

Novel heteroleptic ruthenium complexes for dye sensitized solar cells



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ABSTRACT

A new heteroleptic complex, $[\text{Ru}(\text{dcbH}_2)(\text{bpy})(9\text{AA})\text{Cl}]^{2+}$, **Ru-9AA** (9AA = 9-aminoacridine), was synthesized, characterized and used along with the previously synthesized $[\text{Ru}(\text{dcbH}_2)(\text{bpy})(\text{TCNE})\text{Cl}]$, **Ru-TCNE** (TCNE = tetracyanoethylene), in dye-sensitized solar cells (DSCs). The photoelectrochemical data were evaluated in comparison to the standard $[\text{Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$ dye, **N3**. DSCs sensitized by these compounds exhibit overall efficiency conversion of 0.95 and 2.82% for **Ru-9AA** and **Ru-TCNE**, respectively, while that for **N3** is 5.65% in the same condition. In spite of presenting lower global efficiencies than the standard dye, the **Ru-TCNE** complex present adequate electron injection efficiency and convert light into electricity effectively.

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1. Introduction

Polypyridyl ruthenium(II) complexes have been extensively studied due to their thermal stability, interesting photochemical, photophysical and electrochemistry properties [1,2], which can be adjusted by the insertion of different Lewis bases. These features have driven the development of several applications of ruthenium (II) complexes (e.g., artificial photosynthetic frameworks [3,4], sensors [5], and catalysis [6–8]). Among these applications, dye-sensitized solar cells (DSCs) have caught significant attention as an alternative to conventional silicon photovoltaic devices [9,10]. A pioneer study on DSC was performed by Grätzel and O'Regan in 1991 [11] using the dye complex *cis*- $[\text{Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$ (**N3**), where $\text{dcbH}_2 = 4,4'$ -dicarboxy acid-2,2'-bipyridine.

It is well-known that the mechanism of sensitization of a wide band gap semiconductor (e.g., TiO_2) in DSCs containing Ru-based dyes, such as **N3**, relies on a light-driven metal-to-ligand charge-transfer (MLCT) transition followed by charge-injection into the anode [12–14]. The design of new optimal sensitizer is a challenging task to improve light harvesting and hence the DSC efficiency. Most strategies rely on new Ru-based chromophores with broad high extinction coefficient MLCT bands, which fulfill an intense absorption the visible region. Usually, the first approach for broadening the absorption band and enhance the molar absorption

coefficient is to increase the conjugation length of the bipyridyl ligand. In relation to the red-shifted absorption band [15], the coordination of two kinds of Lewis bases are typically employed: (i) polypyridyl ligands of lower π^* manifold; (ii) strong donor ligands that raise the energy of the metal-based highest occupied molecular orbital (HOMO). Therefore, thiocyanate (NCS^-), which is a strong donor ligand, has been successfully used as an ancillary ligand in many ruthenium sensitizers [16–19]. However, several systems have been reported focusing on the replacement of NCS^- , due to the decrease in the stability associated to the labilization of this ligand from the Ru(II) coordination sphere [20–22]. Among the so-synthesized compounds, the best solar conversion efficiency ($\eta = 10.1\%$) was observed for $[\text{Ru}(\text{dcbH}_2)_2(2-(2,4\text{-difluorophenyl})\text{pyridine})]$, in which both NCS^- ligands were replaced [20]. Bomben et al. [22] expanded the series through design strategies to develop Ru(II) complex dyes for the purpose of TiO_2 sensitizers, achieving initial efficiencies of 2–4%. These relatively low efficiencies have been ascribed by authors to insufficient driving force for dye regeneration by the electrolyte.

In order to develop new molecular engineered sensitizers in DSCs to enhance its stability, we have investigated NCS^- replaced ruthenium complexes containing the 9-aminoacridine (9AA) and tetracyanoethylene (TCNE) ligands. The former ligand has received particular attention for being one of the most versatile chromophores for fluorescence probes [23] with interesting photophysical and photochemical properties, while the unsaturated polynitrile TCNE ligand is an interesting electron acceptor because of its very high electron affinity (3 eV [24]). In addition, despite its

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simple structure, the non innocent TCNE ligand presents intense charge transfer absorption bands in the visible. Besides, very few works have been reported on photophysical and electrochemical properties of ruthenium bis(diimine) X_2 complexes where X represents a pyridinyl-based ligand [25]. The obtained complexes, referred as **Ru-9AA** and **Ru-TCNE**, are represented in Fig. 1. Photoelectrochemical parameters of DSCs using these new compounds are presented along with those having **N3** for comparison.

2. Experimental

2.1. General

Reagents and solvents were obtained from commercial sources and used as received: 9-aminoacridine (9AA), *N*-methylmorpholine (NMM), 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-dipyridyl, ruthenium(III) chloride hydrate, methanol, dimethylformamide (DMF), tetra-*n*-butylammonium perchlorate (tbpap) species were purchased from Aldrich. The ESI mass spectra were recorded by using an on-trap mass spectrometer (LCMS-IT-TOF, Shimadzu) equipped with an orthogonal ESI source operated in the positive ion mode. The heated capillary temperature and electrospray voltage were set at 150 °C and 3.5 kV, respectively. Infrared (IR) spectra were recorded with an ABB Bomem FTLA 2000-102 FTIR spectrometer, using KBr pallets. Nuclear magnetic resonance (NMR) experiments were performed on a Bruker DRX-500 spectrometer (Bruker Biospin, Rheinstetten, Germany) at room temperature using CD₃OD-*d*₄ as solvent (Cambridge Isotope Laboratories). Conductivity of a 10⁻³ mol L⁻¹ solution in methanol was measured in a QUIMIS Q795M2 conductivitymeter.

