# Efficient near IR sensitization of nanocrystalline $TiO_2$ films by ruthenium phthalocyanines

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**Bis(3,4-dicarboxypyridine)(1,4,8,11,15,18,22,25-octamethylphthalocyaninato)ruthenium(II) (JM3306) anchored to nanocrystalline $TiO_2$ films through the axial pyridine 3,4-dicarboxylic acid ligands is an efficient near IR sensitizer for photovoltaic injection cells based on nanocrystalline $TiO_2$ films.**

Nanocrystalline solar cells have attracted significant attention as low cost alternatives to conventional solid state photovoltaic devices.[1] The most successful charge transfer sensitizers employed so far in these cells are polypyridyl-type complexes of ruthenium[2,3] yielding overall AM 1.5 solar to electric power conversion efficiencies of up to 10–11% and stable operation for millions of turnovers.[4] In order to improve further the performance of these devices it is imperative to enhance their near IR response which is weak owing to the small absorption coefficient of such ruthenium complexes above 650 nm. Phthalocyanines possess intense absorption bands in the near IR region and are known for their excellent stability rendering them attractive for photovoltaic applications.[5] They have been repeatedly tested in the past as sensitizers of wide band gap oxide semiconductors.[6,7] However, poor incident photon to electric current conversion yields were obtained remaining under 1% with these systems which is insufficient for solar cell applications. Here we report on the use of ruthenium phthalocyanines (RuPC) as a charge transfer sensitizer. While RuPC derivatives have been tested as agents for photodynamic cancer therapy[8,9] they have not been employed as redox sensitizers so far. The choice of Ru as a central metal offers the advantage to attach the chromophore through axial ligands to the surface of the oxide semiconductor. Using 3,4-dicarboxypyridine to anchor the dye to mesoscopic $TiO_2$ films we have achieved for the first time strikingly high photocurrent yields with phthalocyanines exceeding 60% in the near-IR region.

Bis(3,4-dicarboxypyridine)(1,4,8,11,15,18,22,25-octamethylphthalocyaninato)ruthenium(II) (JM3306) was synthesized according to literature procedure[10] and isolated as $[(PCMe_8)Ru\{3,4\text{-py}(CO_2)_2H\}_2]\cdot 3THF$. Elemental analysis (calculated mass% in parentheses): C, 62.05 (62.11); H, 4.86 (4.86); N, 10.79 (10.98). The absorption and emission spectra of an ethanol solution of this dye are shown in Fig. 1. The absorption band in the visible [Fig. 1(*a*)] has a maximum at 650 nm ($\varepsilon$ = 49 000 $dm^3\ mol^{-1}\ cm^{-1}$) and that of the phosphorescence [Fig. 1(*b*)] is located at 895 nm the triplet state lifetime being 474 ± 5 ns under anaerobic conditions. The emission is entirely quenched [Fig. 1(*c*)] when JM3306 is adsorbed onto a nanocrystalline $TiO_2$ film. The dye was deposited by dipping a mesoscopic anatase film (thickness *ca.* 10 μm, coated onto conducting glass, LOF TEC 10, fluorine doped $SnO_2$ sheet resistance $10\ \Omega\ \square^{-1}$) as previously described[2] for several hours in a $2 \times 10^{-5}$ M solution in ethanol containing 40 mM 3α,7α-dihydroxy-5β-cholic acid (Cheno) and 2.5% $Me_2SO$. The presence of Cheno is necessary to avoid surface aggregation of the sensitizer. The vibible band in the absorption spectrum of JM3306 is red shifted by 10 nm upon adsorption.

