizers is of major importance for practical applications as well as for fundamental studies, and several efforts have been made to accomplish this task. An example is offered by the step by step synthesis of tris-heteroleptic Ru(II) of the type $[\text{Ru}(\text{dcbH})(\text{dmb})(\text{ddtc})]$ and $[\text{Ru}(\text{dcbH}_2)(\text{dmb})(\text{NCS})_2]$, where the ligands (dcbH₂ = 4,4'-dicarboxy-2,2'-bipyridine, dmb = 4,4'-dimethyl-2,2'-bipyridine and ddtc = diethyl dithiocarbamate) are introduced sequentially.²¹ The IPCE values were found in the range 30–50%, in agreement with our results obtained with similar compounds.¹⁴ A considerable increase in photocurrent conversion efficiency has been observed with $[\text{Ru}(\text{dcbH})(\text{dmb})(\text{ddtc})]$ in the presence of chenodeoxycholic acid as coadsorbant. This effect is interpreted in terms of the formation of aggregates of sensitizer molecules due to hydrogen bonding of the carboxy group and the nitrogen of the ddtc ligand or the stacking of bipyridine rings, in the absence of deoxycholic acid.²¹

The outstanding photoelectrochemical performances given by the mononuclear complex $[\text{Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$ have been recently surpassed by an analogous species based on the terpyridine ligand.²² TiO₂ electrodes covered with the complex $[\text{Ru}(\text{L})(\text{NCS})_3]$ (L = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine) displayed very efficient panchromatic sensitization covering the whole visible spectrum and extending the spectral response in the near IR region up to 920 nm, with maximum IPCE values comparable to that obtained with the dithiocyanate complex. Another species based on a substituted terpyridine is the mixed ligand complex $[\text{Ru}(\text{HP-terpy})(\text{dmb})(\text{NCS})]$ where P-terpy = 4-phosphonato-2,2':6,2''-terpyridine and dmb = 4,4'-dimethyl-2,2'-bipyridine.²³ A quantitative study of dye adsorption on TiO₂ has shown that complexes containing the phosphonated terpyridine ligand adsorb more efficiently and strongly, giving an adsorption constant about 80 times larger than that for the dicarboxy bipyridine compounds. 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, a search for a 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.²⁴ The photoaction spectra of TiO₂ electrodes sensitized with the $[\text{Ru}(\text{4-phenylboronic-2,2'-bipyridine})_2(\text{CN})_2]$ complex showed IPCE values comparable to those observed for $[\text{Ru}(\text{dcbH}_2)_2(\text{CN})_2]$,⁸ indicating that the new type of linkage does not reduce the electronic coupling between sensitizer and semiconductor.

4 Supramolecular sensitizers

Studies on sensitization of nanocrystalline TiO₂ with supramolecular species may provide fundamental insights into inter-

facial 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 (photosensitizer, P) and a covalently linked acceptor (A) or donor (D) component on a semiconductor surface, are shown schematically in Fig. 4.

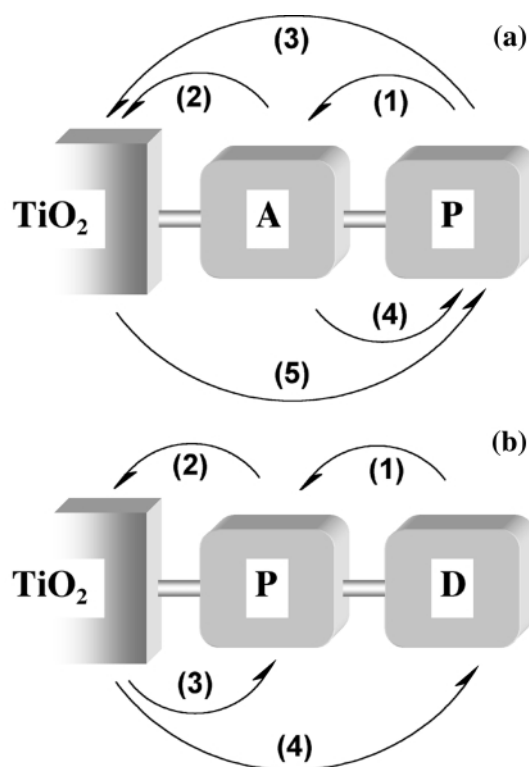


Fig. 4 Sequence of intramolecular and interfacial electron transfer processes involving dyad systems adsorbed on a semiconductor.

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 depicted in Fig. 4, several non-trivial 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 a 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 about 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 Fig. 4a) and the primary charge recombination process (4 in Fig. 4a). It is evident that a good deal of control of 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 Fig. 4 are designed to translate the electron-hole away from the surface and reduce the rate of electron-hole recombination (k_3 in Fig. 1), and thus increase the overall cell efficiency. In principle, an extension from dyads to larger systems can be envisioned keeping in mind

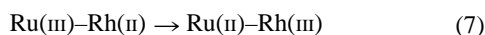
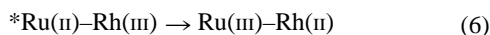
that each additional charge separation step will reduce the driving force which can be stored in the interfacial charge separated state.

