

Comment on “Measurement of Ultrafast Photoinduced Electron Transfer from Chemically Anchored Ru–Dye Molecules into Empty Electronic States in a Colloidal Anatase TiO₂ Film”

Jacques E. Moser,^{*,†} Dimitrios Noukakis,^{‡,§}
 Udo Bach,[†] Yasuhiro Tachibana,[‡] David R. Klug,[‡]
 James R. Durrant,[‡] Robin Humphry-Baker,[†] and
 Michael Grätzel[†]

Laboratory for Photonics and Interfaces, Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland, and Centre for Photomolecular Sciences, Departments of Biochemistry and Chemistry, Imperial College, London SW7 2AY, U.K.

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In a recent Letter published in this journal, Willig et al. reported on the ultrafast electron transfer from photoexcited ruthenium(II) *cis*-di(isothiocyanato)bis(4,4'-dicarboxy-2,2'-bipyridyl),¹ (N3), into titania. This dye has attracted wide attention as a highly efficient charge-transfer sensitizer for mesoporous TiO₂ films.² A key element of Willig et al.'s results was the determination of the absorption spectrum of the one-electron oxidation product of Ru(II)(dcbpy)₂(NCS)₂ which was produced by chemical reaction of N3 with oxidants, such as Br₂, and was reported to peak at 440 nm with negligible near-infrared absorption.

The apparent stability of this species identified as the [Ru(III)(dcbpy)₂(NCS)₂]⁺ cation by Willig et al. in ethanol is at variance with earlier electrochemical studies of the Ru(II)-(dcbpy)₂(NCS)₂/Ru(III)(dcbpy)₂(NCS)₂ redox system in organic solvents where a reversible wave in the cyclic voltammetry was obtained only at high scan rates, yielding for the oxidized Ru(III)(dcbpy)₂(NCS)₂ complex a lifetime of 0.1–1 s, depending on the degree of protonation of the carboxyl substituents.³

The assignment of the 440 nm spectral feature to the Ru(III)(dcbpy)₂(NCS)₂ cation in ref 1 is also in contradiction with laser photolysis data obtained earlier by Durrant et al. which show this species to exhibit a broad near-IR absorption, probably originating from a LMCT transition with a maximum close to $\lambda = 800$ nm.⁴

In view of this controversy, we have scrutinized our earlier results and carried out further experimental verifications which we present here. Our data demonstrate unambiguously that the conclusions of Willig et al. are erroneous and that the data reported by these authors have likely been obtained with samples of degraded sensitizer.

Instead of abstracting an electron from the Ru(II) center, powerful oxidants such as bromine react with N3 by chemical attack of the thiocyanato ligand. The reason for this is the high (0.85 V/SCE) redox potential for the Ru(II)/Ru(III) couple in N3 which is close to that of the –NCS ligand, favoring attack of the latter by the oxidant. The oxidation of –NCS by bromine has been studied by Werner at the beginning of the century, using thiocyanato complexes of Co(III) which is isoelectronic

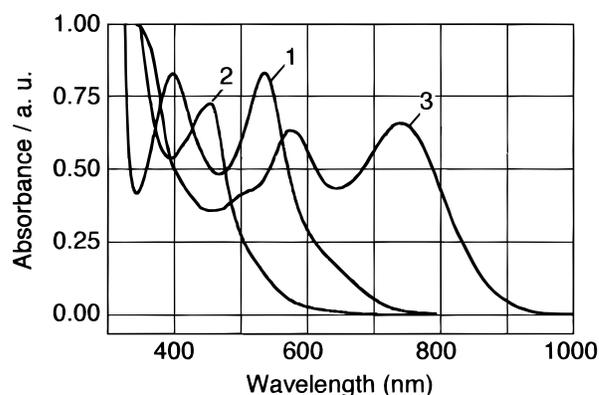


Figure 1. Absorption spectra of the original Ru(II)(dcbpy)₂(NCS)₂ dye in ethanolic solution (1) and of the reaction product of the oxidation of the complex by Br₂ (2). Absorption spectrum (3) is that of the first oxidation product of the uncarboxylated analogue Ru(II)(bpy)₂(NCS)₂ by Ce(IV) in acetonitrile.

