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Stability of the oxidized form of RuLL'(NCS)₂ dyes in acetonitrile in the presence of water and pyridines – Why the Dye-sensitized solar cell electrolyte should be dry.

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Abstract

The detrimental effect of electrolyte water contamination on the light-soaking lifetime of Dye-sensitized Solar Cells (DSCs) prepared with RuLL'(NCS)₂ dyes and N-additives like 4-*tert*-butylpyridine (TBP) is not well understood. A new explanation is presented based on investigation of the stability of the ruthenium(III) complexes Ru(bipy)₂(NCS)₂⁺ (**1**⁺) and RuLL'(NCS)₂⁺ (L = 4,4'-dicarboxy-2,2'-bipyridine, L' = 4,4'-nonyl-2,2'-bipyridine) (Z907⁺) in acetonitrile in the presence of water and pyridines covering a large variation in basicity. **1**⁺ reacts with small amounts of water in the acetonitrile containing a pyridine base (X) according to the overall reaction: 6 Ru(bipy)₂(NCS)₂⁺ + 4 H₂O + 8 X → 5 Ru(bipy)₂(NCS)₂ + Ru(bipy)₂(NCS)(CN) + SO₄²⁻ + 8 XH⁺. The reaction mechanism of **1**⁺ (and Z907⁺) is proposed to be initiated by an attack of OH⁻ giving Ru(bipy)₂(NCS)(NCS-OH). The stronger the base the faster the reaction. Extrapolating the life time of Z907⁺ to a typical TBP concentration of 0.5 M in the DSC gives a degradation rate around 7 s⁻¹. Z907⁺ bound to a layer of nano crystalline TiO₂ surface reacted fast too, when inserted in an acetonitrile solution containing 4-*tert*-butylpyridine. In a “wet” electrolyte, containing more than 500 mM of water the light-soaking lifetime of a DSC prepared with Z907 is predicted to be about 10 days at out-door light soaking

conditions, whereas trace amounts of water (< 25 mM) in a “dry” electrolyte is used up by consumption of only 10% of the Z907 in a typical DSC. Therefore, the DSC is expected to have a long light-soaking lifetime with a “dry” electrolyte.

Introduction

Ruthenium bipyridine complexes with the general composition $\text{RuLL}'(\text{NCS})_2$ e.g. Z907 (see Fig. 1) have been widely used as sensitizers in Dye-sensitized Solar Cells (DSCs) (Hagfeldt et al. 2010; Gratzel 2009; Cao et al. 2009; Kohle et al. 1997), since the introduction of *cis*-di(thiocyanato)bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (N3) in 1993 (Nazeeruddin et al. 1993). The popularity is due to high light to electricity efficiencies (up to 11%) (Chiba et al. 2006) and high light-soaking stabilities of DSCs prepared with this class of ruthenium dyes (Wang et al. 2005; Harikisun and Desilvestro 2011). However, the light-soaking performance and stability depends on the composition of the DSC electrolyte (Nakade et al. 2005; Wang et al. 2005; Lenzmann and Kroon 2007). The “classic” DSC electrolyte is comprised of a mixture of a nitrile solvent e.g. 3-methoxypropionitrile plus an ion-liquid together with iodide/iodine as redox mediator and a N-additive e.g. 4-*tert*-butylpyridine to enhance the light to electricity efficiency (Hinsch et al. 2001). Several reports have demonstrated that water in the electrolyte may decrease the light-soaking stability of the DSC (Bella et al. 2015; Lu, Lee, et al. 2011; Lu, Shen, et al. 2011). The harmful effect of water has been explained by hydrolytic cleavage of the dyes from the TiO_2 anode (Greijer, Lindgren, and Hagfeldt 2003), replacement of a SCN^- ligand with OH^- ions (Greijer, Lindgren, and Hagfeldt 2003) and reaction of water with iodide to form IO_3^- (Barkschat et al. 2008; Grunwald and Tributsch 1997). The proposed explanations have been questioned (Bella et al. 2015) and no mechanism is well accepted. In this work it is investigated how water and the added pyridine influence the stability of the $[\text{RuLL}'(\text{NCS})_2]^+$ ion.

The oxidized form of the sensitizer $[\text{RuLL}'(\text{NCS})_2]^+$ is a key intermediate in the DSC cell cycle. (Fig. 1). In order for the DSC to be able to function for 20 years under normal outdoor light conditions every sensitizer molecules should be able to sustain 1×10^8 cell (Grätzel 2006). The turn-over number N can be calculated from eq. (1), where k_{reg} is the rate of regeneration of $\text{RuLL}'(\text{NCS})_2$ from $[\text{RuLL}'(\text{NCS})_2]^+$ by the mediator e.g. I^- and k_{deg} is the rate of degradation of $[\text{RuLL}'(\text{NCS})_2]^+$.

$$N = k_{\text{reg}}/k_{\text{deg}} \quad (1)$$

Grätzel has performed an experiment in which the ruthenium(II) complex Z907 without any addition of N-additives was oxidized in acetonitrile by NOBF_4 to Z907^+ and obtained a lifetime of Z907^+ equal to 75 min indicating a turn-over number $N \gg 1 \times 10^8$ (Grätzel 2006).

The oxidation chemistry of $\text{RuLL}'(\text{NCS})_2$ complexes has been investigated by several authors (Kohle et al. 1997; Wolfbauer, Bond, and MacFarlane 1999; Cecchet et al. 2002; Hansen, Gervang, and Lund 2003; Nour-Mohammadi et al. 2007; Nour-Mohhamadi et al. 2005) and it is well recognized that both electrochemical (Hansen, Gervang, and Lund 2003; Wolfbauer, Bond, and MacFarlane 1999) and chemical oxidation of $\text{RuLL}'(\text{NCS})_2$ (Kohle et al. 1997) partially leads to oxidation of one or both of the thiocyanate ligands to cyanide. No detailed investigation of the exact stoichiometry of the oxidation reaction including the fate of the eliminated sulphur has been presented. Except for the lifetime study of Z907^+ (Grätzel 2006) very little, if any, information has been published on $[\text{RuLL}'(\text{NCS})_2]^+$ degradation rates in the presence of N-additives and impurities of water.

In the present work $\text{Ru}(\text{bipy})_2(\text{NCS})_2$, **1**, (Fig. 1) was selected as a model compound of the $\text{RuLL}'(\text{NCS})_2$ DSC complexes due to the reasonably high solubility of **1** in acetonitrile. We have investigated the degradation chemistry and kinetics of **1**⁺ and Z907^+ in acetonitrile solutions in the presence of the six different pyridine derivatives shown in Fig. 1, covering a wide basicity range. Finally, the reactivity of Z907^+ attached to a TiO_2 photo anode was studied by insertion into an

acetonitrile solution containing various pyridine derivatives. The results are summarized with an estimate of the lifetime of a DSC prepared with the Z907 dye as a function of the amount of water in the electrolyte.