In the following section a series of heterotriad systems based on TiO₂ nanocrystals, chromophoric unit, and a covalently bound electron donor or acceptor moiety, will be discussed. Besides these systems, we also studied several polynuclear complexes in which the sensitizer unit is connected to chromophoric moieties acting as antenna units. In this type of heterosupramolecular system we have observed remote charge injection, stepwise electron transfer, and an enhancement of the interfacial charge separation.

4.1 Ru(II)–Rh(III) polypyridine systems

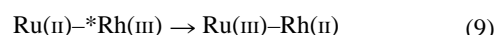
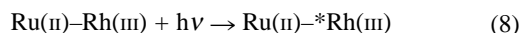
A first attempt to model a charge separating sensitizer of the type sketched in Fig. 4a is represented by the dyad and heterotriad shown in Fig. 5.²⁵ The dyad is hereafter indicated as Rh–Ru, where Ru represents the (4,4'-dimethyl-2,2'-bipyridine)bis(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) moiety and Rh represents the tris(4,4'-dimethyl-2,2'-bipyridine)rhodium(III) moiety. For the heterotriad we used the following systems: TiO₂–Rh'–Ru(dmb)₂ and TiO₂–Rh'–Ru(dmp)₂, where Ru(dmp)₂ represents bis(4,7-dimethyl-1,10-phenanthroline)ruthenium(II), Ru(dmb)₂ bis(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II), and Rh' represents the tris(4,4'-dicarboxy-2,2'-bipyridine)rhodium(III) moiety.

Both in the dyad and heterotriads the Ru unit was designed to play the role of P and the Rh unit that of A in Fig. 4a. Upon excitation of the Ru unit in the dyad, (eqn. (5)), the typical MLCT emission of this unit is strongly quenched with respect to that of a free Ru model, indicating the occurrence of efficient excited-state electron transfer (eqn. (6)).



An approximate value for the rate constant of this process ($\sim 1\text{--}2 \times 10^8 \text{ s}^{-1}$ in methanol) can be measured from the emission decay. Laser flash photolysis at 440 nm, corresponding to excitation of the Ru chromophore, did not show any transient accumulation of the electron transfer product. Therefore the back electron transfer process (eqn. (7), process (4), Fig. 4a) is faster than the forward reaction.²⁵

Upon laser excitation at 298 nm, corresponding to excitation of the Rh chromophore, a transient absorption difference spectrum of the electron transfer product is observed. This experiment shows that electron transfer from Ru to excited Rh (eqn. (9)), can also take place in this system ($k = 3 \times 10^{10} \text{ s}^{-1}$), and most usefully, yields a charge separated state with measurable lifetime ($\tau = 140 \text{ ps}$), unobtainable by excitation of the Ru moiety.



The kinetics of the three electron transfer steps can be qualitatively rationalized by standard electron transfer theory on the basis of the energetics of the system (Fig. 6).

The forward electron transfer following Rh excitation is much faster than that following Ru excitation, as both processes lie in the “normal” free energy region, and the former is much more exergonic than the latter. The fact that the back electron transfer process, which has a very large driving force, appears relatively slow (*e.g.*, slower than the forward process arising from the Rh localized excited-state) is most probably a result of the Marcus “inverted region” effect. The kinetics of the electron transfer process, involving the excited Ru chromophore and the covalently bound Rh(III) moiety (eqn. (6)), has also been studied for the systems Rh'–Ru(dmb)₂ and Rh'–Ru(dmp)₂ in solution. The observed rate constants of these processes were: $k = 3.3 \times 10^7 \text{ s}^{-1}$ for Rh'–Ru(dmb)₂ and $k = 2 \times 10^8 \text{ s}^{-1}$ for Rh'–Ru(dmp)₂. Also in these complexes the forward electron transfer (eqn. (5)) was slower than the recombination step (eqn. (7)), as shown by the lack of accumulation of the Ru(II)–Rh'(III) electron transfer product.