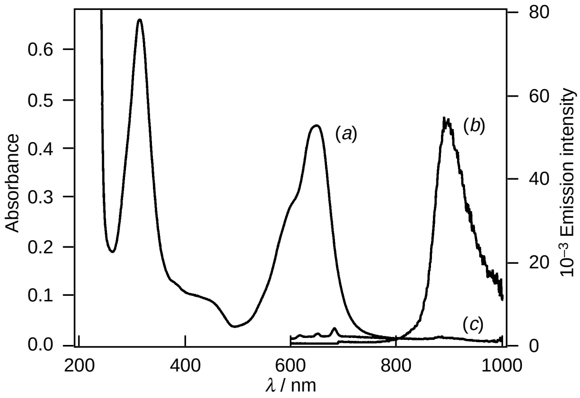

**Fig. 1** Absorption (*a*) and emission (*b*) spectra of JM3306 in ethanol, concentration = $9 \times 10^{-6}$ M; (*c*) quenched emission of JM3306 adsorbed onto the nanocrystalline $TiO_2$ film

The very efficient quenching of the emission of JM3306 was found to be due to electron injection from the excited triplet state of the phthalocyanine into the conduction band of the $TiO_2$. The photocurrent action spectrum is shown in Fig. 2 where the incident photon to current conversion efficiency (IPCE) is plotted as a function of wavelength. The feature is extending well into the near IR region displaying a maximum

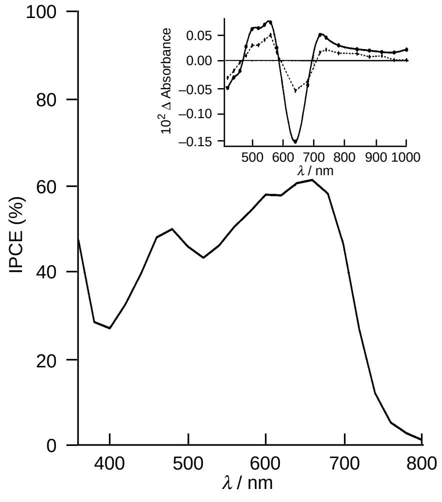

**Fig. 2** Photocurrent action spectrum obtained with a nanocrystalline $TiO_2$ film supported onto a conducting glass sheet and derivatized with a monolayer of JM3306 and coadsorbed with Cheno. The incident photon to current conversion efficiency is plotted as a function of wavelength. A sandwich type cell configuration was used to measure this spectrum. The redox electrolyte was 0.5 M LiI–0.05 M $LiI_3$ in propylene carbonate solvent. Insert shows the transient spectra of JM3306 on a $TiO_2$ film, at time slices of 8 and 32 μs after the 532 nm (0.3 mJ) exciting pulse from a Nd-YAG laser.

around 660 nm where the IPCE exceeds 60%. Despite the fact that the pyridyl orbitals do not participate in the π–π*-excitation which is responsible for the 650 nm absorption band of JM3306, electronic coupling of its excited state to the Ti 3d conduction band manifold is strong enough through this mode of attachment to render charge injection very efficient. Bignozzi and coworkers[11] achieved very recently sensitization of $TiO_2$ with ruthenium polypyridyl type complexes where the coupling of the MLCT excited state to the conduction band manifold was through space and did not involve the anchoring group.

The occurrence of electron transfer was further confirmed by time resolved nanosecond laser experiments shown in the inset of Fig. 2. The end of the pulse transient spectrum indicates bleaching of the ground state absorption of JM3306 and the appearance of new features in the wavelength range 700–800 and 480–580 nm. These bands are attributed to the formation of the cation radical of the phthalocyanine.[9] The recovery of the ground state specrum due to charge recombination occurs on a time scale of several hundred microseconds indicating that recapture of the conduction band electron by the oxidized dye is a relatively slow process.

Our results establish a new pathway for grafting phthalocyanines to oxide surfaces through axially attached pyridine ligands. Using such a film in a sandwich type cell configuration[2] in conjunction with a 1 $\text{M}$ LiI–0.05 $\text{M}$ $LiI_3$ redox electrolyte photocurrents close to 10 mA $cm^{-2}$ were readily obtained under simulated AM 1.5 solar radiation. These are by far the highest conversion efficiencies obtained with phthalocyanine type sensitizers. These findings open up new avenues for improving the near IR response of our nanocrystalline injection solar cell. In addition, important applications can be foreseen for the development of photovoltaic windows transmitting part of the visible light. Such devices would remain transparent to the eye, while absorbing enough solar photons in the near IR to render efficiencies acceptable for practical applications.

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## Notes and References

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