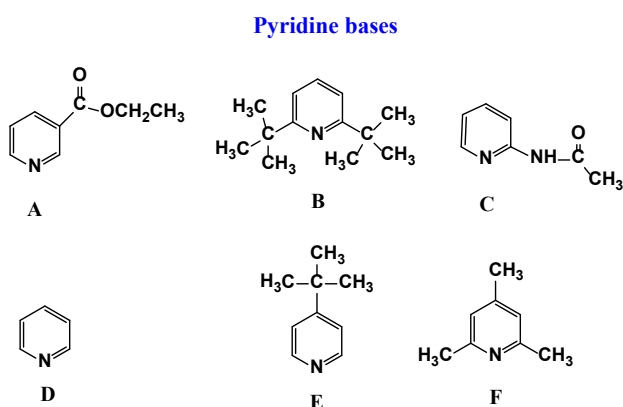
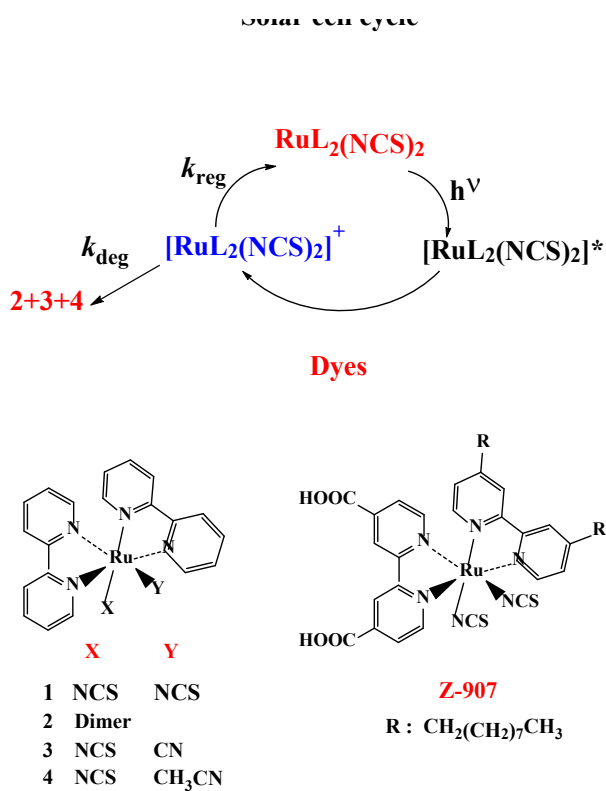


Fig. 1 The DSC cell cycle of the RuL₂NCS₂ sensitizer. Molecular structures of the model ruthenium complex **1**, Z907, the degradation products **3** and **4** and the applied six pyridines A-F. **2** is an unidentified ruthenium dimer – see Table 2.

2. Experimental

2.1 Materials

The ruthenium dye Z907 was purchased from Great Cell Solar Limited, Australia. Pyridine derivatives, 4-*tert*-Butylpyridine, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, LiCF_3SO_3 , LiClO_4 , Bu_4NBF_4 , KCN, KSCN, dimethyl formamide (DMF) and $\text{Ru}(\text{bipy})_3(\text{PF}_6)_2$ were obtained from Sigma-Aldrich. HPLC grade acetonitrile (Chemsolute) was obtained from TH. Geyer (Germany). 4-*tert*-Butylpyridine was distilled under reduced pressure. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was dried for two days at 130 °C before use. Transparent FTO|TiO₂ electrodes (10 µm layer of 20 nm TiO₂ particles on FTO glass, area= 0.36 cm², catalogue number 74111) were obtained from Solaronix, Aubonne, Switzerland

2.2 Syntheses

cis-Bis(2,2'-bipyridine)dithiocyanatoruthenium(II), $(\text{Ru}(\text{bipy})_2(\text{NCS})_2)$ (**1**), was obtained from *cis*- $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (Lay et al. 2007) through a modified literature method (Nazeeruddin et al. 1993): *cis*- $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (1.56 g, 3.0 mmol), DMF (70 ml) and potassium thiocyanate (6.3 g, 65 mmol) dissolved in water (8 ml) was heated at 150 °C for 3 hours under stirring and a flow of nitrogen. While still warm, the reaction mixture was slowly poured into 75 mL ethanol (99.8%) under stirring. The mixture was cooled in ice overnight and filtered to give a microcrystalline red product, which was washed twice with 50 mL 30% ethanol/water followed by three 40 ml portions of diethyl ether. Yield 1.32 g (81%) of pure product. (See NMR data in Supplementary).

2.3 Electrooxidations

$\text{Ru}(\text{bipy})_2(\text{NCS})_2$ (**1**) (22.14 mg, 0.0418 mmol) was oxidised to the corresponding blue $\text{Ru}(\text{bipy})_2(\text{NCS})_2^+$ complex in acetonitrile (30 ml) containing LiCF_3SO_3 as supporting electrolyte. The electrolysis was performed with magnetic stirring at +0.70 V vs. a silver wire as reference electrode using a platinum net electrode as anode and a carbon rod as cathode. After 3.78 C had passed through

the cell (corresponding to having extracted 0.94 electron from each molecule of the ruthenium(II) complex), the current stopped and the solution was dark blue of the ruthenium(III) complex **1**⁺.

Z907 (23.0 mg, 0.0264 mmol) was oxidised at +0.80 V following the same procedure as described above. Z907 is insoluble in acetonitrile and the oxidation current was low in the beginning of the electrolysis and increased slightly during the electrolysis due to some further oxidation of the soluble green Z907⁺ complex. The electrolysis was stopped after 3.58 C. The oxidation of Z907 to Z907⁺ requires 2.55 C while the last 0.97 C probably has been spent on the oxidation of 5-10% of the Z907 to [RuLL'(NCS)(CN)] in analogy to **1** (see Results 3.3).

2.4 LC-UV/Vis-MS

In a typical experiment 1 ml of the blue **1**⁺ solution (~1.5 mM) obtained from the electrolysis was mixed with an excess of one of the six pyridines in Fig. 1 (1 ml 100 mM solution in acetonitrile). After the reaction had finished and the colour had changed from blue to red, the mixture was analysed by LC-UV/Vis-ESI-MS. The applied analytical equipment was comprised of a Dionex Ultimate 3000 UHPLC and diode array detector interfaced with a HESI electro spray ion source to a Thermo Finnigan LTQ-XL linear ion-trap mass spectrometer. The chromatographic separation was performed with a Phenomenex Phenylhexyl Kinetix analytical 10 cm column with an internal diameter of 2.1 mm (Product no. ØØD-4500-AN). An 18 min gradient elution was performed with a flow of 0.2 ml/min and application of three mixtures of A = 90% methanol+ 9.9% H₂O + 0.1 % formic acid and B = acetonitrile with 0.1% formic acid. The initial eluent composition (95% A, 5 % B) was linearly changed to A:B = 50:50 during 13 min. Final composition after 18 min was 5% A, 95% B. The HESI probe and the heated ESI capillary temperatures were both 200 °C.

2.5 Stopped-flow experiments

Kinetic experiments were performed with a RX1000 rapid kinetics spectrometer accessory from Applied Photophysics coupled by fibre-optics to a Redtide USB650 UV diode-array spectrophotometer from Ocean Optics. The light source was an Ocean Optics LS-1 tungsten halogen lamp. In a typical experiment the electrochemically prepared solutions of either 1^+ or $Z907^+$ was transferred to the A-syringe (5 ml) and the B-syringe (5 ml) was filled with e.g. 4-*tert*-butylpyridine dissolved in acetonitrile (10-200 mM). Three hundred diodearray spectra (400-800 nm) were recorded through a single stopped-flow experiment with time intervals between the spectra from 25 msec. to 10 sec. The decays of 1^+ and $Z907^+$ were followed at 750 and 770 nm respectively.