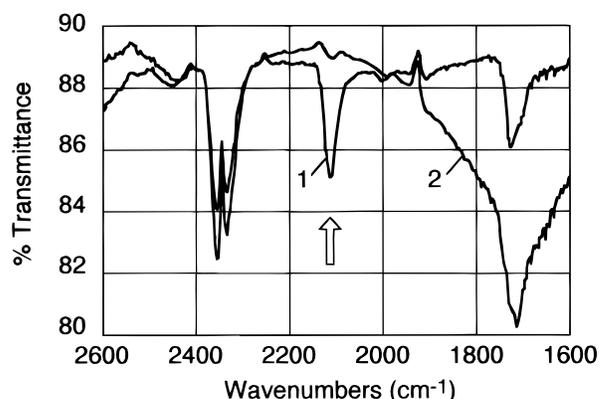


Figure 2. FTIR liquid film spectra of ethanolic solutions of the Ru(II)(dcbpy)₂(NCS)₂ complex dye (1) and of the yellow product (absorption maximum at 440 nm) of the oxidation of N3 by bromine (2). Disappearance of the C≡N bond stretch characteristic band at 2139 cm⁻¹ indicates that the original isothiocyanato ligands of the sensitizer have been decomposed.

with Ru(II).⁵ Cleavage of the C≡N bond was observed yielding amino complexes. A similar decomposition of the –NCS ligands in the presence of strong oxidants is also expected to occur in the case of N3.

Similar to Willig et al., we obtain a yellow product upon oxidation of Ru(II)(dcbpy)₂(NCS)₂ in ethanol by a number of oxidants, i.e., Br₂, LiOCl, NOBF₄, WCl₆, or Ce(NH₄)₂(NO₃)₆ (Figure 1). The coloration of the solution at this stage is not stable and evolves within seconds (or minutes, depending on the excess of oxidant added) to yield a spectrum which is similar to that of the original N3 dye. The IR spectra of the latter stable compound and of the yellow oxidized product clearly indicate the absence of the characteristic SCN band at 2139 cm⁻¹ (Figure 2), confirming that cleavage of the C≡N bond has taken place quantitatively upon chemical oxidation of the dye. Therefore, attribution by Willig et al. of the 440 nm absorption of the product formed by bromine oxidation of N3 to Ru(III)(dcbpy)₂(NCS)₂ is erroneous.

The uncarboxylated analogue of N3, Ru(II)(bpy)₂(NCS)₂, is a complex which, due to its lower oxidation potential (0.5 V/SCE), is less prone to decomposition of the thiocyanato ligand by chemical oxidants. Except for a 20 nm blue shift of its

* Corresponding author. E-mail: je.moser@epfl.ch.

† Present address: Elsevier Science S.A., 1003 Lausanne, Switzerland.

‡ Ecole Polytechnique Fédérale.

§ Imperial College.

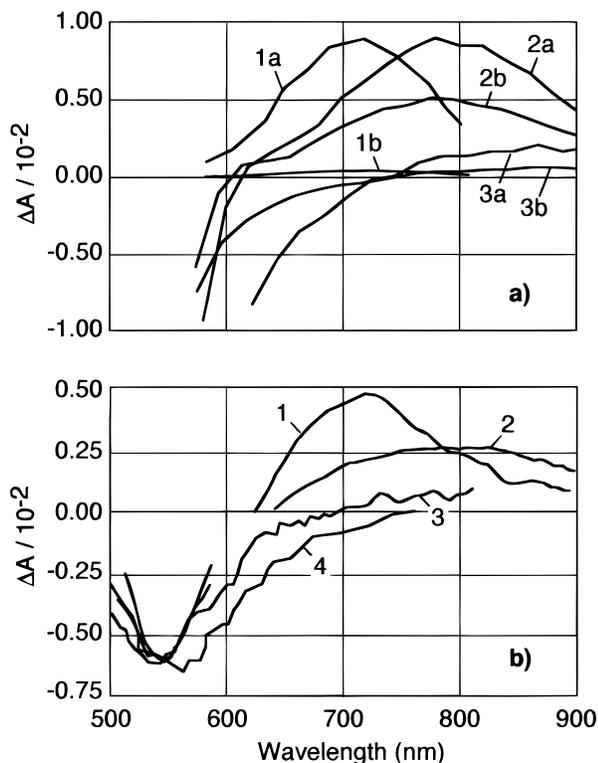


Figure 3. (a) Transient absorption spectra obtained upon nanosecond pulsed laser excitation of Ru(II)(dcbpy)₂(NCS)₂ dye in ethanolic solution (1), of a fresh N3-sensitized TiO₂ transparent film (2), and of the same dye-loaded titania sample after storage for 1 day in the air (3). Spectra were recorded 50 ns (1a, 2a, 3a) and 0.5 μs (1b, 2b, 3b) after the laser excitation pulse ($\lambda = 600$ nm, 5 ns duration) was applied. (b) Transient absorption spectra recorded 6 ps after ultrafast laser excitation ($\lambda = 600$ nm, 150 fs pulse duration) of Ru(II)(dcbpy)₂(NCS)₂ dye in ethanolic solution (1), of a fresh N3-sensitized TiO₂ transparent film (2),⁴ and of a similar dye-loaded titania sample after degradation upon storage for several days in the air (3). The transient spectrum reported by Willig et al.¹ is displayed for comparison (4). All spectra are scaled to the same absorption change at $\lambda = 550$ nm.