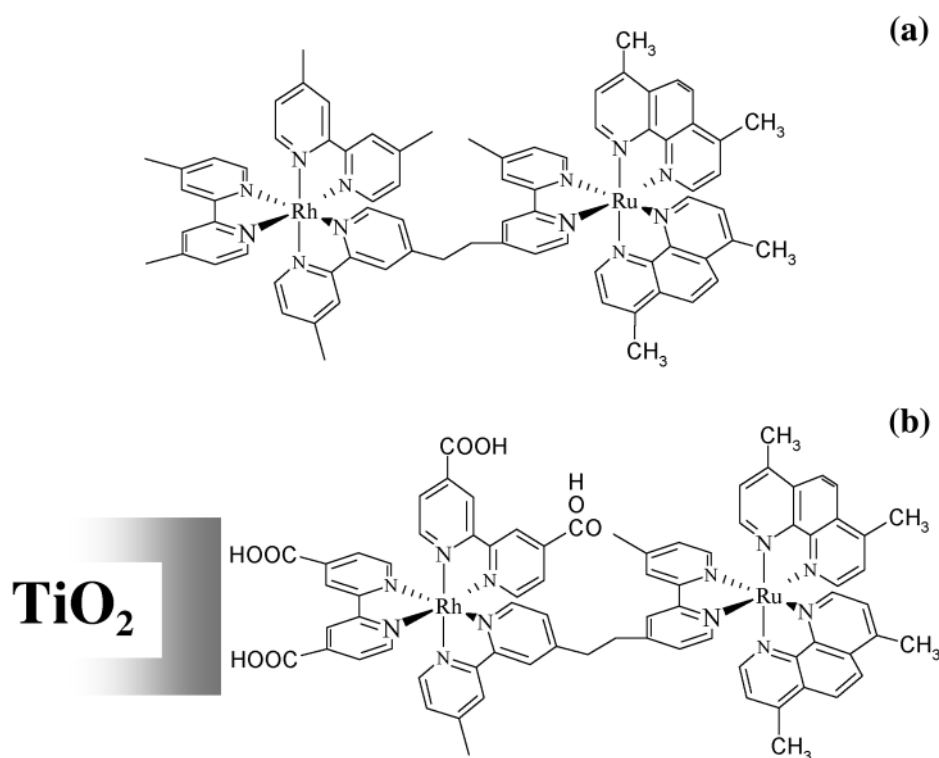


Fig. 5 Schematic structure of the complexes (a) Rh–Ru and (b) TiO₂–Rh'–Ru(dmp)₂.

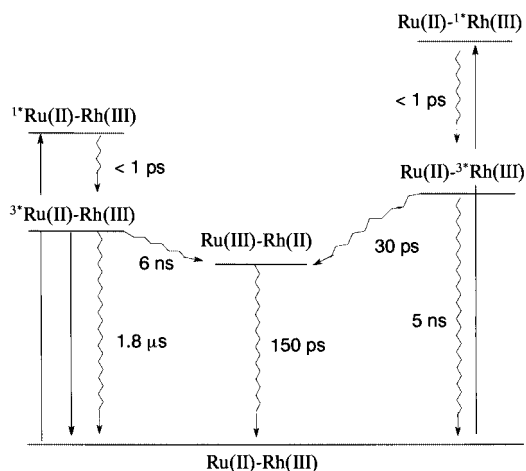


Fig. 6 Excited-state electron-transfer quenching processes in the Rh–Ru sensitizer.

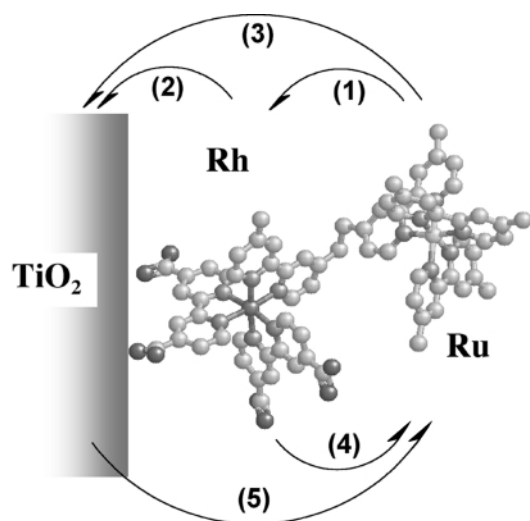


Fig. 7 Sequence of intramolecular and interfacial electron transfer processes in the TiO_2 -Rh–Ru system.

The photophysical behaviour of the heterosupramolecular systems TiO_2 -Rh'–Ru(dmb)₂ and TiO_2 -Rh'–Ru(dmp)₂ are shown schematically in Fig. 7. Besides the electron transfer processes (1) and (4), which can occur in the dyad, at least three new processes can be added, *e.g.* a stepwise charge injection to TiO_2 (1, 2), remote injection from the Ru moiety (3), and back electron transfer to a remote group (5).

A preliminary study showed that the Rh'–Ru dyads anchored to TiO_2 could be used as efficient sensitizers, giving rise to maximum IPCE values of the order of 40–50%. A detailed laser flash photolysis study showed that after excitation of the Ru-chromophore, the charge separated state $\text{TiO}_2(\text{e}^-)\text{-Rh'–Ru(III)}$ was formed.²⁶ Since the lifetimes of the residual emission from the Ru* moieties on TiO_2 were similar to those observed for the binuclear Rh'–Ru(dmb)₂* and Rh'–Ru(dmp)₂* species in solution, it was concluded that the charge injection process was mediated by the Rh centre, as shown in Fig. 7, processes (1) and (2). The lifetime of the charge separated state, $\text{TiO}_2(\text{e}^-)\text{-Rh'–Ru(III)}$, was *ca.* 200 ps. Within this lifetime, charge injection from the Rh' centre to TiO_2 occurs, resulting in the interfacial $\text{TiO}_2(\text{e}^-)\text{-Rh'–Ru(III)}$ charge separated state. This fast electron injection is in agreement with injection rates from mononuclear dye molecules ($k = 10^{12}\text{--}10^{13} \text{ s}^{-1}$).²⁷ The translation of the electron-hole, away from the surface, is expected to lead to an extended lifetime for the interfacial charge separated state as was indeed observed for the charge separated state $\text{TiO}_2(\text{e}^-)\text{-Rh'–Ru(III)}$ with respect to that of the model system $\text{TiO}_2(\text{e}^-)\text{-Ru(III)}$.²⁶