2.6 Cyclic voltammetry

Cyclic voltammograms were recorded with a standard three-electrode electrochemical setup comprised of a VersaSTAT 3F potentiostat from Princeton Applied Research, a platinum electrode ($d=3$ mm) as working electrode, a Ag/AgCl pseudo reference electrode and a platinum wire as counter electrode. The solvent was acetonitrile with Bu_4NBF_4 (0.1 M) as supporting electrolyte. In some CV experiments attempts were made to remove water from the solvent: The acetonitrile/ Bu_4NBF_4 solution was first dried with 4Å molecular sieves (dried at 200 °C) followed by passing the solution through a column of activated aluminium oxide (dried with a heat-gun at 0.1 mbar).

2.7 Sulphate determination

28.82 mg of **1** (0.0544 mmol) in acetonitrile (total volume 27.8 ml) was oxidised at +0.7 V with 0.1 M $LiClO_4$ as supporting electrolyte. The electrolysis stopped after 5.01 C and 10.0 ml of the blue solution was transferred to a round bottomed flask, 2,4,6-trimethylpyridine (10.0 ml, 100 mM in acetonitrile) was added and after 10-15 min the solvent was removed at reduced pressure to give a red solid. The solid was first dissolved in methanol (2.0 ml) and then re-precipitated by the addition of water (8.0 ml).

The mixture was filtered through a 45µm Sartorius filter and an aliquot of the filtrate (10 µl) was injected on a Thermo Scientific ion-chromatograph equipped with a DionexIonPacTMAS14A anion column and suppressed conductivity detection. The eluent consisted of an aqueous solution of Na₂CO₃ (8 mM) and NaHCO₃ (1 mM). The sulphate ions eluted as a clean peak after 10.56 min well separated from the large ClO₄⁻ peak at 60 min. The concentration of sulphate 24.2 mg/L was obtained by comparison of the peak area with a standard sulphate calibration curve obtained from Dionex seven anion standard samples (Product no. 056993).

2.8 NMR

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400 MHz for ¹H-NMR and at 100.61 MHz for ¹³C NMR. Spectra were recorded in CD₃CN or in mixtures of CH₃CN and (CD₃)₂SO at ambient temperature. The solvent resonance of CD₂HCN was used as reference.

Ru(bipy)₂(NCS)₂⁺ (1⁺): The NMR sample of 1⁺ was prepared by withdrawing an aliquot (10 ml) of the blue electrolysis solution of 1⁺ and removing the acetonitrile by rotatory evaporation. The blue solid, i.e. the trifluoromethane sulphonate salt of 1⁺, was dissolved in 1.5 ml CD₃CN.

2.9 The reaction of Z907⁺ on a TiO₂ surface

Transparent FTO|TiO₂ electrodes were soaked overnight in a 0.5 mM solution of Z907 in methanol. The red-dyed electrode was inserted in a solution of [Ru(bipy)₃]³⁺ prepared by electrooxidation of Ru(bipy)₃(PF₆)₂ following a similar electro-oxidation procedure as described for 1. Within less than 1 min. the red FTO|TiO₂|Z907 electrode became oxidized with formation of a surface of the green Z907⁺ ions. The electrode was carefully rinsed in acetonitrile to remove remaining [Ru(bipy)₃]³⁺. The

UV/Vis of the FTO|TiO₂|Z907⁺ electrode showed the characteristic absorption peaks of Z907⁺ at $\lambda = 590$ and 770 nm. Green FTO|TiO₂|Z907⁺ electrodes were soaked in 4-*tert*-butylpyridine (25 mM in acetonitrile) after which the green colour immediately changed to red.

3. Results

3.1 Ru(III) formation and reaction

The ruthenium(III) species **1**⁺ and Z907⁺ were obtained by electrochemical oxidation of the corresponding ruthenium(II) complexes in acetonitrile at a platinum electrode at 0.7-0.8 V vs. (Ag/Ag⁺). Fig. 2 shows the UV/Vis spectra of the blue **1**⁺ and the green Z907⁺ electrolysis solutions diluted 10 times in acetonitrile. When 4-*tert*-butylpyridine (TBP) in excess was added to the solutions, they both quickly turned red. The product spectrum of **1**⁺ is very similar to a reference spectrum of **1** (red) indicating that **1**⁺ is transformed primarily to the starting ruthenium(II) complex **1**. The visible spectrum of the Z907⁺ + TBP reaction (black) shows an absorption peak at 523 nm close to the 527 nm absorption band of an authentic sample of Z907. Therefore, both the **1**⁺ and Z907⁺ are reduced predominately to their parent ruthenium(II) complexes. Absorption maxima, molar absorption coefficients and redox potentials of the above mentioned ruthenium complexes are listed in Table 1.

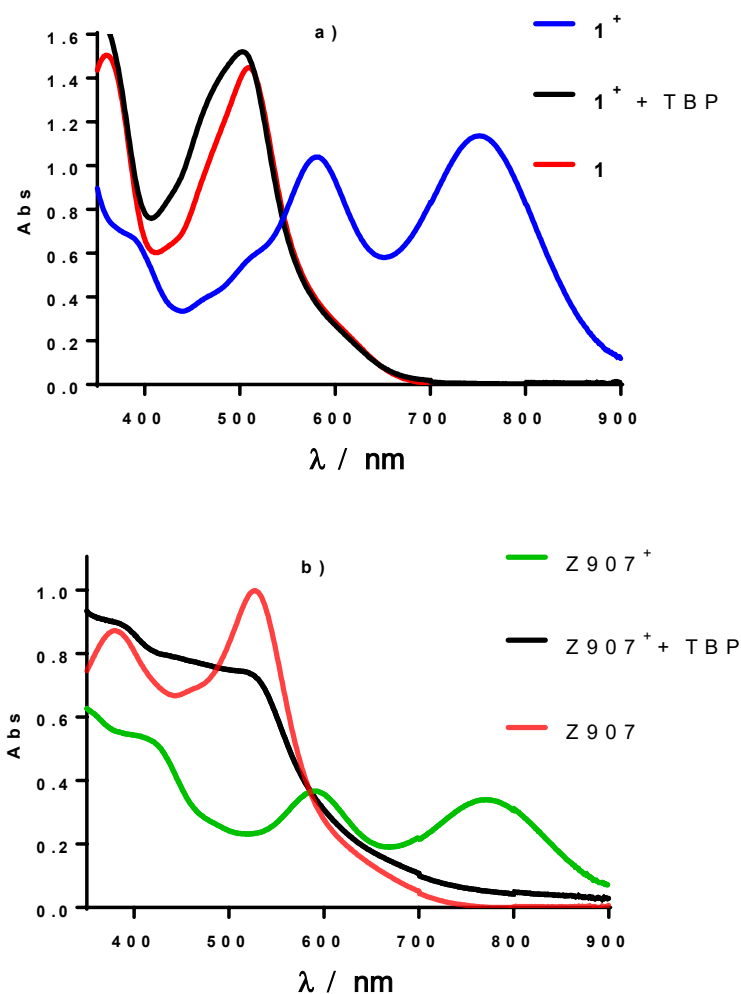


Fig. 2 a) Blue spectrum: 1^+ , (0.16 mM), black: TBP (10 μL) added to the cuvette, red: 1 , (0.16 mM). b) Green spectrum: Z907^+ (0.12 mM), black: TBP (10 μL) added to the cuvette, red: Z907 (0.12 mM).

Table 1 Absorption maxima and molar absorption coefficients in acetonitrile

Complex	λ_1 /nm	λ_2 /nm	ϵ_1 / $\text{M}^{-1}\text{cm}^{-1}$	ϵ_2 / $\text{M}^{-1}\text{cm}^{-1}$	E^0 /V ^b
1	359	509	9300	9000	+0.80
1^+	581	751	6400	7000	
Z907^{a}	380	527	9000	10300	+0.86
Z907^+	590	770	3800	3800	

^a Z907 dissolved in 10% DMF and 90% acetonitrile. b) E^0 : Average potential of the oxidation and

reduction CV peak potentials in acetonitrile measured relative to ferrocene and transferred to the NHE scale by adding 0.530 V (Eberson 1987).

