PTA-based ruthenium complexes as photosensitizers for dye-sensitized solar cells

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ABSTRACT

Two novel ruthenium complexes are synthesized, photo-characterized and tested as photosensitizers in dye-sensitized solar cells (DSCs): [RuCl₂(mPTA)₃(H₂O)](CF₃SO₃)₃ (C₁) (m: methyl; PTA: 3,5,7-triaza-phosphaadamantrane) and [Ru(C = C = CPh₂)Cp(PTA)(PPh₃)](CF₃SO₃) (C₂). The complexes are soluble in organic solvents and, interestingly, in water, which makes them useful for water-based photochemical processes. They possess excellent photon-absorption over a wide range of the spectrum with intense peaks at ~ 330 nm for both sensitzers. A second peak is found for C₂ at 525 nm, wider than the corresponding to the N719 standard dye. DSCs using these sensitzers are evaluated against different electrolytes. The solar cell performance was similar for both complexes and strongly dependent on the electrolyte nature, with a maximum conversion efficiency of 0.32% for the iodide/triiodide electrolyte.

1. Introduction

The use of dye-sensitized solar cells (DSCs) is a well established strategy for solar energy conversion because of their efficiency, inexpensive manufacturing and environmental friendly nature [1,2]. DSCs are sandwich-type electrochemical devices based on

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nanocrystalline metal oxide semiconductors sensitized by molecular dyes [3,4]. The dye (or photosensitizer) is able to absorb over a wide range of the solar spectrum to reach its excited state, then producing electrons injected into the conduction band of the semiconductor (photoelectrode), as depicted in Fig. 1. The semiconductor often consists of a mesoporous TiO2 film deposited on a transparent fluorine-doped tin oxide (FTO) conducting glass; this provides a large surface area to maximize the light absorption while ensures the dye-electrolyte electrical connection. Injected electrons flow towards the counter electrode, a platinized FTO glass substrate, and are transferred to the redox pair present in the electrolyte (usually I\textsuperscript{-}/I\textsuperscript{3+}). The circuit is completed when the oxidized dye is regenerated to its ground state by electron donation from the electrolyte. As a result, DSCs perform an electrical work through a regenerative photo-electrochemical cycle without consumption of chemical species [5].

DSCs use indistinctly natural or synthetic dyes to harvest energy from light [6]. Artificial dyes, usually based on transition metal coordination complexes such as Ru, Os and Pt, are widely employed since they yield greater efficiencies [7,8]. Ruthenium-based complexes satisfy a few key requirements to work properly, such as photon absorption across a broad range of wavelengths, chelation to TiO2 surface, and chemical stability. Among these complexes, polypyridyl ruthenium coordination complexes such as Ru, Os and Pt, are widely employed since the redox pair present in the electrolyte (usually I\textsuperscript{-}/I\textsuperscript{3+}). The circuit is completed when the oxidized dye is regenerated to its ground state by electron donation from the electrolyte. As a result, DSCs perform an electrical work through a regenerative photo-electrochemical cycle without consumption of chemical species [5].

2. Materials and methods

2.1. Materials

Conducting glass plates (FTO) (F-doped SnO\textsubscript{2}, with resistance 11–13 Ω/sq, Nippon Sheet Glass) are used to fabricate the electrodes of the DSCs. TiO\textsubscript{2} and Pt films are fabricated from TiO\textsubscript{2} (P-25, Degussa), Triton X-100 (Merck) and H\textsubscript{2}PtCl\textsubscript{6} (Aldrich). Iodine (99.9%, Aldrich), LiI (99.9%, Aldrich), LiF (99.9%, Aldrich), 4-tert-butylpyridine (TPB) (96%, Aldrich), 1-methyl-3- propylimidazolium iodide (MPII) (98%, Aldrich), N-Methylbenzimidazole (NMBI) (99%, Aldrich), Guanidinium thiocyanate (GNC) (99%, Sigma) and 3-methoxypropionitrile (98%, Aldrich) are employed to prepare the electrolyte solutions. The dye N719 (95%) and all the other chemicals are purchased from Sigma-Aldrich with reagent grade and used as received.

2.2. Synthesis and characterization of the ruthenium complexes

All reactions were carried out under dry nitrogen atmosphere by standard Schlenk-tube techniques. Solid complexes were collected on sintered glass-frits and washed as described later. The following products for the synthesis were prepared according to reported procedures: PTA [23, [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] [24,25], [RuC\textsubscript{p}Cl(PPh\textsubscript{3})\textsubscript{2}] [26] and [RuC\textsubscript{p}Cl(PTA)(PPh\textsubscript{3})] [27,28].

