An investigation of the photosubstitution reaction between N719-dyed nanocrystalline TiO$_2$ particles and 4-*tert*-butylpyridine

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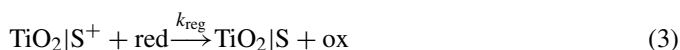
Abstract

The effect of high concentrations of the solar cell additive 4-*tert*-butylpyridine (**4-TBP**) on the stability and lifetime of the sensitizer [Ru(Hdcbpy)$_2$(NCS)$_2$]$^{2-}$, 2(n-C$_4$H$_9$)$_4$N$^+$, (H$_2$dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid), known as **N719**, has been evaluated based on kinetic data obtained from simple model experiments. In these experiments, colloidal solutions of **N719**-dyed nanocrystalline TiO$_2$ particles in acetonitrile were irradiated with 532-nm laser light in the presence of 0–1 mol/l of **4-TBP**. Five degradation products were identified using LC–ESI-MS: the 4-*tert*-butylpyridine substitution product [Ru(H$_2$dcbpy)(Hdcbpy)(NCS)(4-TBP)] (**SP**) and the products [Ru(H$_2$dcbpy)$_2$(NCS)(CN)], [Ru(H$_2$dcbpy)(Hdcbpy)(NCS)(CH$_3$CN)], [Ru(H$_2$dcbpy)(Hdcbpy)(NCS)(H$_2$O)] and [Ru(H$_2$dcbpy)$_2$(CN)$_2$] (**3–6**). The sum of the quantum yields of the five products, $\Phi_{deg} = (1.3 \pm 0.2) \times 10^{-4}$, was found to be independent of **4-TBP** concentration. Based on this observation, a degradation mechanism was proposed, in which the reaction proceeds through the rate-determining formation of a common intermediate complex, $I = [Ru^{II}(H_2dcbpy)_2(NCS)(NCS\cdot)]^+$. An average degradation rate of $k_{deg} = 6 \times 10^{-3}$ s^{-1} was obtained from the value of Φ_{deg} and the back electron-transfer rate, k_{back} of the reaction TiO$_2$ + e$^-$ | N719$^+$ → TiO$_2$ | N719, obtained by means of photo-induced absorption (PIA) measurements. The lifetime of the solar cell sensitizer **N719** was estimated to be between 34 years, based on k_{deg} and an average literature value of the regeneration rate, $k_{reg} = 2 \times 10^6$ M^{-1} s^{-1}, of the reaction between TiO$_2$ | N719$^+$ and iodide. We conclude that the addition of **4-TBP** to dye-sensitized solar cells (DSSC) does not decrease the lifetime of the **N719** dye during normal solar cell operation at room temperature.
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Keywords: N719; *tert*-Butylpyridine; Dye-sensitized solar cells; Stability; LC–ESI-MS

1. Introduction

Nanocrystalline dye-sensitized titanium dioxide solar cells (nc-DSSC) have attracted significant attention because of their good efficiency of solar-to-electric power conversion and lower cost compared to those of silicon solar cells [1–6]. The chemistry at the photo anode is described by Eqs. (1)–(3):

$$TiO_2|S \xrightarrow{h\nu} TiO_2|S^* \tag{1}$$

$$TiO_2|S^* \xrightarrow{k_{inj}} TiO_2 + e^-|S^+ \tag{2}$$

$$TiO_2|S^+ + red \xrightarrow{k_{reg}} TiO_2|S + ox \tag{3}$$

The sensitizer, S, is first excited by a photon; this is followed by an ultra-fast electron injection from S* to the conduction band of the TiO$_2$ semiconductor. The cell cycle finishes after the regeneration of S by the reduced form of the mediator, which in most cases is iodide. One of the most popular sensitizers is the ruthenium dye known as **N719**, i.e., [Ru(Hdcbpy)$_2$(NCS)$_2$]$^{2-}$, 2(n-C$_4$H$_9$)$_4$N$^+$, (H$_2$bdcbpy = L = 2,2′-bipyridine-4,4′-dicarboxylic acid), due to its high efficiency and stability [1–4]. The molecular structure is depicted in Fig. 1.

Various additives have been introduced into the cell electrolyte to improve cell performance [7–13]. One of the most commonly used additives is 4-*tert*-butylpyridine (**4-TBP**), as it has been shown to increase the open circuit voltage, V_{oc}, of the cell by 80–100 mV. It does this by suppressing the dark current arising from the recombination of electrons in the conduction band with the oxidized form of the mediator (I$_3^-$) [14,15].

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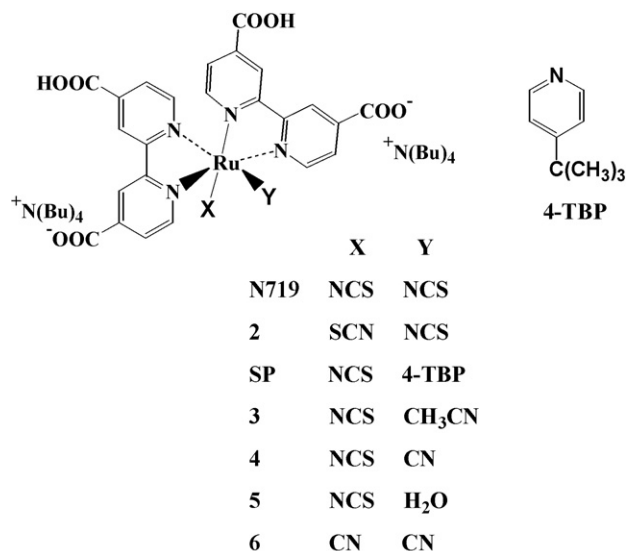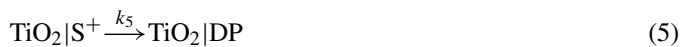 *E-mail address:* tlund@ruc.dk (T. Lund).