3.2 LC-MS analysis

Aliquots of the electrolysis solution of the blue $\mathbf{1}^+$ was mixed with a pyridine derivative dissolved in acetonitrile. When the blue solution had changed to red within seconds to minutes depending on the pyridine, the solutions were analysed by LC-UV/Vis-MS. Fig. 3a shows the HPLC chromatogram of the products obtained in the reaction of $\text{Ru}(\text{bipy})_2(\text{NCS})_2^+$, ($\mathbf{1}^+$) with 4-*tert*-butylpyridine. The main product (75%) is $\text{Ru}(\text{bipy})_2(\text{NCS})_2$ ($\mathbf{1}$), in accordance with the UV/Vis results in the previous paragraph. Product $\mathbf{3}$ has an electro-spray mass spectrum with a ruthenium isotope pattern around $m/z = 499$ (Fig. 3c). This ion may be assigned to the formula $[\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CN})+\text{H}]^+$. The ESI-MS of product $\mathbf{4}$ (Fig. 3d) shows the ions $m/z = 513$ and 472 , which may be identified as the molecular ion $\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CH}_3\text{CN})^+$ and fragmentation ion $\text{Ru}(\text{bipy})_2(\text{NCS})^+$, respectively. Finally the broad HPLC peak of product $\mathbf{2}$ (Fig. 3b) has a complicated ruthenium isotope pattern around $m/z = 498$ with a peak separation of 0.5 mass units indicating a doubly charged ion corresponding to the formula $[(\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CN}))_2]^{2+}$. Furthermore, the spectrum (Fig. 3b) contains a doubly charged fragment ion at $m/z = 472$ corresponding to the formula $[\text{Ru}(\text{bipy})_2(\text{NCS})]_2^{2+}$. UV/Vis and MS data of the products $\mathbf{1-4}$ and the relative product quantification of the four pyridine reactions with $\mathbf{1}^+$ is shown in Table 2 and 3, respectively. The products $\mathbf{1-4}$ are assumed to have equal molar absorption coefficients at their respective absorption maxima in the interval 400-800 nm (Nour-Mohammadi et al. 2007).

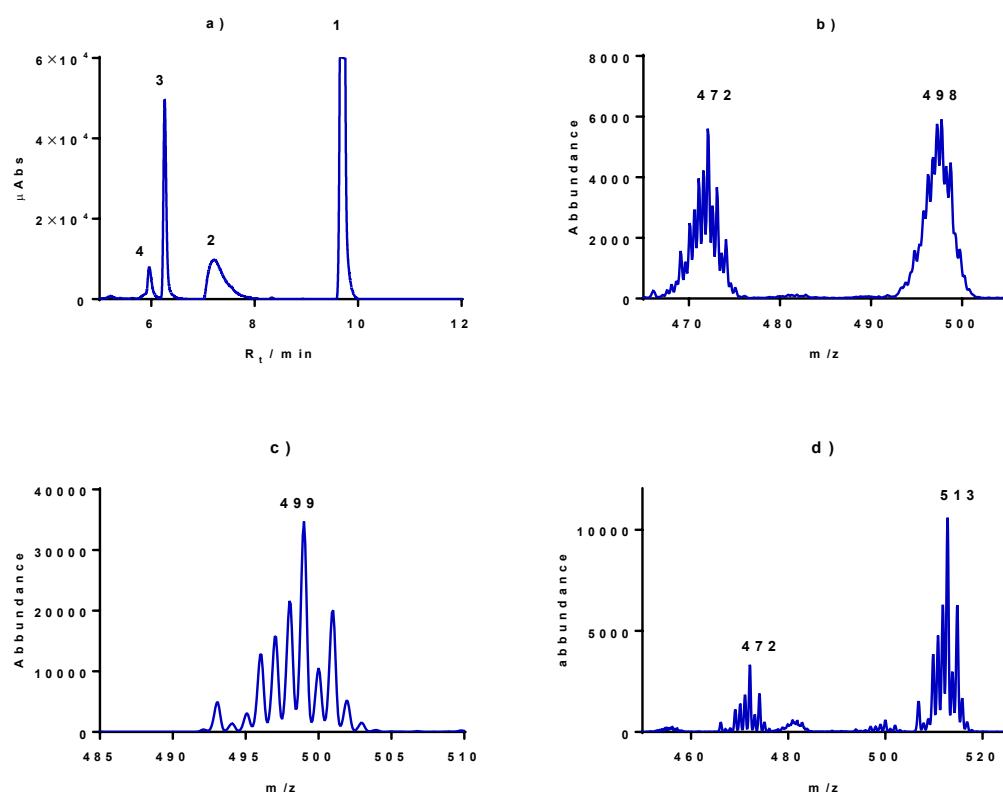


Figure 3 LC-UV/Vis-MS analysis of the reaction between with 1^+ and TBP (50 mM) in acetonitrile. a) LC-UV/Vis chromatogram showed in λ_{\max} mode between 400-800 nm. b) Electro-spray mass spectrum of product **2**. c) ESI-MS of product **3**. d) ESI-MS of product **4**.

Table 2 Product identification of **1-4**

Compound	Identification (M)	R_t min	λ_{\max} ^{a)} nm	ESI-MS m/z
1	$\text{Ru}(\text{bipy})_2(\text{NCS})_2$	9.70	492	530 $[\text{M}]^+$
2	$(\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CN}))_2$	7.22	445	498 $[\text{M}]^{2+}$
3	$\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CN})$	6.26	465	499 $[\text{M}+\text{H}]^+$
4	$\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CH}_3\text{CN})$	5.96	445	513 $[\text{M}]^+$

^a UV/Vis obtained in HPLC eluent of water/acetonitrile solution with 0.1% formic acid.

Table 3 LC-UV/Vis-MS product analysis (area %) of the reactions of **1**⁺ (1.2 mM) with some pyridine derivatives X in acetonitrile. ^{a)-b)}

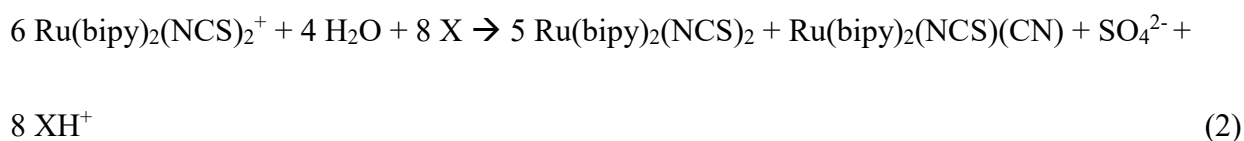
Pyridine X	1	2	3	4
Ethyl nicotinate	85	1.4	10	3.2
Pyridine	79	7.5	11.1	2.9
4- <i>tert</i> -butylpyridine	75	11	11.8	2.3
2,4,6-Trimethylpyridine	77	7.9	12.6	2.9

a) The pyridine X (1 ml, 100 mM) was added to a blue solution of **1**⁺ (1 ml, 1.4 mM)

b) The LC-UV/Vis chromatograms were plotted in the maximum absorption mode in the wavelength interval 400-800 nm.

3.3 The overall reaction

The product analysis is consistent with the following overall reaction shown in eq. (2) as discussed below.