absorption bands compared to N3, spectral properties of this compound and of its oxidized form are not likely to be affected significantly by the lack of carboxylic substituents on the bipyridyl ligands. The controlled oxidation by Ce^{IV}(NH₄)₂(NO₃)₆ (10⁻² M in CH₃CN) of this analogue complex in acetonitrile leads in effect to a blue product, the optical spectrum of which is characterized by a broad absorption band with maxima at 578 and 746 nm (Figure 1). While this blue compound is clearly the first oxidation step product of Ru(II)(bpy)₂(NCS)₂, further addition of ceric salt produces the discoloration of the solution and appearance of the familiar yellow color (absorption maximum at 428 nm).

The observed broad absorption band peaking at 746 nm, which is assigned to the [Ru(III)(bpy)₂(NCS)₂]⁺ cation, is comparable to the spectral feature obtained in transient spectra recorded upon laser excitation of fresh N3-sensitized TiO₂ films (Figure 3), whose band peaking around 780–800 nm has been attributed in ref 4 to a LMCT transition of the -NCS ligands to the Ru(III) metal center in the Ru(III)(dcbpy)₂(NCS)₂ oxidized form. This LMCT transition is shifted ca. 80 nm to the blue to $\lambda \approx 720$ nm for the MLCT excited state of the dye. Therefore, as discussed previously,⁴ the N3 dye cation and excited state

can be readily distinguished by the position of this absorption band. Nanosecond transient spectra (Figure 3a) show moreover that the signal corresponding to the N3⁺ species formed upon electron injection into the conduction band of TiO₂ is characterized by a lifetime exceeding 0.5 μs, which is more than 1 order of magnitude longer than that of the dye excited state in solution ($\tau \approx 50$ ns).²

Degradation of Ru(II)(dcbpy)₂(NCS)₂ adsorbed on dry TiO₂ films has been observed in the dark leading to a slight blue shift of the sample absorption. The decomposition of the dye is significantly accelerated by visible light irradiation and by the presence of acidic centers at the surface. In high vacuum the TiO₂ surface is expected to dehydroxylate forming coordinatively unsaturated Ti(IV) ions that act as Lewis acids. Surface acidity is further augmented by the protons released by adsorption of N3 dye molecules. These acid centers are likely to be the cause of irreversible N3 oxidation under high-vacuum conditions used by Willig et al. Wetting of the dyed oxide surface by a solvent is expected to attenuate these effects and indeed allows to keep samples in the laboratory environment for days without noticeable degradation. Results obtained by application of various analytical techniques to the degraded samples are consistent with the transformation of the original dye into the stable Ru(II)(dcbpy)₂(CN)₂ complex through sulfur loss and isomerization.^{6,7}

Transient spectra recorded upon nanosecond and subpicosecond laser excitation of samples stored for a few hours in air, and whose sensitizer is partially degraded, are drastically different from those obtained with fresh samples (Figure 3). Degradation of the sensitizer results in a loss of the characteristic 800 nm absorption increase assigned to a LMCT transition from the dye's -NCS groups and thus to a shift of the isosbestic point toward the red to $\lambda \approx 750$ nm. This loss of the LMCT transition is consistent with our conclusion above that dye degradation is associated specifically with modifications to the thiocyanato ligands.⁸

The similarity of the spectra we have obtained with degraded samples and those measured by Willig et al. (Figure 3b) is striking and strongly suggests that the data reported by these authors are in fact obtained from a degraded form of the original Ru(II)(dcbpy)₂(NCS)₂ sensitizer.

References and Notes

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- (8) This transient spectrum is also consistent with the transformation of the original N3 dye into Ru(II)(dcbpy)₂(CN)₂. Contrary to Ru(II)(dcbpy)₂(NCS)₂, the dicyano complex does not exhibit a LMCT transition band in the near-IR in its MLCT excited state, nor in its Ru(III) oxidized form.