# Photoinduced electron transfer and redox-type photochromism of a $TiO_2$-anchored molecular diad

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**A linear, rigid molecular diad constituted of an electron donor (triarylamine, D) linked to a chromophore [Ru–bis(terpyridine), S] is synthesized; upon anchoring onto a nanocrystalline $TiO_2$ electrodes this produces a charge-separated state $D^{+}$–S $|(e^{-})$ $TiO_2$ under illumination decaying with $k = 7 \times 10^{7}$ $s^{-1}$ (70%), $3 \times 10^{5}$ $s^{-1}$ (20%) and $4 \times 10^{3}$ $s^{-1}$ (10%) and yielding a photochromic effect at positive polarization.**

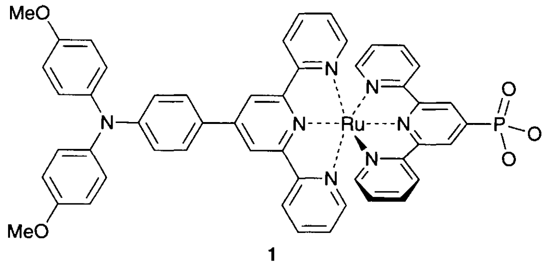
Light-induced charge separation exploiting molecular chromophores has followed two parallel paths. Extensive work has been carried out to synthesize molecular assemblies of donors, chromophores and acceptors (diads, triads, tetrads) to achieve charge separation in solution or in monolayers.[1] On the other hand, charge separation at chromophore–semiconductor interfaces has allowed the development of efficient photovoltaic systems.[2] Combining molecular and interfacial light-induced charge separation is expected to further improve the efficiency of the process.

Sauvage and coworkers observed efficient light-induced charge separation in the linear, rigid diad complex [(daap–terpy)Ru(ttp)]$^{2+}$, where daap–terpy = 4′-[(*N,N*-di-*p*-anisylamino)phenyl)]-2,2′ : 6′,2″-terpyridine and ttp = 4′-*p*-tolyl-2,2′ : 6′,2″-terpyridine.[3] In order to study the photoelectrochemical behaviour of a similar compound at a semiconducting interface, we have synthesized the diad **1**, in which the phosphonate group ensures strong adsorption on $TiO_2$.[4]

Photochromism is also a sought after property. The high absorption coefficient and good stability of oxidized triarylamines should allow light-induced modification of the absorption spectrum of the adsorbed diad **1** under positive polarization of the photoanode in reductant-free solution (redox-type photochromism). To our knowledge, the only related phenomenon described is UV-induced photochromism of Prussian blue on flat $TiO_2$.[5]

The molecular diad **1** [(daap–terpy)Ru(terpy–$PO_3$)] where terpy–$PO_3^{2-}$ = 2,2′ : 6′,2″-terpyridine-4′-phosphonate and the model compound **2** [(4,4′,4″-$Me_3$terpy)Ru(terpy–$PO_3H$)$^{+}$]-$ClO_4^{-}$ were prepared.†

The UV–VIS absorption spectrum of **1** in EtOH shows two ligand-centred absorption maxima at 274 nm ($\varepsilon$ = 45600 dm$^3$ mol$^{-1}$ cm$^{-1}$) and 311 (58300) and an MLCT band at 504 nm ($\varepsilon$ = 27700 dm$^3$ mol$^{-1}$ cm$^{-1}$). The substantial bathochromic–hyperchromic effect of the linked daap is seen by comparison with complex **2** ($\lambda_{max}$ = 482 nm, $\varepsilon$ = 15300 dm$^3$ mol$^{-1}$ cm$^{-1}$) and [Ru(daap–terpy)$_2$][$PF_6$]$_2$ (a byproduct of the synthesis of **1**) ($\lambda_{max}$ = 516 nm, $\varepsilon$ = 51000 dm$^3$ mol$^{-1}$ cm$^{-1}$). Electrochemical oxidation† of the daap moiety leads to weakening and blue-shifting of the MLCT band ($\lambda_{max}$ = 488 nm, $\varepsilon$ = 22500 dm$^3$ mol$^{-1}$ cm$^{-1}$). In parallel, an absorption band characteristic of a triarylamine radical cation develops at 750 nm, with $\varepsilon \geqslant$ 15600 dm$^3$ mol$^{-1}$ cm$^{-1}$.