First, this overall reaction predicts that 83% of **1**⁺ is transformed to **1**; the observed average percentage of 79% found from the four pyridine experiments in Table 3 is close to this prediction. Second, 0.25×10^{-5} mole of sulphate was found by ion chromatography in an experiment with 1.86×10^{-5} mole of **1**⁺ and excess of 2,4,6-trimethylpyridine (TMP) predicting 0.31×10^{-5} mole of sulphate which compares reasonably well with observation. Third, the only source of the sulphate oxygen atoms is the water present in the acetonitrile. (See section 3.5). Finally, the pyridine molecule acts as a base taking up liberated protons (see section 3.4.3). When various small amounts of TMP were added to cuvettes with an excess of **1**⁺, equilibrium absorptions at 750 nm were obtained after several hours of reaction. The absorption decrease corresponding to a decrease of [**1**⁺] was a function of added TMP and followed very closely the expected decrease predicted by equation (2) (See Fig. S1 in the supplementary material).

3.4 NMR

3.4.1 The ^1H NMR spectrum of the blue solution of $\mathbf{1}^+$ in CD_3CN (see Experimental 4.8) clearly shows that the compound is paramagnetic. Broad resonances are seen at 17.05, 14.52, 9.01 (sharp), 1.4, -5.37, -16.65, -20.25 and -34.9 ppm. The latter is very broad. The one at 1.4 ppm is hidden underneath the solvent signal. In addition, weak resonances originating from the diamagnetic $\text{Ru}(\text{bipy})_2(\text{NCS})_2$ are also seen. The ^1H NMR spectra of $\mathbf{1}^+$ and $\mathbf{1}$ are shown in Suppl. Mat Figs. 2 and 3.

3.4.2 *Addition of 4-tert-butylpyridine.* To a blue solution of $\mathbf{1}^+$ was added 4-*tert*-butylpyridine and after it had turned red, the ^1H -NMR spectrum was by and large that of $\mathbf{1}$, but showed resonances from a small amount of $\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CN})$. The molar ratio between $\mathbf{1}$ and water in the NMR sample was determined from the integrals to be 1:40. The concentration of $\mathbf{1}^+$ was 1.34 mM in the electrolysis solution and the water concentration might therefore be estimated to 55 mM assuming that no water disappeared during the preparation of the NMR sample.

3.4.3 *Addition of pyridine- ^{15}N .* Pyridine- ^{15}N was added to the blue solution of $\text{Ru}(\text{bipy})_2(\text{NCS})_2^+$ instead of 4-*tert*-butylpyridine. The ^1H NMR spectrum of the ruthenium species was identical to that resulting from the addition of 4-*tert*-butylpyridine. The protonation shift of pyridine in DMSO-d_6 is 101.6 ppm (Duthaler and Roberts 1978). After addition of a slight excess of pyridine- ^{15}N over ruthenium(III) complex (molar ratio 2.5:1), the ^{15}N NMR spectrum resonance shifted 49.2 ppm, corresponding to approximately half of the pyridine being protonated. This experiment was conducted with $\mathbf{1}^+$ for which tetrabutylammonium tetrafluoroborate had been used as electrolyte, due to the fact that lithium ions binds to pyridine (Nguyen, Hansen, and Lund 2013).

3.5 Kinetics

Fig. 3 shows a typical stopped-flow kinetic experiment of the reaction between 1^+ and TBP (50 mM in acetonitrile). The decay of 1^+ and the raise of the **1** absorptions monitored at 750 and 506 nm respectively, does not follow a perfect first order exponential decay/raise. The decay is slightly too fast in the beginning of the process and too slow in the middle of the decay compared with a first order fit, indicating a slightly more complex reaction mechanism than a simple first order process. We have chosen to report the experimental half-life $t_{1/2}$ determined as the time where $(A-A_\infty)/(A_0-A_\infty) = 0.5$.

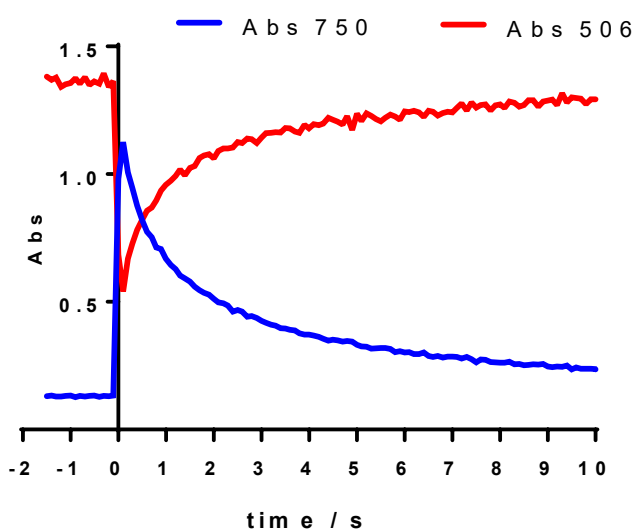


Fig. 3 Stopped-flow experiment of the reaction between 1^+ and 4-*tert*-butylpyridine (50 mM) in acetonitrile. Values of $t_{1/2}$ was fitted from the decay of the blue 1^+ monitored at 750 nm ($t_{1/2} = 1.5$ s) and from the formation of Ru(II) products at 506 nm ($t_{1/2} = 1.0$ s). Standard deviation = 3 % in both fits.

The reactions follow to a good approximation first order in base concentration as shown in Fig. 4 in the cases where 1^+ and $Z907^+$ react with different amounts of TBP added.

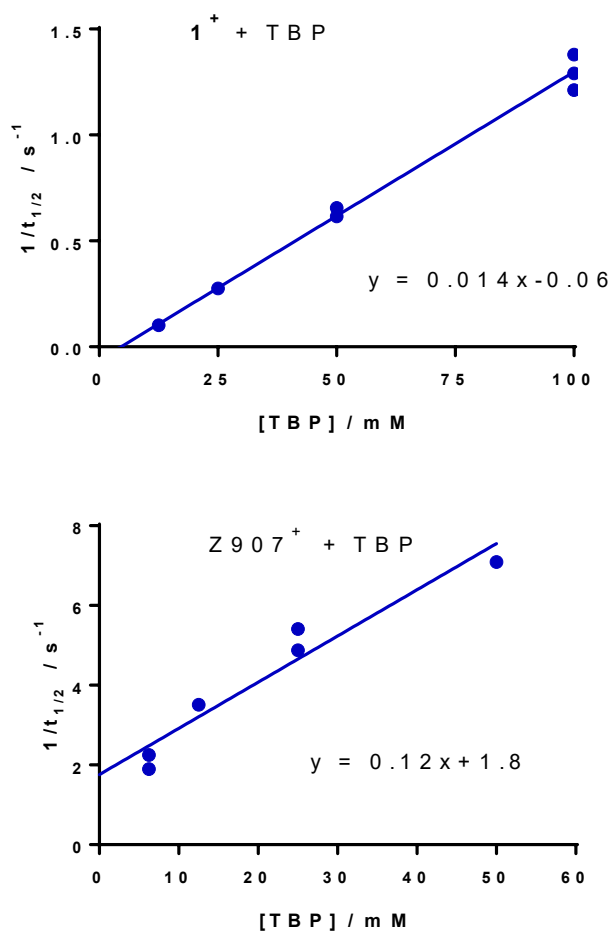


Fig. 4 Measured half-lives $t_{1/2}$ of the reaction between $\text{Ru}(\text{bipy})_2(\text{NCS})_2^+$ (1^+) and Z907^+ with *tert*-butylpyridine (TBP) in acetonitrile at 22 °C

Since the degradation reaction from $\text{Ru}(\text{III})$ to $\text{Ru}(\text{II})$ (cf. eq. (2)) only takes place in the presence of a base, degradation reaction rates have been demonstrated to be quite dependent on the basicity of the base. With hydroxide, the reaction is extremely fast, while the very weakly basic ethyl nicotinate exhibits a rather slow reaction. Half-lives have been estimated for the reactions between $[\text{Ru}(\text{bipy})_2(\text{NCS})_2]^+$ and six different pyridine derivatives plus cyanide and hydroxide. Data are given in Table 4 together with a measure of the basicity of the eight bases. The pK_a values refer to aqueous solutions, but give an indication of the relative basicity of the bases in acetonitrile and correlate with the degradation data.