4.2 Ru(II) polypyridine–phenothiazine system

The alternative approach to vectorially translating the electron-hole away from the surface is by using a system of the type depicted in Fig. 4b. The dyad system, Ru–PTZ, which was prepared to model this function, is shown in Fig. 8. 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.²⁸

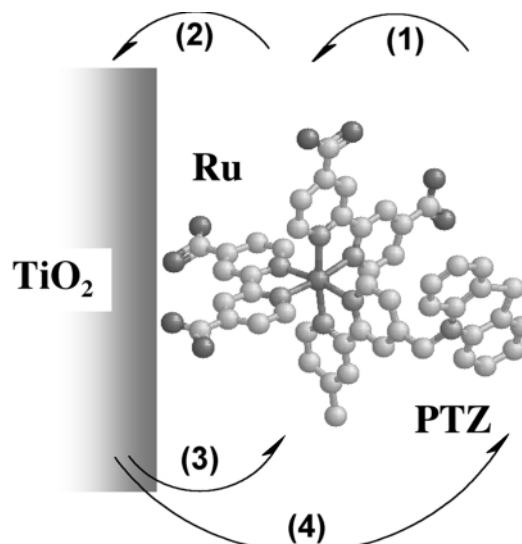


Fig. 8 Sequence of intramolecular and interfacial electron transfer processes in the TiO_2 -Ru–PTZ system.

Irradiation with visible light in solution results in the population of the Ru(III)(dcbH⁻)³MLCT excited-state, which is followed by reductive quenching of the excited-state by the PTZ moiety. The reductive quenching of the excited-state (Fig. 9) 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.

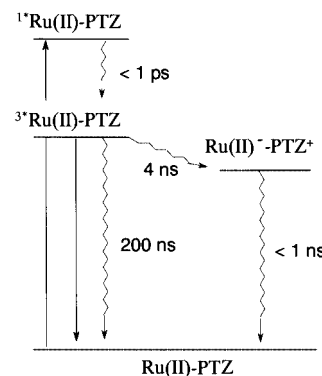


Fig. 9 Excited-state electron-transfer quenching processes in the Ru–PTZ sensitizer.

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_2 , excitation of the Ru chromophore can result in a new charge separated state, $\text{TiO}_2(\text{e}^-)\text{-Ru-PTZ}^+$. In principle there are two possible pathways available to reach this charge separation. In pathway (1) (Fig. 10), charge injection is followed by the charge shift to the donor, while in 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-

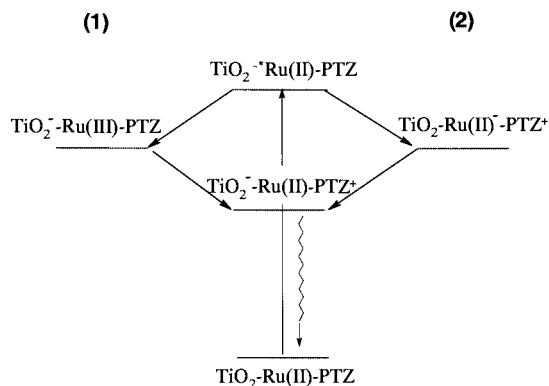


Fig. 10 Possible sequences of intramolecular and interfacial electron-transfer processes for the heteromolecular $\text{TiO}_2\text{-Ru-PTZ}$ system.

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 $\text{TiO}_2(\text{e}^-)\text{-Ru(II)-PTZ}^\bullet$. 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 $[\text{Ru}(\text{dmb})(\text{dcbH})_2]$ gives rise to the formation of the charge separated state $\text{TiO}_2(\text{e}^-)\text{-Ru(III)}$, whose recombination kinetics are complex and can be analysed by a distribution model, with an average rate constant of $k_3 = 3.9 \times 10^6 \text{ s}^{-1}$. Translating the hole from the Ru centre to the pendant PTZ moiety produces a delay in recombination rates (k_3) by three orders of magnitude.²⁸

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 (eqn. (3)) gave the predicted increase of V_{oc} of 200 mV, which was in agreement with the obtained value (180 mV).²⁸ It is therefore encouraging that an increase of the lifetime of the interfacial charge separated state $\text{TiO}_2(\text{e}^-)\text{-Ru(III)-PTZ}^\bullet$ has a direct influence on the overall efficiency of the cell.