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Cyclic voltammetry† shows two quasi-reversible oxidation waves, at 0.95 and 1.50 V *vs.* NHE, respectively assigned to the daap–daap$^{\cdot +}$ and the Ru$^{II}$–Ru$^{III}$ couples. The driving force for the daap $\rightarrow$ Ru$^{III}$ electron transfer is thus 0.55 V. A quasi-reversible wave, attributed to ligand reduction, appears at −1.09 V.

Resonance-Raman spectroscopy was used to elucidate the localization of the electron density upon excitation.[6] By selecting a wavelength $\lambda$ = 530.9 nm, just to red of $\lambda_{max}$ at 504 nm, RR shows a spectrum whose fingerprint in terms of peak positions is analogous to the daap–terpy ligand. At 415.4 nm, the RR spectrum shows predominant peaks that resemble the terpy–$PO_3$ ligand fingerprint. The lowest-energy MLCT corresponds to the daap–terpy ligand on the RR time-scale. When **1** is absorbed onto a nanocrystalline $TiO_2$ film‡ the RR clearly shows the same MLCT, at wavelengths even further to the red (568.2 nm) due to less experimental interference from the natural emission of the dye.

Laser flash photolysis was applied to $TiO_2$ nanocrystalline films‡ sensitized by adsorption of a monolayer of **2** (S) and **1** (D–S), respectively. Excitation at $\lambda$ = 430 nm by ns pulses resulted in the injection of electrons into the conduction band of the oxide and production of the oxidized dye at the surface [eqns. (1a) and (1b), respectively].

$$S^{*}\ |TiO_2 \rightarrow S^{+}|(e^{-})\ TiO_2 \tag{1a}$$

$$D\text{–}S^{*}\ |TiO_2 \rightarrow D\text{–}S^{+}\ |(e^{-})\ TiO_2 \tag{1b}$$

The charge-recombination process (2) for **1** and **2** is characterized by a slow, complex multiexponential kinetics in the 100 μs to ms time scale with $k = 3 \times 10^{5}$ $s^{-1}$ (80%) and $4 \times 10^{3}$ $s^{-1}$ (20%) components, identical for both compounds [eqns. (2a) and (2b), respectively].

$$S^{+}\ |(e^{-}_{cb})\ TiO_2 \rightarrow S\ |TiO_2 \tag{2a}$$

$$D\text{–}S^{+}\ |(e^{-}_{cb})\ TiO_2 \rightarrow D\text{–}S\ |TiO_2 \tag{2b}$$

For diad **1** in propylene carbonate, rapid oxidation of about half of the D moieties (estimated using the $\varepsilon$ values of **1** and oxidized **1** in solution) was observed within the laser pulse, yielding a large transient absorbance signal with $\lambda_{max}$ = 750 nm. It must be stressed that reaction (2b), being much slower, does not compete with (3). Alternatively, charge separation can take place *via* reductive quenching of S* by D before electron injection into $TiO_2$, following eqn. (4). Mechanisms (4) and (1a) + (3) cannot be distinguished, the process occurring within the laser pulse and leading to the same states.

$$\mathrm{D{-}S^+ \rightarrow D^+{-}S} \qquad (3)$$

$$\mathrm{D{-}S^* \,|TiO_2 \rightarrow D^+{-}S^- \,|TiO_2 \rightarrow D^+{-}S \,|(e^-_{cb})\, TiO_2} \qquad (4)$$

Reaction (3) is not observed when dry films are irradiated in air, indicating that the oxidation potential of D is quite sensitive to the environment. Adsorption of the dye on various sites of the oxide surface is likely to involve different surroundings, more or less favourable to the intramolecular electron transfer.

