Preparation of Phosphonated Polypyridyl Ligands to anchor Transition-metal Complexes on Oxide Surfaces: Application for the Conversion of Light to Electricity with Nanocrystalline TiO_2 Films

Péter Péchy, François P. Rotzinger, Mohammed Khaja Nazeeruddin, Oliver Kohle,
Shaik Mohammed Zakeeruddin, Robin Humphry-Baker and Michael Grätzel*
Institut de Chimie Physique, Ecole polytechnique fèdèrale de Lausanne, CH-1015 Lausanne, Switzerland

To anchor transition-metal compounds onto metal oxide surfaces 2,2′:6′,2″-terpyridine-4′-phosphonic acid (4′-PO_3H_2-terpy) is synthesized; strong surface adhesion as well as efficient charge-transfer sensitization of nanocrystalline TiO_2 films has been observed with a ruthenium complex involving this ligand.

Grafting of redox-active molecules onto oxide surfaces through interlocking groups providing intimate electronic coupling between the metal centre and the semiconductor support is an important target in molecular electronics.[1–4] Recently, we described ruthenium complexes endowed with 4,4′-dicarboxy-2,2′-bipyridine ligands for the anchorage on to nanocrystalline TiO_2 films.[5] The adsorbed complex acts as a charge-transfer sensitizer injecting electrons in the conduction band of the oxide upon metal-to-ligand charge transfer (MLCT) photo-excitation. Very high incident photon-to-current conversion efficiencies approaching 100% have been achieved, but the sensitizer desorbs in aqueous solution above pH 5. The present study reports the synthesis and characterization of the diethyl ester of the novel ligand 2,2′:6′,2″-terpyridine-4′-phosphonic acid (4′-PO_3H_2-terpy), and the complex [Ru(4,4′-Me_2-2,2′-bipy)(4′-PO_3H-terpy)(NCS)] **1**. The phosphonate group strongly enhances the adsorption onto the TiO_2 surface and provides sufficient electronic coupling with the oxide to achieve efficient light-induced charge separation.

The preparation of diethyl-2,2′:6′,2″-terpyridine-4′-phosphonate† involved the phosphonation of 4′-bromo-2,2′:6′,2″-terpyridine‡ with diethyl phosphite in the presence of tetrakis(triphenylphosphino)palladium(0) and triethylamine. The reaction is a modification of Hirao's pyridine-3-phosphonic acid diethyl ester synthesis.[7]

The ruthenium complex **1** was synthesized as follows: an equimolar ratio of $RuCl_3 \cdot 3H_2O$ and 4′-PO_3Et_2-terpy refluxed in ethanol gave [Ru(4′-PO_3Et_2-terpy)Cl_3]. This compound was subsequently refluxed with 4,4′-dimethyl-2,2′-bipyridine in DMF, then the phosphonate functionality was hydrolysed by refluxing the product in dilute HCl yielding [Ru(4,4′-Me_2-2,2′-bipy)(4′-PO_3H_2-terpy)Cl]Cl. To the methanolic solution of the latter chloro complex an alkaline solution of NaNCS was added. [Ru(4,4′-Me_2-2,2′-bipy)(4′-PO_3H-terpy)(NCS)] **1** was isolated as a neutral complex at the isoelectric point by acidification with dilute aqueous trifluoromethanesulfonic acid. The resulting solid was thoroughly washed with acetone and dried under vacuum.§ Further experimental and spectral details will be given elsewhere.

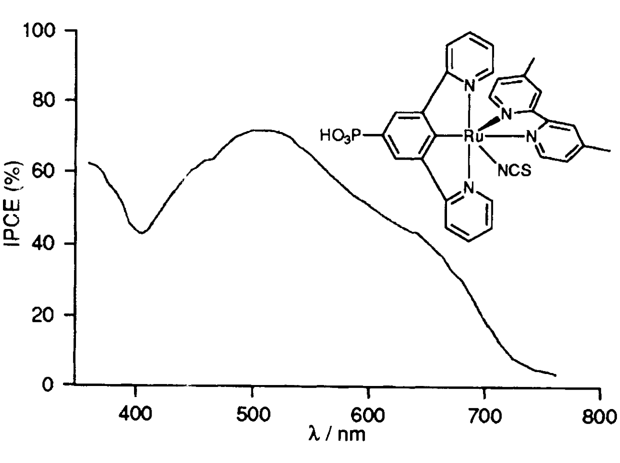

Fig. 1 Photocurrent action spectrum obtained with a nanocrystalline TiO_2 film supported onto a conducting glass sheet and derivatized with a monomolecular layer of complex **1**. The incident photon-to-current conversion efficiency is plotted as a function of wavelength. A sandwich-type cell configuration[5] was used to measure the spectrum; the redox electrolyte consisted of a solution of 0.5 mol dm^{-3} KI and 0.05 mol dm^{-3} KI_3 in ethylene carbonate and propylene carbonate mixture (50:50 *v*/*v*).