4.3 Re(I)-Ru(II) polypyridine system

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 $(\text{CH}_2)_n$ spacers, such as those depicted in Fig. 11, were used in

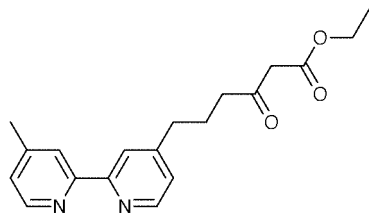


Fig. 11 Schematic structure of the ligand bpy-acac .

molecular dyes.²⁹ 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 Fig. 12. The binuclear compound is based on the $-\text{Re(I)}(\text{dcbH}_2)_2$ and $-\text{Ru(II)}(\text{bpy})_2$ moieties, undergoing ultra-fast and efficient photoinduced $\text{Re}^* \rightarrow \text{Ru}$ energy transfer.³⁰ Due to the facial geometry of the surface-bound Re-moiety, the $-\text{Ru}(\text{bpy})_2$ unit is forced to be close to the surface.

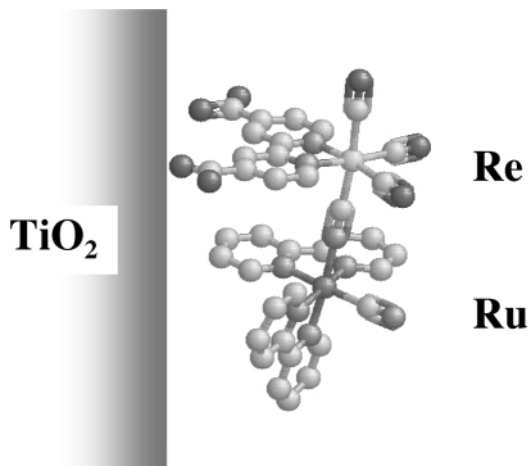


Fig. 12 Schematic structure of the $\text{TiO}_2\text{-Re-Ru}$ system.

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 $\text{TiO}_2(\text{e}^-)\text{/Re(I)-Ru(III)}$ 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 ($\text{bpy}^- \rightarrow \text{dcbH}_2$) electron hopping from $\text{Ru(III)}(\text{bpy}^-)$ to $\text{Re(I)}(\text{dcbH}_2)$, occurs within the laser pulse ($k > 5 \times 10^7 \text{ s}^{-1}$). 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 photo-physics of the binuclear complex $[\text{Ru}(\text{dcbH}_2)_2(\text{Cl})\text{-BPA-Os}(\text{bpy})_2\text{Cl}]^{2+}$ (BPA = 1,2-bis(4-pyridyl)ethane) on transparent TiO_2 films.³¹ At monolayer coverages the binuclear complex gives rise to ca. $\frac{1}{2}$ molecular adsorption with respect to the model complex $[\text{Ru}(\text{dcbH}_2)_2(\text{Cl})(\text{py})]^\bullet$, indicating that the binuclear complex lies on the nanocrystals of TiO_2 in a more or less extended conformation, as shown in Fig. 13a,c.

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 $\text{TiO}_2(\text{e}^-)\text{-Ru(II)-Os(III)}$. This state can either be formed through charge injection from the excited Ru chromophore followed by intramolecular $\text{Os(II)} \rightarrow \text{Ru(III)}$ electron transfer, or *via* remote electron transfer from the $^3\text{MLCT}$ excited-state localized on the $\text{Os}^{\text{II}}(\text{bpy})_2$ unit.

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.