The back-electron transfer [eqn. (5)] from the conduction

$$\mathrm{D^+{-}S \,|(e^-_{cb})\, TiO_2 \rightarrow D{-}S|\, TiO_2} \qquad (5)$$

band to $D^+$ takes place with typically $k = 7 \times 10^7\ \mathrm{s^{-1}}$ (70%), $3 \times 10^5\ \mathrm{s^{-1}}$ (20%) and $4 \times 10^3\ \mathrm{s^{-1}}$ (10%) kinetic components. In an inverted region regime, the decrease of the driving force for charge recombination by 0.5 V and the build-up of a large solvent reorganization energy due to the amine moiety could explain why reaction (5) is faster than (2a) and (2b), in spite of the assumed longer separation.

In photovoltaic experiments,§ **1** and **2** gave similar incident photon-to-current efficiencies (IPCE) indicating efficient interception of both $S^+$ and $D^+$ by iodide.

Photochromism was expected with adsorbed diad **1** when recombination (5) is prevented by positive polarization of the supporting $TiO_2$ anode. Thus, $TiO_2$ film‡ on $SnO_2$ conducting glass, derivatized with **1**, was kept at +0.55 V in propylene carbonate or, better, the liquid salt 1-ethyl-3-methyl bis[(trifluoromethyl)sulfonyl]amide.[7] Under illumination with white light, the electrode absorption spectrum changed within a few seconds, with development of an absorption maximum at 750 nm, corresponding to the formation of $D^+$ (Fig. 1). The initial spectrum (S–D) was regenerated by applying a potential of −0.3 V. Several cycles were realized without modification of the respective spectra.

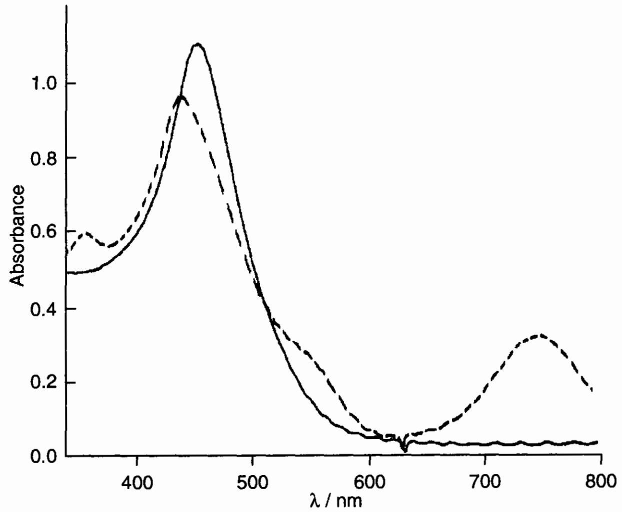

**Fig. 1** Photochromism of a nanocrystalline $TiO_2$ film‡ on $SnO_2$ conducting glass, derivatized with a monolayer of complex **1**. The photoanode immersed in 1-ethyl-3-methyl bis[(trifluoromethyl)sulfonyl]amide was kept at +0.55 V. The initial spectrum (D–S, —) changed under illumination to the $D^+$–S spectrum (---). The original spectrum was regenerated by applying a potential of −0.3 V to the $TiO_2$ electrode.

In conclusion, diad **1** did not allow more efficient charge separation at the $TiO_2$ surface, due to the very fast recombination reaction (5). However, it did allow the realization of photochromic electrodes with promising applications for information storage or smart windows. Research is in progress to synthesize diads with longer D–S distance and less coupling for longer $\mathrm{D^+{-}S\,|(e^-)\,TiO_2}$ charge-separated lifetimes and better charge separation in solar cells. Equally, diads are being produced which contain electrochromophores with higher absorptivity in the oxidized state, in order to further increase the photochromic effect.

The Swiss National Science Foundation and COST program are acknowledged for financial support.

## Footnotes

† Details concerning syntheses, analyses and electrochemistry will be given elsewhere.

‡ 7 μm thick, transparent, nanocrystalline $TiO_2$ film deposited on glass, roughness factor ≈ 700.

§ 1 mol $dm^{-3}$ LiI, 0.01 mol $dm^{-3}$ $LiI_3$ in propylene carbonate; solar cell as previously described.[2]

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*Received, 28th December 1995; Com. 5/08390G*