2.2. Synthesis of the compounds

The standard dye **N3** was purchased from DyeSol, and the complexes *cis*-[Ru(dcbH₂)(bpy)Cl₂] and *cis*-[Ru(dcbH₂)(bpy)(TCNE)Cl]·H₂O [26] were synthesized according to the literature procedure with slight modification.

2.3. *cis*-[Ru(dcbH₂)(bpy)(9AA)Cl]²⁺

0.034 g (0.17 mmol) of 9AA was dissolved in 10 mL of DMF followed by addition of 30 μL of *N*-methylmorpholine (NMM) under stirring. After 10 min, 0.100 g (0.17 mmol) of [Ru(dcbH₂)(bpy)Cl₂] was added, and the mixture was kept under stirring and reflux for 24 h. At the end of the reaction, the solid is filtered off and the solvent was removed from the filtrate by rotary-evaporator under vacuum. The residue was dissolved in a minimum amount of

methanol and loaded on a P2 column. The desired complex was eluted with 20–80% of methanol–H₂O containing 20 mM KCl as a dark red fraction, which was concentrated by rotary-evaporator under vacuum till near dryness. The thick slurry obtained was then precipitated by adding NH₄PF₆. The precipitate was filtered off, washed with acetone, and dried under vacuum. After then, the solid was recrystallized in methanol. Yield: 55%. Anal. calcd for C₃₅H₂₆N₆O₄ClRuP₂F₁₂: C, 41.17; H, 2.57; N, 8.23; found: C, 41.50; H, 2.79; N, 8.77. HRMS calcd for C₃₅H₂₆N₆O₄ClRu: 731.1401 and [C₃₅H₂₆N₆O₄ClRu]²⁺ (base peak): 365.5366. Found: 731.0732 and 365.5365 (Fig. S1 in the Supporting Information). Λ_M (methanol, 10⁻³ mol L⁻¹) = 170 μS cm⁻¹ mol⁻¹. IR (KBr pallet, cm⁻¹) 1718 (ν_{COOH}), 1420 (δ_{CH} + δ_{NH}), 843 (ν_{PF₆}).

2.4. Electrochemical experiments

The electrochemical experiments were carried out at room temperature in freshly distilled DMF containing 0.1 mol L⁻¹ tbap under argon atmosphere. These measurements were performed by using an electrochemical analyzer from Bioanalytical Systems Inc. (BAS), model EPSILON. A single compartment electrochemical glass cell was used with glassy carbon, Pt disk and Ag/AgCl as working, auxiliary and reference electrodes, respectively. The potentials referred in this text do not include the liquid potential junction.

2.5. Photophysical experiments

UV–vis absorption spectra were recorded on a Hewlett-Packard, 8453A diode array spectrophotometer. Steady-state emission spectra were recorded in a PTI fluorescence spectrophotometer in a T-format. A xenon lamp (λ_{exc} = 500 nm, 1 nm bandwidth) was used as excitation light source for steady-state. The absorbance of sample solutions in methanol was set between 0.1 and 0.3 in a four polished face cuvette with 1.00 cm optical length. Solutions were deoxygenated with argon for at least 10 min prior to measurement. Emission quantum yields were calculated relative to [Ru(bpy)₃]²⁺ in CH₃OH with φ = 0.045.

2.6. Photoanodes preparation

TiO₂ nanoparticles were prepared by the sol–gel method as described previously [27,28] or obtained from Dyesol (18-NRT paste). A semiconductor film was deposited over transparent Fluorine doped Tin Oxide (FTO) substrates (Pilkington, TEC-15, 15 Ω per square) by screen-printing to fabricate photoanodes. After drying at room temperature, the electrodes were sintered at

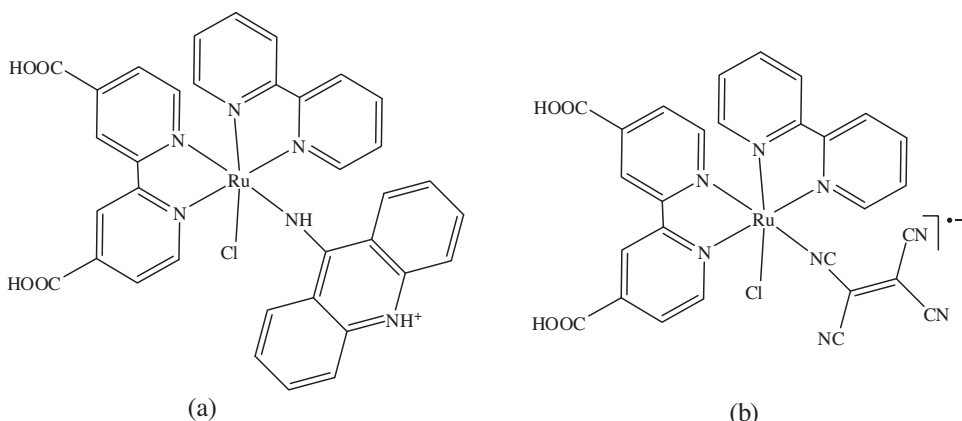


Fig. 1. Structures of complexes: (a) *cis*-[Ru(dcbH₂)(bpy)(9AA)Cl]²⁺ and (b) *cis*-[Ru(dcbH₂)(bpy)(TCNE)Cl], referred as **Ru-9AA** and **Ru-TCNE**.

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