The UV–VIS absorption spectrum of complex **1** in ethanol shows an intense MLCT band[8] at 498 nm (ε = 8500 $dm^3\ mol^{-1}\ cm^{-1}$). Intraligand π–π^* charge-transfer absorption bands are located at 280 and 320 nm. Complex **1** luminesces in ethanol in the presence of alkali at pH 10 at room temp. ($\lambda_{em,max}$ = 708 nm, ϕ = 0.0044, τ = 15 ns). The excitation spectrum matches the absorption spectrum showing the complex to be free of any other emissive impurities. The emission quantum yield of complex **1** is one order of magnitude smaller than that of $[Ru(bipy)_3]^{2+}$. The cyclic voltammogram of [Ru(4,4′-Me_2-2,2′-bipy)(4′-PO_3H-terpy)(NCS)] shows a quasi-reversible oxidation wave at 0.86 V (*vs.* SCE, 100 mV s^{-1}, 0.1 mol dm^{-3} $NBu^t_4CF_3SO_3$ in Me_2SO).

A monolayer of complex **1** was adsorbed from a dilute solution in ethanol onto a *ca.* 8 μm thick nanocrystalline TiO_2 (anatase) film prepared as previously described.[5] The Langmuir adsorption constant was estimated to be 8×10^6 which is *ca.* 80 times larger than that obtained for [Ru{4,4′-$(CO_2H)_2$-2,2′-bipy}$_2$$(NCS)_2$] under similar conditions. Thus, one phosphonate group on the terpyridyl ligand shows much stronger adhesion of the complex than the four carboxylates of [Ru{4,4′-$(CO_2H)_2$-2,2′-bipy}$_2$$(NCS)_2$]. Important for practical applications is the fact that complex **1**, in contrast to the carboxylated analogues, does not desorb from the surface of the nanocrystalline TiO_2 film if this is exposed to water. The adsorbed state is maintained over a wide pH domain ranging from pH 0 to at least pH 9.

Despite its relatively short excited-state lifetime, complex **1** is an excellent charge-transfer sensitizer for nanocrystalline TiO_2 films. The photocurrent action spectrum is shown in Fig. 1 where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The broad feature covering a large part of the visible spectrum displays a maximum around 510 nm where the IPCE exceeds 70%. Taking into account the loss of photons through absorption and scattering by the conducting glass supporting the film, the conversion yield of photons to electric current is practically quantitative at this wavelength. These characteristics render the new phosphonated polypyridyl complexes very attractive for applications in molecular photovoltaic devices.

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Footnotes

† Yield (after column chromatography): 80.5%, mp 140–152 °C (ethanol). MS (EI): *m*/*z* (rel. int.) 369 (M^+, 29.1). ^1H NMR (200.00 MHz, $CDCl_3$): δ 1.35 (t, 6H, 7 Hz), 4.21 (m, 4H), 7.30 (ddd, 2H, 7.5,

5, 2 Hz), 7.82 (dt, 2H, 8, 2 Hz), 8.56 (d, 2H, 8 Hz), 8.68 (d, 2H, 4.5 Hz), 8.82 (d, 2H, $^3J_{P-H}$ = 14 Hz). ^{13}C NMR (50.29 MHz, $CDCl_3$): δ 16.29 (d, $^3J_{C-P}$ = 6 Hz), 62.58 (d, $^2J_{C-P}$ = 6 Hz), 121.11(s) 122.58 (d, $^2J_{C-P}$ = 10 Hz), 124.00(s), 136.70(s), 139.54 (d, $^1J_{C-P}$ = 186 Hz), 149.20(s), 155.27 (d, $^4J_{C-P}$ = 2 Hz), 155.79 (d, $^3J_{C-P}$ = 14 Hz). ^{31}P NMR (80.96 MHz, $CDCl_3$): δ 15,59.

‡ Bromination of 2,6-bis(2′-pyridyl)-4-pyridone[6] with $POBr_3$ gave 4′-bromo-2,2′ : 6′,2″-terpyridine in 80% yield (after column chromatography). ^{1}H NMR (200.00 MHz, $CDCl_3$): δ 7.38 (ddd, 2H, 7.6, 4.9, 1.2 Hz), 7.88 (dt, 2H, 7.9, 1.8 Hz), 8.59 (dt, 2H, 7.9, 0.9 Hz), 8.66 (s, 2H), 8.72 (ddd, 2H, 4.9, 1.8, 0.9 Hz). ^{13}C NMR (50.29 MHz, $CDCl_3$): δ 121.40(d), 124.20(d), 135.06(s), 136.93(d), 149.21(d), 154.96(s), 156.49(s).

§ ^{1}H NMR [200.00 MHz, $(CD_3)_2SO$]: δ 2.31 (3H, s), 2.74 (3H, s), 6.99 (2H, d, 5.8 Hz), 7.06 (d, 2H, 5.8 Hz), 7.39 (dd, 2H, 6.4 Hz), 7.65 (d, 2H, 5.0 Hz), 7.98 (m, 3H), 8.50 (s, 1H), 8.71 (s, 1H), 8.76 (d, 2H, 6.8 Hz), 8.95 (d, 2H, $^3J_{P-H}$ = 10.8 Hz), 9.38 (d, 1H, 5.8 Hz). ^{31}P NMR [$(CD_3)_2SO$]: δ 3.09.

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