Tabel 4 Measured half-lives $t_{1/2}^a$ of the reactions between $[\text{Ru}(\text{bipy})_2(\text{NCS})_2]^+$ with bases, (50 mM) the pyridines (A-F), cyanide and hydroxide, in acetonitrile at 22 °C

Base	pK _a ^b	$t_{1/2}/\text{s}$	$1/t_{1/2}/\text{s}^{-1}$
Ethyl Nicotinate (A)	2.92 ^{c,d}	199	0.0050
2,6-Di- <i>tert</i> -butylpyridine (B)	3.58 ^{c,e}	242	0.0041
N-(2-Pyridyl)acetamide (C)	4.09 ^{c,f}	23	0.043
Pyridine (D)	4.89 ^{c,d,e}	4.3	0.23
4- <i>tert</i> -Butylpyridine (E)	6.03 ^{c,e}	1.6	0.63
2,4,6-Trimethylpyridine (F)	7.22 ^{c,g}	0.41	2.4
Tetrabutylammonium cyanide	9.2 ^h	0.012	86
Tetrabutylammonium hydroxide	15.7 ⁱ	0.009	111

^a $t_{1/2}$ determined as the time where $(A_0 - A_\infty)/(A_0 - A_\infty) = 0.5$. [Base] = 50 mM. All the pyridines were measured at 50 mM concentration and tetrabutylammonium cyanide and hydroxide at 5 mM and the $t_{1/2}$ results extrapolated to 50 mM.

^b $\log(\text{Stability constant})$ for $\text{B} + \text{H}^+ \leftrightarrow \text{BH}^+$

^c Numbers collected from IUPAC Stability constants database (Pettit 2006). The numbers refer to measurements in alcohol/water mixtures and values for the single species varies rather much with the alcohol percentage of the solvent. However, the order of basicities indicated by the tabulated numbers seems trustworthy.

^d Numbers given (Niazi and Molin 1987) for 10% ethanol/water. Considerable variations due to different composition was found for pK_a's in this study (Niazi and Molin 1987), e.g. 1.68 and 3.54 respectively for 72% ethanol/water.

^e (Rochester and Waters 1982)

^f (Jones and Katritzky 1959)

^g (Wiczling et al. 2006)

^h IUPAC recommended value (Water, Ionic strength 0.0 M) (Beck 1987)

ⁱ Based on pK_w = 14.0

As indicated in eq. (2) water is involved in the reaction of the $\text{Ru}^{\text{III}}\text{LL}'(\text{NCS})_2^+$ complexes. Indeed,

the reaction rate was found to increase when increasing amounts of water was added. For example, the half-life of reaction ($[TBP]=50\text{mM}$) decreased by a factor of 4 by adding water up to 1M. The effect of water was further investigated by cyclic voltammetry of **1** in carefully dried acetonitrile/ $0.1\text{ M Bu}_4\text{NBF}_4$. As seen from Fig. 5 the voltammogram of **1** is nicely reversible. When TBP is added, **1**⁺ reacts near the electrode surface with regeneration of **1** according to eq. (2) with the result that the oxidation peak increases in height and the reduction peak is reduced. This effect is clearly enhanced by the addition of water. If traces of water had been removed completely from the CV-cell, the shape of the voltammogram should not have been affected by the addition of TBP. However, we have apparently not been able to remove all traces of water from the CV cell.

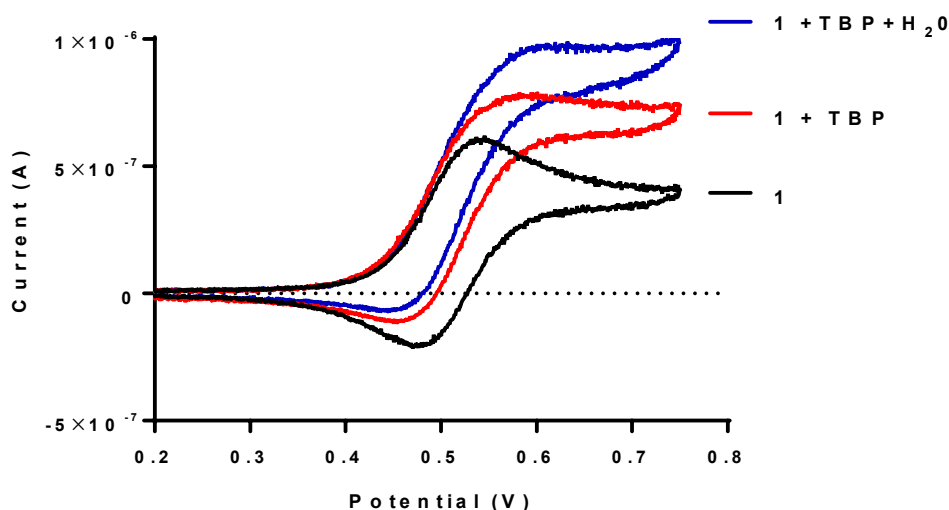


Fig. 5 Cyclic voltammograms of **1** (1mM) in dried $0.1\text{ M Bu}_4\text{NBF}_4$ in acetonitrile (black), with addition of TBP (3.5 mM) (red) and with addition of TBP (3.5 mM) and H_2O (280 mM) (blue). Scan rate equal to 10 mV/s .

3.6 Degradation on a TiO_2 surface of a solar cell

In addition to the fast reactions of **1**⁺ and Z907^+ in homogeneous acetonitrile solutions with the solar cell N-additive 4-*tert*-butylpyridine (TBP), the reaction of Z907^+ on the surface of the nano crystalline

TiO₂ anode of a DSC was investigated: Z907 was attached to TiO₂ photoanodes by dye soaking in methanol. The resulting red photoanodes were inserted into an electrochemically generated solution of Ru(bipy)₃³⁺ which is several hundred mV stronger as oxidation agent than Z907⁺. The red Z907 on the surface was within a few minutes oxidized to the green Z907⁺. After washing the electrode in acetonitrile, it was placed in an acetonitrile solution of TBP (50 mM) and instantaneously the green colour changed to red. This simple experiment demonstrates that the reduction of Z907⁺ on the TiO₂ surface in a basic acetonitrile solution is very fast like the homogeneous reaction.

