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Note

A mass spectrometric analysis of sensitizer solution used for dye-sensitized solar cell

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Dedicated to Professor Michael Grätzel.

Abstract

We report a mass spectrometric study of ruthenium(II) sensitizer $((C_4H_9)_4N)_2[Ru(4\text{-carboxy-}4'\text{-carboxylate-}2,2'\text{bipyridine})_2(NCS)_2]$ (N719) in various organic and aqueous solvents. At the equilibrium different species were found, depending on solution properties. After stoichiometry confirmation through high-resolution mass spectra and isotopic pattern analysis, the formation of these complexes was found to strongly depend from the polarity and the ionic strength of solvent medium. Mass spectra obtained in acetonitrile/*tert*-butanol (1:1) mixture, used for the absorption of N719 on TiO_2, suggests that the main species involved in the adsorption process is the dicarboxylate form of N719 with one $(C_4H_9)_4N$ as counter ion. The photovoltaic data of the N719 sensitizer adsorbed on TiO_2 films exhibited a remarkable power conversion efficiency, 11.20% at 1 sun.

Keywords: Ru(II) complex; ESI-MS; Noncovalent complexes; N719 sensitizer; Dye-sensitized solar cell

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1. Introduction

Dye-sensitized solar cells are currently attracting widespread academic and commercial interest for conversion of sunlight into electricity because of its low cost and high efficiency [1–23]. At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles, and the sensitizer, which allows electronic conduction and harvesting of solar radiation, respectively. Various ruthenium complexes containing anchoring groups such as carboxylic acid, dihydroxy, and phosphonic acid on pyridine ligands have been used as sensitizers [24]. The anchoring groups serve to immobilize the sensitizer onto nanocrystalline TiO_2 surface, which upon photoexcitation injects electrons into the TiO_2 conduction band and the concomitant hole transfer to the redox electrolyte [25,26].

The anchoring groups of the sensitizer that contain protons, upon adsorption, transfer most of its protons to the TiO_2 surface charging it positively and thereby the Fermi level moves down (positively). However, the positive shift of the Fermi level decreases the gap between the redox couple iodide/triiodide and the Fermi level, resulting in lower open-circuit potential. On the other hand, if the sensitizer carries zero protons, then the Fermi level moves negatively, due to adsorption of anionic complex, and the cations thereby have a higher value for open-circuit potential while that of short circuit current is low [27–29]. Therefore, there should be an optimal degree of protonation of the sensitizer for which the product of short circuit photocurrent

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and open circuit potential is high that determines the power conversion efficiency of the cell.

cis-Dithiocyanatobis(4-carboxy-4′-carboxylate-2,2′-bipyridine)ruthenium(II) ditetrabutylammonium salt, (N719), is a high performance sensitizer in Grätzel photovoltaic cells [30]. It is adsorbed on mesoporous anatase TiO_2 as tetrabutylammonium double salt from a solution of acetonitrile/*tert*-butanol (1:1) mixture. The two hydrophobic cations were used in order to increase the solubility of sensitizer in organic solvent.

The high performance achieved using $((C_4H_9)_4N)_2$[Ru-(4-carboxy-4′-carboxylate-2,2′bipyridine)$_2$(NCS)$_2$] (N719) sensitized TiO_2 solar cell can be related to several factors, such as broad range of visible light absorption, relatively long-lived excited states, its excited energy almost matching those of TiO_2 conduction band, and the effect of protons and the cations carried by the sensitizer. It is therefore important to analyze in detail the structure of the sensitizer from adsorbing solution in order to design and develop tailored sensitizers. In this paper, we report detailed HPLC (High Pressure Liquid Chromatography) and mass analysis of the N719 sensitizer.