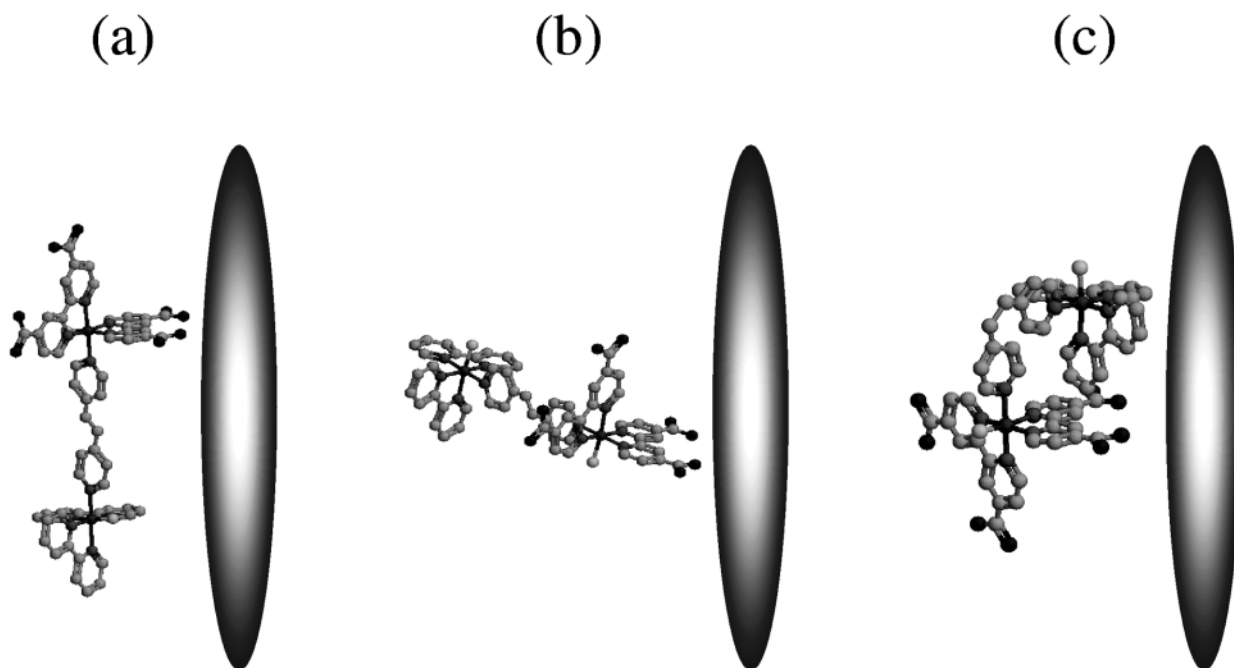


Fig. 13 Different orientations of the TiO_2 -Ru-Os system.

4.4 Antenna effect

As far as the antenna effect is concerned, different schemes can be conceived in order to increase the light harvesting efficiency on a semiconductor surface. Two simple prototypes, following the “branched” or “one-dimensional” design are shown schematically in Fig. 14.

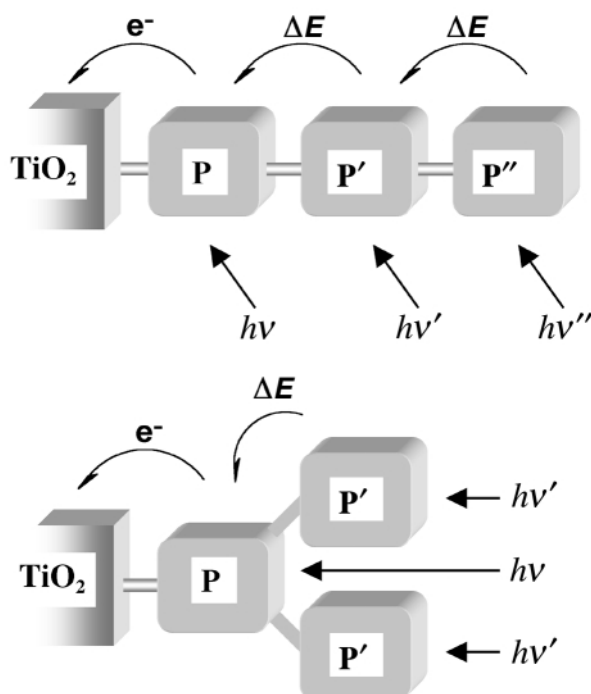


Fig. 14 Possible sequences of intramolecular and interfacial electron-transfer in linear and branched antenna systems adsorbed on a semiconductor.

Extension of the two types of design to larger antenna systems is intuitive. The obvious requisites for the supramolecular species to be used in such systems are: (i) an efficient antenna effect, leading the absorbed energy towards the

molecular component; (ii) the capability for the molecular component bound to the semiconductor surface, once excited, to inject electrons into the conduction band. For a supramolecular system considered as an independent photochemical molecular device, an obvious expectation is that “the larger the antenna system, the larger the light harvesting efficiency”. The same is not necessarily true for light-to-energy conversion on a semiconductor. A highly branched supramolecular system projects a much larger area than a simple molecular sensitizer onto the semiconductor surface. At saturation coverage, this would strongly reduce the gain represented by the antenna effect. From this point of view, the one-dimensional design would look superior to the branched one, as one could think of increasing the nuclearity of the supramolecular system without substantially increasing the occupied area.

The idea of using sensitizer–antenna molecular devices in the sensitization of semiconductors stems from the observed inefficiency of multilayers of adsorbed mononuclear sensitizers.¹⁰ In a first attempt to investigate the feasibility of such an approach, the $[(\text{NC})\text{Ru}(\text{bpy})_2(\text{CN})\text{Ru}(\text{dcbH}_2)_2(\text{NC})\text{Ru}(\text{bpy})_2(\text{CN})]^{2+}$ trinuclear complex has been developed.¹⁰