4. Discussion

4.1 Mechanism

The electrochemically generated blue solutions of **1**⁺ and the green solution of Z907⁺ are stable for several weeks. The addition of small (or large) amounts of hydroxide or a weaker base causes a colour change back to red indicating a reduction back to ruthenium(II) with a stoichiometry as shown in eq. (2). Since the rate of reactions depends on the identity of the base and increases with its basicity, it is tempting to rationalize the initial part of the reaction being dependent on the [OH⁻] concentration as has been shown to be the case when Ru(bipy)₃³⁺ is reduced in aqueous base (Mønsted and Nord 1991). The quantitative dependence on [OH⁻] of reaction rates of the degradation of the ruthenium(III) complexes with base in acetonitrile solvents has not yet been fully studied (Josephsen, Lund, and Hansen). The mechanism could be initiated by a direct coordination of the pyridine to the ruthenium(III) complex. However, 2,6-di-*tert*-butylpyridine (DTBP), being sterically crowded at the nitrogen and not able to coordinate still reacts in line with the other bases as seen from Table 4. This seems to indicate that OH⁻ binds to the ruthenium(III) complex, the pyridines acting as bases. We have suggested a reaction mechanism with several steps as shown in Fig. 6 to account for the observed products and stoichiometry. The first step is an attack of hydroxide (formed by the added base and water in acetonitrile) on the partially positively charged thiocyanate sulphur of the ruthenium(III) complex (reaction 2 in Fig. 6) followed by formation of “S-OH” and Ru(bipy)₂(NCS)(NC) which further rearrange to Ru(bipy)₂(NCS)(CN), (reactions (3) and (4)). “S-OH” is stepwise oxidized by five [Ru(bipy)₂(NCS)₂]⁺ to SO₄²⁻ consuming four water molecules and transferring protons to the base

(B) (reaction (8) in Fig. 6) The eliminated sulphur is here symbolised by “SOH”, a species which has not been detected or identified in the literature; for example a report on the oxidation of thiocyanate in aqueous hydrogenperoxide to sulphate does not mention any partly oxidised sulphur compound (Wilson and Harris 1960). However, any low valent oxygen containing sulphur species is reducing and will turn into sulphate in an oxidising environment.

Reactions 5-7 are side reactions suggested by the LC-MS analyses. The small amount of solvent substituted product $\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CH}_3\text{CN})^+$ is likely to be formed as suggested in reaction 5. Trace amounts of the $\text{Ru}(\text{bipy})_2(\text{NCS})(\text{TBP})^+$ characterized by $m/z = 607$ $[\text{M}]^+$ was observed in reactions of $\mathbf{1}^+$ with high concentrations of TBP (0.5M) (reaction (7)). Surprisingly a by-product corresponding to $[\text{Ru}(\text{bipy})_2(\text{NCS})(\text{CN})]_2$ (reaction 6) was also detected. This kind of product was not found in the blue solution before base addition.

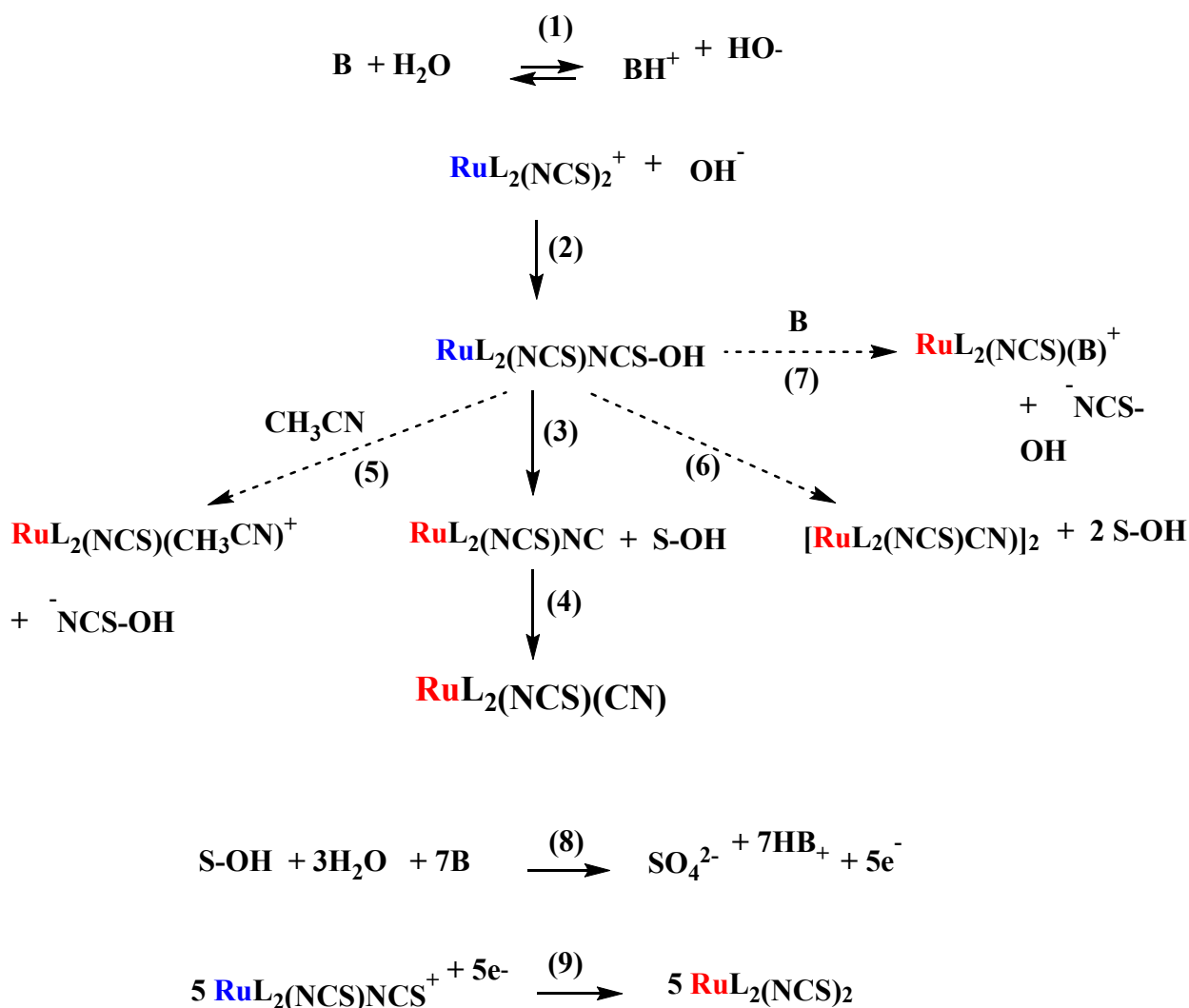


Fig. 6 Reaction mechanism of $\text{RuL}_2(\text{NCS})_2^+$ in acetonitrile containing a base B (e.g. a pyridine) and water. L = bipy. **Ru** (in blue) is Ru(III), whereas **Ru** (in red) is Ru(II)

The oxidation products $\text{RuL}_2(\text{NCS})(\text{CN})$, $\text{RuL}_2(\text{NCS})(\text{CH}_3\text{CN})^+$ and $\text{RuL}_2(\text{NCS})(\text{B})^+$ has also been detected in real DSCs (Kohle et al. 1997; Rendon et al. 2015; Tihihonen et al. 2015) and in model experiments (Nour-Mohhamadi et al. 2005; Nour-Mohammadi et al. 2007) prepared with N719 as dye (L = 4,4'-dicarboxy-2,2'-bipyridine). However, a higher amount of the N-additive substitution product $\text{RuL}_2(\text{NCS})(\text{B})^+$ was reported compared to what is found in this work for 1^+ . This difference may be related to the fact that **1** and N719 differ in structure and our experiments were performed in homogenous solutions and not with the dye attached to a TiO_2 surface.