2.2.1. Complex C1: [RuCl\textsubscript{2}(mPTA)(H\textsubscript{2}O)](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}\

We first prepared the compound mPTA(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}, which is one of the reactants to accomplish the synthesis of complex C1. To this end, MeCF\textsubscript{3}SO\textsubscript{3} (0.56 mL, 5.08 mmol) was added to a stirred PTA (0.6 g, 3.82 mmol) solution prepared in CHCl\textsubscript{3} (60 mL). A white suspension is formed, further stirred for 30 min at room temperature. The resulting white precipitate was filtered, washed against CHCl\textsubscript{3} and air-dried.

Yield: 91.3%.

Complex C1 was synthesized by reacting mPTA(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} and [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] in MeOH according to Scheme 1. The complex [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (450 mg, 0.47 mmol) was dissolved in MeOH (60 mL) and then mPTA(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} (460 mg, 1.43 mmol) was added. The MeOH used for the synthesis was not dried, providing the water required for the reaction. After 6 h of reaction at room temperature, a yellow-orange solution was obtained. Next, the solvent was reduced to 15 mL and 20 mL of Et\textsubscript{2}O were added. The yellow precipitate was finally filtered under inert atmosphere, washed against Et\textsubscript{2}O and vacuum-dried. Yield: 84%.

The yellow complex C1 is soluble and stable in water at room temperature (S<sub>25 °C</sub> = 89 mg mL<sup>-1</sup>). The molecular structure consists of a distorted octahedral ruthenium atom bonded to two mPTA trans to each other, two Cl ligands trans to each other and one mPTA trans to [Ru(C = C phenyl)Cp(PTA)(PPh\textsubscript{3})](CF\textsubscript{3}SO\textsubscript{3}) (C2), with m: methyl, and PTA: 3,5,7-triaza-phosphaadamantane. PTA ligands make these complexes soluble in aqueous solvents, becoming them useful for water-based photochemical processes [21]. Both complexes present intense photon-absorption bands at ~ 330 nm and C2 also displays a much stronger absorption at 525 nm. Moreover, chelation to the titania film can be accomplished via the PTA groups, similarly to the anchoring provided by phosphate groups [22]. The efficiency of DSCs containing the complexes in combination with three electrolytes is evaluated and compared to N719. The electrochemical behavior is similar for both complexes with a strong influence of the electrolyte nature.

![Scheme 1. Synthesis of the ruthenium complex C1.](image)
one water molecule [29]. The positive charge of the complex is balanced by three CF₃SO₃⁻ counter-ions. Characterization data can be found in the supplementary material.

2.2.2. Complex C2: \([\text{Ru}(C≡C\text{Ph}_2)\text{Cp}(\text{PTA})(\text{PPh}_3)](\text{CF}_3\text{SO}_3)\]

The allenylidene-ruthenium complex was prepared as described in Scheme 2. Ag(CF₃SO₃) (0.03 g, 0.12 mmol) dissolved in CHCl₃ (2 mL) was added to a stirred solution of \([\text{RuCpCl}(\text{PTA})(\text{PPh}_3))] (0.072 g, 0.12 mmol) prepared in 30 mL of CHCl₃. The solution reacted with 1,1-diphenyl-2-propyn-1-ol (0.18 g, 0.81 mmol) for 5 min at room temperature. The resulting mixture was filtered to remove the precipitated AgCl, yielding a purple solid after solvent evaporation. The solid corresponding to complex C2 was washed against Et₂O (2 x 5 mL) and dried under vacuum. Yield: 94%.

Complex C2 is soluble in common organic solvents and slightly soluble in water (S25°C = 0.1 mg mL⁻¹). The complex formation is confirmed by \(^{13}\text{C}\{1\text{H}\} \text{NMR} [30].\) Spectra reveal a neat triplet slightly below 293.7 ppm corresponding to the allenylidene α-carbon coupled to the two phosphines P-atoms. Signals ascribable to both β- and γ-carbons are detected at the expected chemical shifts. The complex keeps its nature in solid state, as confirmed by the characteristic allenylidene stretching absorption band observed by IR spectra, \(\nu(C≡C): 1930\) cm⁻¹. The cone angles of the PPh₃ and PTA phosphines are obtained from the structure of a parent complex, as C1 does not form crystals. These angles are 133° for the PPh₃ and 109° for the PTA, in agreement with those found for other ruthenium complexes with PPh₃ and PTA ligands [30]. Further characterization results are shown in the supplementary data.