Efficient energy funneling from the peripheral chromophores to the central $-\text{Ru}(\text{dcb})_2-$ unit in this trinuclear complex was demonstrated by conventional photophysical experiments and by time-resolved resonance Raman.³² In experiments carried out using TiO_2 coated electrodes in aqueous solution at pH 3.5, photocurrents were obtained upon irradiation with visible light. The photoaction spectrum was observed to reproduce the absorption spectrum of the complex, indicating that the efficiency of absorbed light conversion is constant throughout the spectrum, regardless of whether the incident light is absorbed by the central unit or by the terminal ones. Subsequent experiments on this complex adsorbed on polycrystalline TiO_2 gave an overall conversion efficiency of *ca.* 7% with turnover numbers of at least five million without decomposition. Considerable efficiencies were also observed with related compounds containing $[\text{Ru}(4,4'\text{-X}_2\text{bpy})\text{Ru}(\text{CN})_2]$ ($\text{X} = \text{COOH}, \text{CH}_3, \text{C}_6\text{H}_5$) and phenanthroline-containing analogues, as lateral units.³³

The antenna effect is expected to be of relevance for applications requiring very thin TiO_2 layers. This is exemplified

by the comparison between the photoaction spectra of the mononuclear $[\text{Ru}(\text{dcbH}_2)(\text{CN})_4]^{2-}$ and of the trinuclear species $[\text{Ru}(\text{dcbH}_2)(\text{CN})_3(\text{CN})\text{Ru}(\text{bpy})_2(\text{CN})\text{Ru}(\text{bpy})_2(\text{CN})]$ shown in Fig. 15.

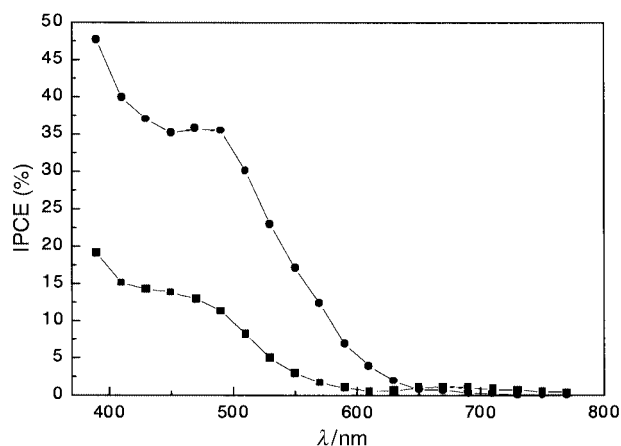


Fig. 15 Comparison between the photoaction spectra of $[\text{Ru}(\text{dcbH}_2)(\text{CN})_4]^{2-}$ (—■—) and $[\text{Ru}(\text{dcbH}_2)(\text{CN})_3(\text{CN})\text{Ru}(\text{bpy})_2(\text{CN})\text{Ru}(\text{bpy})_2(\text{CN})]$ (—●—).

Time resolved resonance Raman and emission spectroscopy show that energy transfer processes, from MLCT excited-states localized on the $\text{Ru}(\text{bpy})_2(\text{CN})$ chromophoric units to MLCT states localized on the $\text{Ru}(\text{dcbH}_2)(\text{CN})_3^-$ moiety, occur with unitary efficiency.³⁴ Fig. 15 shows the photoaction spectra of monolayers of the two molecular species on 2 μm thick TiO_2 photoanodes and the corresponding absorption spectra. It appears evident that the polynuclear sensitizer gives rise to higher photocurrents than the mononuclear species, as expected on the basis of the increased LHE term. Analogous observations were previously made by comparing the photoaction spectra of the mononuclear $[\text{Ru}(5,5'\text{-dcbH}_2)_2(\text{CN})_2]$ and of the trinuclear $[(\text{NC})\text{Ru}(\text{bpy})_2(\text{CN})\text{Ru}(5,5'\text{-dcbH}_2)_2(\text{CN})\text{Ru}(\text{bpy})_2(\text{CN})]^{2+}$ sensitizers.³² These results confirm that antenna-sensitizer complexes can be profitably used to increase the light harvesting efficiency of sensitized semiconductor materials.

5 Conclusions

Simple strategies for the design of mononuclear sensitizers and of artificial supramolecular systems, featuring functions such as photoinduced charge separation and the 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 pre-determined built-in functions can now be rationally designed and synthesized.

Upon functionalization in appropriate positions, molecular devices can be grafted onto the semiconductor surface and profitably used in the sensitization process. Studies on model systems suggest the possibility of preventing interfacial charge recombination in sensitized semiconductor cells, by taking 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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7 References