Fig. 1. Molecular structures of the starting dye **N719** (including its minor isomer **2**) and the observed photolysis products **SP** and **3–6**.

Recently we found the substitution product, **SP**, i.e., Bu_4N^+, $[Ru(Hdcbpy)_2(NCS)(4\text{-}TBP)]^-$ (see Fig. 1), in dye extracts from light-exposed nc-DSSC using **N719** as the sensitizer [16]. To the best of our knowledge, there have been no previous reports of possible side reactions of **N719** with 4-*tert*-butylpyridine in solar cells. The observation prompted us to investigate the kinetics of the substitution reaction, to be able to evaluate the influence of this reaction on the long-term stability of nc-DSSC.

The 4-*tert*-butylpyridine may react with the sensitizer in all its three states, i.e., S, S^*, and S^+. The substitution product, however, was mainly found in solar cells that had been exposed to light at room temperature [16]. Furthermore preliminary results from our laboratory show that **N719** does not react thermally with **4-TBP** in acetonitrile at room temperature. These observations indicate that at room temperature, the substitution product, **SP**, is mainly formed through the dye states S^* or S^+. The injection rate of S^* into the conduction band of the TiO_2 semiconductor is extremely fast ($k_{inj} = 10^{13}$ s^{-1}) [17], and the pyridine additive therefore does not have enough time to react with S^*. Thus, it is most likely that the substitution reaction is initiated from the oxidized state of the sensitizer S^+ (Eq. (4)):

$$TiO_2|S^+ + 4\text{-}TBP \xrightarrow{k_4} TiO_2|SP \tag{4}$$

$$TiO_2|S^+ \xrightarrow{k_5} TiO_2|DP \tag{5}$$

$$TiO_2 + e^-|S^+ \xrightarrow{k_{back}} TiO_2|S \tag{6}$$

Besides the substitution reaction Eq. (4) S^+ may undergo intramolecular and solvent dependant degradation reactions Eq. (5). In the case of S = **N719** these products lead to the degradation products **3–6** [18,21].

In this work, we have measured the quantum yield of the substitution product, Φ_{SP}, and the quantum yield of the sum of the degradation products **3–6**, Φ_{DP}, through model experiments similar to those by which we obtained the oxidative degra-

dation reaction rate, k_5 [18]. The quantum yield experiments were performed by irradiating colloidal solutions of **N719**-dyed nanocrystalline TiO_2 particles in acetonitrile in the presence of high concentrations of 4-*tert*-butylpyridine. The chemistry of the model experiments is described by Eqs. (1), (2), and (4)–(6).

The work investigates the mechanism of the photo-initiated substitution reaction and evaluates the effect of 4-*tert*-butylpyridine on the overall $TiO_2 | S^+$ degradation rate, k_{deg}, with **N719** being used as the sensitizer. Based on the k_{deg} value, we have estimated the intrinsic lifetime of **N719** in light-exposed solar cells.

2. Experimental

2.1. Chemicals

The bis(tetrabutylammonium) salt of the complex *cis*-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II), with the trade name ruthenium 535-bis TBA and referred to as **N719**, was obtained from Solaronix SA (Aubonne, Switzerland). The *N,N*-dimethylformamide (DMF) and acetonitrile (ACN) used were of HPLC grade and were obtained from Merck. The 4-*tert*-butylpyridine used was purchased from Sigma–Aldrich and was used as received. The applied titanium dioxide was P25 from Degussa AG (Dusseldorf, Germany).

2.2. Instrumentation

The HPLC–UV/vis–MS equipment and procedure, light sources, and photon-counting device have recently been described [18]. The heated capillary of the ion trap mass spectrometer was set to 200 °C. ^{1}H NMR was obtained using a 600-MHz INOVA spectrometer from Varian Inc. (Palo Alto, CA, USA).

2.3. Synthesis of Bu_4N^+, $[Ru(Hdcbpy)_2(NCS)(4\text{-}TBP]^-$

N719 (25 mg, 0.021 mmol) and a large excess of 4-*tert*-butylpyridine (320 μl, 2.14 mmol) were dissolved in DMF (5 ml). The solution was deaerated with argon and heated to approximately 120 °C under a small argon flow. After ~24 h, the solvent was removed by means of rotary evaporation and the remaining solids were dissolved in a small amount of methanol. The solution was separated on a column packed with Sephadex LH20 resin and with the application of a starting eluent of water/acetonitrile/formic acid (94/5/1). Methanol was added during the elution process until all ruthenium complexes were eluted. The eluted fractions were analyzed using LC–UV/vis–MS; the fractions containing the desired substitution product were collected and the solvent was removed by means of rotary evaporation. The remaining solid product was dissolved in 1.1 g of D_2O and 40 μl of a basic solution of 1 g D_2O and 100 mg NaOD, and the solution was analyzed using ^{1}H NMR.