



Ruthenium polypyridine complexes as sensitizers in NiO based p-type dye-sensitized solar cells: Effects of the anchoring groups

Yann Pellegrin^a, Loïc Le Pleux^a, Errol Blart^a, Adèle Renaud^a, Benoit Chavillon^b, Nadine Szuwarski^a, Mohammed Boujtita^a, Laurent Cario^b, Stéphane Jobic^b, Denis Jacquemin^{a,**}, Fabrice Odobel^{a,*}

^a CEISAM, Université de Nantes, CNRS, 2 rue de la Houssinière, 44322 Nantes Cedex 3, France

^b Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière, 44322 Nantes Cedex 3, France

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ABSTRACT

In this contribution, we investigate the photovoltaic performances of four ruthenium trisbipyridine complexes in NiO based dye-sensitized solar cells (DSSC). The four complexes differ by the nature of the anchoring groups, which are either carboxylic acids, biscarbodithioic acids catechol or methyl phosphonic acids. The properties of the dyes were studied by electrochemistry, absorption and emission spectroscopies, surface binding measurements, time-dependent density functional theory (TDDFT) as well as by determining their photoconversion efficiencies in DSSCs under AM 1.5. We show that these simple dyes are relatively efficient sensitizers in NiO-based DSSCs, since some of them give photoconversion efficiencies comparable to that of a standard benchmark dye coumarin **C343**. We also demonstrate that both catechol and methyl phosphonic acid are promising binding groups for NiO sensitizers to replace classical carboxylic acids in NiO sensitizers and finally we report molecular design rules to elaborate a new generation of better performing ruthenium polypyridine sensitizers.

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1. Introduction

There is currently a growing interest in the development of dye-sensitized solar cells (DSSCs) based on p-type inorganic semiconductors (p-SCs) such as nickel oxide [1]. This new type of solar cell is based on the hole injection in the valence band of the p-SC from the photoexcited sensitizer. Accordingly, the specific electronic properties of the ideal sensitizer for p-SCs significantly differ from those designed for classical Grätzel cells based on the sensitization of a n-type semiconductor (n-SC) such as titanium dioxide. In the latter case, the dye must be a strong reducer in its excited-state to inject an electron in the conduction band of the n-SC. Actually, the electronic requirements of the sensitizers for p-SCs are just the opposite of those for n-SC. In addition, the sensitizers must be functionalized with anchoring groups, first to firmly graft them on the semiconductor surface and second to provide a significant electronic coupling with the semiconductor wavefunction in order to ensure an efficient charge tunnelling from the sensitizer excited-state into the semiconductor [2–5]. For hole injection into a p-SC, this parameter is optimized when the highest occupied molecular

orbital (HOMO) of the dye significantly extends on the anchoring groups in order to overlap with the valence band (VB) orbitals of the semiconductor. Let us notice that the majority of dyes tested with p-type semiconductors were immobilized through carboxylic acid groups [1], which is not necessarily optimal for hole injection, since they generally bear large densities of the lowest unoccupied molecular orbital (LUMO) rather than of the HOMO [2–5]. For an efficient hole injection into the VB of a p-SC, a vectorial electron shift from the anchoring group towards the extremity of the dye is sought. As a result, electron withdrawing anchoring groups do not fulfil this requirement and would rather lead to a situation where positive charge density is moved in an unfavourable direction to assist the hole injection and to prevent the charge back recombination. Besides, with a view of performing charge photoinjection reactions, charge transfer excited-states such as those found in polypyridine ruthenium complexes are particularly relevant. Indeed, polypyridine ruthenium complexes perform particularly well as sensitizers in classical Grätzel DSSCs [6–8] and more generally as dyes in molecular devices for solar energy conversion [9,10]. In addition, the strong reducing potential of these complexes makes this class of compounds particularly appealing in view of performing photocatalytic processes with such photocathodes [11–15]. Surprisingly, synthetic ruthenium polypyridine complexes were never tested in p-type DSSCs.

In this paper, we report: (1) the electrochemical and the photophysical properties; (2) the surface binding properties; (3)

* Corresponding author. Tel.: +33 251125429; fax: +33 251125402.

** Corresponding author. Tel.: +33 251125564; fax: +33 251125402.

E-mail addresses: Denis.Jacquemin@univ-nantes.fr (D. Jacquemin), Fabrice.Odobel@univ-nantes.fr (F. Odobel).