2.3. FTO electrical resistance

The influence of the thermal treatment on the FTO electrical resistance, \(R_s\), was studied according to the Van der Pauw method [31]. Initial resistance value, \(R_0 = (12.60 \pm 0.20)\) Ω/sq, changes to \(R_s = (13.45 \pm 0.15)\) Ω/sq after cleaning with isopropanol and activation by temperature (420°C, 30 min). The FTO is a suitable material for solar cell fabrication, provided that the thermal treatment does not increase significantly the sheet resistance [32].

2.4. Fabrication of photoelectrodes

A concentrated paste of TiO₂ (15 wt.%) was prepared by dispersing TiO₂ nanoparticles in a mixture of ethanol (61 wt.%) and nitric acid (24 wt.%) under 12 h stirring at room temperature. Surfactant Triton X-100 (0.2 wt.%) was added and the mixture stirred for additional 12 h.

FTO substrates were covered with transparent adhesive tape (Scotch, 50 μm in thickness), leaving a square-shaped free surface of \(\sim 0.4\) cm². A drop of the TiO₂ paste was spread using a glass rod over the square area by the so called doctor-blade technique. The paste was allowed to dry at room temperature for 1 h under ethanol atmosphere. The substrate was placed into a muffle furnace (450°C, 1 h) to calcine the paste, then forming the mesoporous TiO₂ film. This procedure yields high quality TiO₂ films without granular features or cracks on the surface [33].

The different ruthenium complexes were adsorbed onto the TiO₂ film by adding an excess of dye solution. The reference dye N719 was prepared in ethanol at 3.10⁻⁴ M, C1 in H₂O at 3.10⁻² M, and C2 in chloroform at 3.10⁻³ M. Adsorption processes were conducted in dark at room temperature for 24 h. The non-adsorbed dye was removed by rinsing with ethanol.

The platinized counter electrodes were made by coating FTO substrates with a thin layer of Pt. A droplet of the H₂PtCl₆ solution (0.01 M in ethanol) was spread on the surface before heating at 380°C for 20 min.

2.5. DSC assembly and characterization

The solar cells were assembled following the procedure stablished by Ito et al. [34,35]. The dye-sensitized electrode and the counter electrode were assembled in a sandwich-type cell using a thermal adhesive film (Dupont Surlyn, 60 μm) to set the inter-electrode gap and make the solar cell airtight. The electrolytes penetrate the gap by capillary action from a tiny hole drilled on the counter electrode. As a result, we obtain solar cells with an active electrode area of 0.36 cm².

Photocurrent density-voltage (J–V) curves were determined under direct sun radiation. The solar irradiation, measured with a thermopile-based pyranometer, was similar in all experiments: 399.3 W/m² (admitting 5% error tolerance). J–V curves were determined by digital source meters without any external bias. The electrical data were averaged over three samples in each case, which also allowed to check the reproducibility.

3. Results and discussion

3.1. UV–vis properties

The UV–vis absorption spectra were recorded using a high resolution diode array spectrophotometer (HR4000, Ocean Optics). Fig. 2 plots the normalized absorption vs wavelength of the ruthenium complexes, including the well-known spectrum of N719 in ethanol. The electronic spectrum of complex C1 in water is characterized by a strong absorption peak at 326 nm and a smaller one at 448 nm; the absorption

Fig. 2. UV–vis absorption spectra of the ruthenium complexes; N719 was prepared in ethanol at 3.10⁻⁴ M (dot line), complex C1 in H₂O at 3.10⁻² M (orange), and complex C2 in chloroform at 3.10⁻³ M (red). Inset: Dye-sensitized solar cells prepared with the ruthenium complexes C1 and C2. Glass substrates shift allows the electrical contacts (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
coefficient was \( \varepsilon_{\text{max}} \approx 10^3 \text{ M}^{-1} \text{ cm}^{-1} \). On the other hand, complex C2 in chloroform displays a peak at 338 nm as well as a broad absorption band in the visible range, with the maximum located at 520 nm. This band matches to one of the N719 absorption peaks, being the C2 band wider. Furthermore, the first peak of both dyes appears at similar wavelengths than the corresponding to the maximum absorption of N719 (315 nm).

The electronic properties of the ruthenium complexes arise from ligand-centered transitions (LCCT), metal-centered or d-d transitions (MC) as well as metal-to-ligand charge transfer transitions (MLCT). The absorption peaks appearing in the UV range are due to LCCT transitions. At higher wavelengths, the absorption comes from MC and MLCT transitions [36]. The ruthenium complexes show absorption properties similar to those of N719, with strong absorption bands covering a wide range of the spectrum. In view of these results, the ruthenium complexes seem to meet the requirements to sensitize DSCs.