We have previously proposed a mechanism for the degradation of N719^+ initiated by an internal electron transfer between the NCS^- ligand to the ruthenium(III) centre with formation of the intermediate $\text{RuL}_2(\text{NCS})(\text{NCS}^\cdot)$ followed by elimination of NCS^\cdot and formation of $\text{RuL}_2(\text{NCS})^+$ with a free ligand position for solvent and B molecule substitution (see eq. (3)) (Nour-Mohammadi et al. 2007).



a mixture of $\text{Ru(II)L}_2(\text{NCS})(\text{B})^+$ and $\text{Ru(II)L}_2(\text{CH}_3\text{CN})^+$ and $\text{Ru(II)L}_2(\text{NCS})(\text{CN})$ (eq. 3)

Such a mechanism suggests that the NCS^\cdot radical is oxidized in the solution to CN^- followed by its attack on $\text{RuL}_2(\text{NCS})^+$ giving $\text{RuL}_2(\text{NCS})(\text{CN})$. However, unpublished results from our laboratory (Degn 2004) demonstrates that electro oxidation of N719 in the presence of high concentrations of $^{13}\text{CN}^-$ ions does not result in any $\text{RuL}_2(\text{NCS})(^{13}\text{CN})$ indicating that the elimination of sulphur to leave $\text{RuL}_2(\text{NCS})(\text{CN})$ is occurring internally within the complex as suggested in Fig. 6. Furthermore, our previously suggested mechanism (Nour-Mohammadi et al. 2007) through the common transient species $\text{RuL}_2(\text{NCS})(\text{NCS}^\cdot)$ (eq. (3)) cannot account for the high stability of $\mathbf{1}^+$ and Z907^+ in acetonitrile solutions. The fact that $\mathbf{1}^+$ and Z907^+ react fast is in accord with an attack of OH^- on the ruthenium(III) complex being the initiating process as suggested in Fig. 6. We have shown, that the reactions go faster with increasing concentration of N-additive, with increasing basicity of the N-additive, and with increasing concentration of water in the acetonitrile media. However this complexity is not yet fully understood and work is in progress to confirm details of the proposed mechanism (Josephsen, Lund, and Hansen).

4.2 Consequences for DSC stability

Fast degradation kinetics of Z907 was also observed on the surface of the nano crystalline TiO_2 anode of a DSC. If we assume that the heterogeneous surface reaction of Z907^+ has the same reaction rate as

in the homogenous solution, it is possible to estimate the long term light-soaking stabilities of the DSC with water in the electrolyte. Extrapolating the kinetic results in Fig. 4 to a typical TBP concentration of 0.5 M in the DSC gives a $\ln 2/t_{1/2deg} = 40 \text{ s}^{-1}$. Since the reaction (eq. 2) returns five out of six ruthenium(III) (1^+) species as intact ruthenium(II) analogues (**1**), only one of the six 1^+ is truly degraded. Accordingly k_{deg} can be approximated as 7 s^{-1} .

The rate of regeneration of $Z907^+$ to Z907 by iodide in the DSC is between 1×10^5 to $2 \times 10^6 \text{ s}^{-1}$ (Nour-Mohhamadi et al. 2005). Assuming $k_{reg} = 1 \times 10^6 \text{ s}^{-1}$ a turn-over number of Z907 equal to $\approx 1.5 \times 10^5$ may be calculated from eq. (1) which corresponds to less than $20 \text{ years} \times 1.5 \times 10^5 / 1 \times 10^8 \approx 10$ days of light-soaking under normal outdoor solar cell conditions if the amount of water in the electrolyte is unlimited. However, if the total amount of the water in the electrolyte is small compared with the total amount of RuLL' (NCS)_2 dye, then the water is consumed and the degradation reaction according to eq. (2) stops. Table 5 shows an estimate of the total water content in typical DSC as a function of the water content in the electrolyte.

Table 5 Total water content in a typical DSC as a function of the electrolyte water concentration.

$\Gamma_{dye} / \text{mol/cm}^2$	$[\text{H}_2\text{O}] / \text{mM}$ in electrolyte	Electrolyte Volume/ cm^3 ^{a)}	$n_{\text{water}} / \text{mol}$ in DSC	$n_{\text{dye}} / \text{mol}$ degraded
2×10^{-7} ^{b)}	25	0.0025	6.25×10^{-8}	1.56×10^{-8}
2×10^{-7}	500	0.0025	1.25×10^{-6}	3.13×10^{-7}

^{a)} The thickness of the DSC is set to $50 \mu\text{m}$ and the porosity to 50%. Area = 1 cm^2

^{b)} Γ_{dye} is the surface concentration of the dye on the TiO_2 photoanode [ref 5].

The simple calculations in Table 5 demonstrates that for “dry” electrolytes with less than 25 mM of water only $\approx 10\%$ of the Z907 dye will react according to eq. (2). After the small amounts of water in the DSC has been removed the dye can in principle sustain $> 1 \times 10^8$ turn-overs. However, in a “wet” electrolyte with more than 500 mM water ($\sim 1\%$) all Z907 is consumed within 1-2 days during normal light-soaking. The main degradation product RuLL' (NCS)(CN) is also a sensitizer, however, with an

efficiency around 30-40% of that of RuLL'(NCS)₂ dye (Nguyen et al. 2011). These results explain the importance of keeping the water content low in DSCs prepared with RuLL'(NCS)₂ dyes and N-additives. Even though it is generally accepted that DSC's prepared with RuLL'(NCS)₂ dyes can sustain long term light-soaking at temperatures below 60 °C (Desilvestro et al. 2009; Toyoda et al. 2004; Wang et al. 2005) very little information is normally given in the literature on the water content in the DSC and how the applied chemicals including the solvent has been purified. The work of Tiihonen *et al.* demonstrated that especially the 3-methoxypropionitrile purification prolonged the light-soaking lifetime of the DSCs prepared with N719 (Tiihonen et al. 2015). Petterson and Gruzecki express a similar experience (Pettersson and Gruszecki 2001). Yan *et al.* (Yan et al. 2014) monitored the efficiency decrease after 24 hours light-soaking of DSC's prepared with N719 and 0-5 % water in the electrolyte. A DSC with 5% water added to the electrolyte had an initial efficiency of 10.0% and after 24 hours of light-soaking the efficiency had decreased to 8.6 %.

5. Conclusion

The stability of the ruthenium(III) oxidation product of the model complex Ru(bipy)₂(NCS)₂ (**1**) and the widely applied dye-sensitized solar cell ruthenium dye Z907 in acetonitrile depends on the N-additive. While the blue **1**⁺ and the green Z907⁺ complexes themselves are stable in acetonitrile, the addition of a base e.g. a pyridine, causes **1**⁺ (and Z907⁺) to react with impurities of water in the acetonitrile. **1** and Ru(bipy)₂(NCS)(CN) are the main degradation products together with sulphate and pyridinium ions with a stoichiometry shown in eq. (2). Our work provides an explanation of the well-known experience that DSCs prepared with RuLL'(NCS)₂ dyes and N-additives have the longest lifetimes in water free electrolytes. It is predicted, that the lifetime of a DCS prepared with Z907 is only a few days when the concentration of water is 0.5 M in acetonitrile as the electrolyte. With a dry electrolyte, say up to 25 mM of water, the little water will be used up by degradation of only 10% of the dye, leaving the remaining 90% of the Z907 in a water-free environment. In principle this 90%, can

sustain a very large turn-over number with a lifetime > 20 years under normal outdoor light-soaking conditions. Furthermore, reported loss of DSC performance as a function of the light soaking time may in some case be due to the “water effect” – however the observations are interpreted differently.

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