- 1 A. J. Bard, *J. Phys. Chem.*, 1982, **86**, 172.
- 2 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.
- 3 R. S. Wenham and M. A. Green, *Prog. Photovolt.*, 1996, **4**, 3.
- 4 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
- 5 G. Smestad, C. A. Bignozzi and R. Argazzi, *Sol. Energy Mater. Sol. Cells*, 1994, **32**, 259.
- 6 M. K. Nazeeruddin, A. Kay, L. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
- 7 H. Gerisher, *Photochem. Photobiol.*, 1972, **16**, 243.
- 8 R. Argazzi, C. A. Bignozzi, T. A. Heimer, F. N. Castellano and G. J. Meyer, *Inorg. Chem.*, 1994, **33**, 5741.
- 9 T. Gerfin, M. Grätzel and L. Walder, in *Molecular Level Artificial Photosynthetic Materials*, *Prog. Inorg. Chem.*, 1997, **44**, 345.
- 10 C. A. Bignozzi, J. R. Schoonover and F. Scandola, in *Molecular Level Artificial Photosynthetic Materials*, *Progr. Inorg. Chem.*, 1997, **44**, 1.
- 11 A. Kumar, P. G. Santangelo and N. S. Lewis, *J. Phys. Chem. B*, 1992, **96**, 834.
- 12 M. Grätzel, in *Semiconductor Nanoclusters, Studies in Surface Science and Catalysis*, P. V. Kamat and D. Meisel (eds.), Elsevier Science B.V., 1996, vol. 103, p. 353.
- 13 (a) S. Hotchandani and P. V. Kamat, *J. Phys. Chem.*, 1992, **96**, 6834; (b) D. Liu and P. V. Kamat, *J. Phys. Chem.*, 1993, **97**, 1076.
- 14 R. Argazzi, C. A. Bignozzi, G. M. Hasselmann and G. J. Meyer, *Inorg. Chem.*, 1998, **37**, 4533.
- 15 H. Rensmo, "Dye-Sensitized Nanostructured Metal Oxide Electrodes. Photoelectrochemical, Quantum Chemical and Electron Spectroscopic Studies", *Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology*, Uppsala, 1998, p. 372.
- 16 A. C. Lees, B. Evrard, T. E. Keyes, J. G. Vos, C. J. Kleverlaan, M. Alebbi and C. A. Bignozzi, *Eur. J. Chem.*, 1999, 2309.
- 17 O. Kohle, S. Ruile and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 4779.
- 18 C. G. Garcia, N. Y. Murakami Iha, R. Argazzi and C. A. Bignozzi, *J. Braz. Chem. Soc.*, 1998, **9**, 13.
- 19 C. G. Garcia, N. Y. Murakami Iha, R. Argazzi and C. A. Bignozzi, *J. Photochem. Photobiol.*, 1998, **115**, 239.
- 20 Md. K. Nazeeruddin, E. Muller, R. Humphry-Baker, N. Vlachopoulos and M. Grätzel, *J. Chem. Soc., Dalton Trans.*, 1997, 4571.
- 21 S. M. Zakeeruddin, Md. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel and V. Shklover, *Inorg. Chem.*, 1998, **37**, 5251.
- 22 Md. K. Nazeeruddin, P. Pechy and M. Grätzel, *Chem Commun.*, 1997, 1705.
- 23 S. M. Zakeeruddin, Md. K. Nazeeruddin, P. Pechy, F. P. Rotzinger, R. Humphry-Baker, K. Kalyanasundaram, M. Grätzel, V. Shklover and T. Haibach, *Inorg. Chem.*, 1997, **36**, 5937.
- 24 R. Argazzi, S. Bui, C. A. Bignozzi, L. De Cola and B. Schlicke, manuscript in preparation.
- 25 M. T. Indelli, C. A. Bignozzi, A. Harriman, J. R. Schoonover and F. Scandola, *J. Am. Chem. Soc.*, 1994, **116**, 3768.
- 26 C. J. Kleverlaan, M. T. Indelli, C. A. Bignozzi, F. Scandola and G. J. Meyer, *J. Am. Chem. Soc.*, submitted.
- 27 Y. Tachibana, J. E. Moser, M. Grätzel, D. R. Klug and J. R. Durrant, *J. Phys. Chem. B*, 1996, **100**, 20056.
- 28 R. Argazzi, C. A. Bignozzi, T. A. Heimer, F. N. Castellano and G. J. Meyer, *J. Phys. Chem. B*, 1997, **101**, 2591.
- 29 T. A. Heimer, S. T. D'Arcangelis, F. Fazzard, J. M. Stipkala and G. J. Meyer, *Inorg. Chem.*, 1996, **35**, 5319.
- 30 R. Argazzi, C. A. Bignozzi, T. A. Heimer and G. J. Meyer, *Inorg. Chem.*, 1997, **36**, 2.
- 31 M. Alebbi, C. Kleverlaan, C. A. Bignozzi, G. M. Hasselmann and G. J. Meyer, *Inorg. Chem.*, submitted.
- 32 C. A. Bignozzi, R. Argazzi, J. R. Schoonover, G. J. Meyer and F. Scandola, *Sol. Energy Mater. Sol. Cells*, 1995, **38**, 187.
- 33 M. K. Nazeeruddin, P. Liska, J. Moser, N. Vlachopoulos and M. Grätzel, *Helv. Chim. Acta*, 1990, **73**, 1788.
- 34 C. A. Bignozzi, R. Argazzi, M. T. Indelli, F. Scandola, J. R. Schoonover and G. J. Meyer, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1997, **109**, 397.