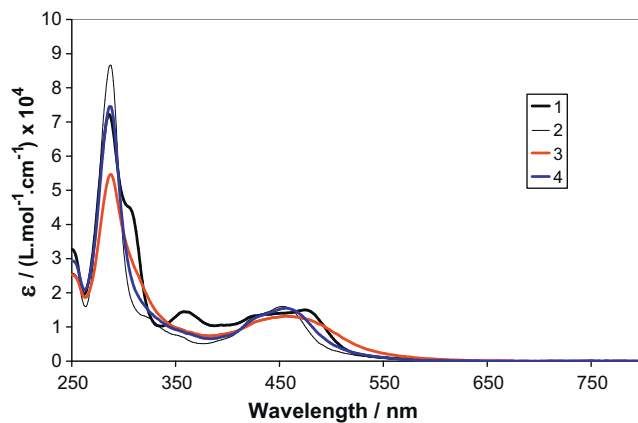


Chart 1. Structures of the ruthenium complexes investigated in this work.

time-dependent density functional theory (TDDFT) simulations; and (4) the photoconversion efficiencies in p-DSSC of a series of four ruthenium(II) trisbipyridyl complexes functionalized with different anchoring groups (Chart 1). The compounds synthesized herein enable not only to test the suitability of ruthenium polypyridine complexes as sensitizers in p-DSSCs but also to explore the pertinence of using other anchoring groups than the classical carboxylic acid group, which is the sole binding group used for NiO DSSCs up to now. These complexes were not prepared to break any photovoltaic records, since it was anticipated that they would display the classical orange colour with a relatively modest extinction coefficient, preventing thus to reach high performances. Similar trisbipyridine ruthenium complexes were also reported to be modest sensitizers in classical TiO₂ based Grätzel cells due to low LHE (Light Harvesting Efficiency) [16,17]. The results of this study firstly demonstrate that both catechol and methyl phosphonic acid are promising binding groups for NiO sensitizers to replace classical carboxylic acids in NiO sensitizers and secondly that through a rational ligand design, it is possible to achieve efficient sensitization of p-type semiconductors with ruthenium polypyridine complexes.

1.1. Materials and general synthetic procedures

Chemicals were purchased from Aldrich, Acros or ABCR and used as received. Air sensitive reactions were carried out under argon in dry solvents and glassware. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh) or with SDS neutral alumina (0.05–0.2 mm mesh). [Ru(bpy)₂(4,4'-biscarboxy-2,2'-bipyridine)](PF₆)₂ **1** [18], [Ru(bpy)₂(4,4'-(CH₂PO₃H₂)₂bpy)](PF₆)₂ **2** [17], complex **4** [19] and *cis*-Ru(bpy)₂Cl₂·2H₂O [20] were prepared according to literature methods. Complex Ru(bpy)₂(4,4'-biscarboxy-2,2'-bipyridine)](PF₆)₂ **3** was prepared by oxidation of the known 4,4'-bis(chloromethyl)-2,2'-bipyridine[bis(2,2'-bipyridine)] ruthenium dichloride [21] by elemental sulphur as described below.

1.1.1. [Ru(bpy)₂(bpy(CS₂H)₂)](PF₆)₂ (**3**)

Elemental sulphur (4 equiv., 69 mg) and sodium methanolate (4 equiv., 116 mg, 2.1 mmol) were placed in anhydrous methanol (50 mL) under argon atmosphere and refluxed until the sulphur was completely dissolved (ca. 2 h). Then [Ru(bpy)₂(4,4'-(CH₂Cl)₂bpy)](PF₆)₂ (1 equiv., 512 mg, 0.54 mmol) was added in the solid form to the reaction mixture, which was refluxed overnight. The solvent was evaporated and the obtained red solid was dissolved in water. Acidification with diluted aqueous hydrochloric

acid led to the precipitation of the complex, which was filtered off and washed several times with water. The product was dissolved in a minimum amount of acetonitrile. Addition of a saturated aqueous solution of NH₄PF₆ led to the precipitation of **3** (465 mg; 86%) as a dark orange solid, which was collected by filtration, washed with H₂O and dried under vacuum. ¹H NMR (300 MHz, CD₃CN): δ 8.49 (m, 6H), 8.05 (m, 6H), 7.72 (m, 4H), 7.39 (m, 6H). Anal. Calcd for C₃₆H₃₅F₁₂N₇O₂P₂RuS₄ (**1** + 2 MeOH and 1 CH₃CN): C, 38.7; H 3.2; N, 8.7; S 11.5. Found: C, 38.5; H, 2.8; N, 8.4; S 11.3.

1.2. Analytical measurements

¹H and ¹³C NMR spectra were recorded on a Bruker ARX 300 MHz. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl₃ δ = 7.26 ppm for ¹H and δ = 77.16 ppm for ¹³C). MALDI-TOF analyses were performed on a Bruker Ultraflex III, microTOF Q spectrometer in positive linear mode at 20 kV acceleration voltage with 2,5-dihydroxybenzoic acid (DHB) or dithranol as matrix. Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a Pt electrode, the auxiliary was a Pt wire of 10 mm long and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supported electrolyte was 0.1 N Bu₄NPF₆ in DMF and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s. UV-visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluoromax fluorimeter.

1.3. Preparation of dye-sensitized nanocrystalline NiO electrodes

Conductive glass substrates (F-doped SnO₂) were purchased from Pilkington (TEC8, sheet resistance 8 Ω/square). Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 minutes before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air. NiO films were prepared in two steps. A first layer of NiO (Nickel oxide nanopowder, Inframat Advanced Materials) was screen printed and annealed at 550 °C for 10 min; second, a layer of F108-templated precursor solution was doctor bladed onto the screen printed NiO, followed by sintering at 450 °C for 30 min

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