2. Experimental

HPLC analyses were performed on a Shimadzu HPLC 10-AVP series equipped with a photodiode array SPD-M 10 Avp as a detector using as solid phase a Luna C-18 (2) column 4.6 mm × 250 mm with a particle size of 5 μm, and water/acetonitrile 1:1, added with 0.1% of formic acid as liquid phase, at a flow rate of 1 ml/min. ESI (Electro Spray Ionization) experiments were conducted with a Thermo Finnigan Advantage Max Ion trap spectrometer in negative ion acquiring mode; sheath gas flow rate was set at 25 (arbitrary unit), auxiliary gas flow rate at 5 (arbitrary unit), spray voltage at 3.25 (KV), capillary temperature at 270 °C, capillary voltage at −7 (V), and tube lens offset at −60.00 (V). Nitrogen was used as sheath and auxiliary gases. High-resolution spectra were recorded on an LTQ Orbitrap Hybrid Mass Spectrometer. Sprayed solutions were prepared starting from a mother solution, obtained by solving 13.8 mg of complex in 10 ml of acetonitrile/*tert*-butanol (1:1); 1 ml of the mother solution was diluted to 10 ml by adding (i) acetonitrile/*tert*-butanol (1:1) mixture, (ii) 5% aqueous methanol solution, and (iii) an aqueous solution of 5 mM ammonium acetate added with 5% of methanol. The solution at basic pH was obtained by adding to aqueous solution some drops of a 30% ammonium hydroxide solution to obtain a concentration solution of 0.1 N; pH was monitored using a pH-metre Crison Basic 20 equipped with a glass electrode Crison 52-02, the reported working pH-range is 0–12; solvents used for MS analysis were purchased from Aldrich and were used without further purification.

The synthesis of N719 sensitizer was reported in our previous paper [10,31]. The chromatographic purification of N719 was carried out three times on a column of Sephadex LH-20 using the following procedure. The N719 complex was dissolved in water containing 2 equiv of tetrabutylammonium hydroxide. The concentrated solution was filtered through a sintered glass crucible and charged onto a Sephadex LH-20 column, which was prepared in water. The adsorbed complex was eluted using water. The main band was collected and the solution pH was lowered to 4.3 using 0.02 M HNO_3 acid. The titration was carried out slowly over a period of 3 h. Then, the solution was kept at −20 °C for 15 h. After allowing flask to 25 °C, the precipitated complex was collected on a glass frit and air dried. The same purification procedure was repeated two more times to get pure N-bonded isomer complex.

3. Results and discussion

Purified N719 was analysed by HPLC using a diode array as detector. HPLC run, reported in Fig. 1a, shows only one peak. Spectral homogeneity across the peak evidences that no coelution occurred, confirming N719 purity (Fig. 1b). The interaction between the solid phase and the TBA counterions of the Ru(II) complex is responsible for the tailored shape of the peak. Structure of complex was confirmed by the integration ratio of aliphatic and aromatic ^1H NMR signals and elemental analyses [32].

In order to characterize charged complexes involved during N719 adsorption on TiO_2 surface, Mass Spectrometry with ESI interface appeared particularly useful because [33] (i) it can directly detect mono and multi-charged ion, (ii) does not alter the connectivity of the complex through disassembly/reassembly sequences and (iii) causes essentially no or very little fragmentation. Recently, Newkome and Wesdemiotis applied this technique to study organometallic assemblies containing bis-terpyridinyl-Ru(II) connectivity [34].

A mother solution of N719 in acetonitrile/*tert*-butanol (1:1) was prepared at the same concentration of that used for the adsorption on TiO_2, then diluted 1:10 to obtain a concentration useful to record mass spectrum by direct injection method.

The mass spectrum reported in Fig. 2 shows a major peak at m/z 946.1 and two minor peaks at m/z 704.9 and at m/z 1187.5. Solvents of relative lipophilic character favour the dissociation of one of the two ion pairs of N719 complex, solvating the hydrophobic TBA cation, and the mono-anion (**E**) (Scheme 1) is mainly observed. Its stoichiometry is confirmed by isotopic pattern as shown in Fig. 3a. On this peak tandem mass spectrometry analysis was performed in order to obtain more structural informations. The complicate fragmentation obtained in MS/MS spectrum revealed that the interactions between the Ru(II) centre and the two bipyridine ligands are very strong. The assignation of the small peak at m/z 704.9 required the use of high resolution mass spectrometry technique. In Fig. 3b are reported experimental and calculated isotopic pattern of peak at m/z 704.9, corresponding to the mono-anion