3.2. Morphology of the Pt electrode

Atomic Force Microscopy (AFM) was used to characterize the morphology, topography and roughness of the counter electrode as these parameters influence the solar cell performance. Fig. 3 shows an AFM surface image of the Pt film deposited on FTO substrate. The image shows a highly textured Pt electrode with 32.3 nm roughness. A surface area of 12.60 \( \mu \text{m}^2 \) was measured for 9.0 \( \mu \text{m}^2 \) scanning area (surface/area ratio = 1.4). This result is very similar to that obtained by Tsai and coworkers [37]. These authors found the best solar cell performance for platinized electrodes with roughness = 28.3 nm and surface/area ratio = 1.17, confirming that our deposition method optimizes the morphology of the Pt counter electrode. The resulting high roughness and surface area enhance the catalytic ability of the electrode for \( \text{I}_3^- \) ions reduction and charge exchange at the Pt/electrolyte interface. As a result, the conversion efficiency of the solar cell is expected to enhance by 10% respect to other electrode morphologies [37].

3.3. Solar cell performance

Cells will be named Cx-ELy, being x, y the numbers of the complex (C) and electrolyte (EL). Three electrolytes are used: EL1: 0.05 M \( \text{I}_2 \), 0.5 M LiI, 0.5 M 4-tert-butylpyridine (TBP) in 3-methoxypropionitrile; EL2: 0.05 M \( \text{I}_2 \), 0.5 M LiI in 3-methoxypropionitrile; EL3: 1.0 M PMII, 0.5 M NMBI, 0.1 M GNCS in 3-methoxypropionitrile. Electrolytes EL1, EL2 are based on the iodide/triiodide redox couple that is considered one of the most efficient charge mediator [32]. Electrolyte EL3 is a liquid ionic composed of imidazolium salts as a source of iodide. It is widely used because of their improved chemical and thermal stability, which is a key requirement for long-lived DSCs [38]. For each complex-electrolyte combination, three solar cells were fabricated to check reproducibility.

Fig. 4 shows average current density–voltage curves for DSCs. Curves allow accessing the electrical parameters: open circuit voltage, \( \text{V}_{\text{OC}} \); short circuit current density, \( \text{J}_{\text{SC}} \); fill factor, FF; and overall efficiency, \( \eta \). The last one represents the percentage amount of solar light converted to electrical output. These parameters are averages from three measurements and are summarized in Table 1. A reference cell is made with dye N719 and electrolyte EL1 (N719-EL1) for comparison.
yields an efficiency of 8.8%, as expected according to previous works [35,39]; this result validates our solar cell manufacturing.

The DSCs prepared with complex C1 and electrolyte EL1 present \( V_{OC} = 550 \text{ mV} \), very close to the value obtained for N719, but a significantly lower \( J_{SC} = 0.444 \text{ mA/cm}^2 \). This leads to an overall conversion efficiency \( \eta = 0.324\% \), which is the best performance achieved with complex C1. The photochemical parameters worsen when C1 works in combination with electrolyte EL2: \( V_{OC} = 396 \text{ mV} \), \( J_{SC} = 0.378 \text{ mA/cm}^2 \), \( \eta = 0.233\% \). The improved performance attained with electrolyte EL1 is due to the presence of 4-tert-butylpyridine (TBP) acting as a redox mediator and the dye regeneration is thus not as good as for the iodide/triiodide redox couple. This ultimately diminishes the solar cell performance [42], as it is observed in our experiments.

The solar cells sensitized with complex C2 exhibited similar performance than complex C1. The characteristic parameters obtained with electrolyte EL1 became worse: \( V_{OC} = 510 \text{ mV} \), \( J_{SC} = 0.306 \text{ mA/cm}^2 \), \( \eta = 0.206\% \). Interestingly, the performance enhances when using electrolyte EL2: \( V_{OC} = 492 \text{ mV} \), \( J_{SC} = 0.397 \text{ mA/cm}^2 \), \( \eta = 0.324\% \). The presence of TBP in this case does not improve the performance since it deprotonates the TiO\(_2\) surface by adsorption, consequently shifting the conduction band of the semiconductor toward negative potentials [40]. The recombination of the photo-injected electrons and the redox mediator is then reduced. Consequently, the open-circuit potential and the overall efficiency of C1-EL1 improve [41]. With the liquid electrolyte, the solar cells C1-EL3 result in even lower photochemical parameters, \( V_{OC} = 256 \text{ mV} \), \( J_{SC} = 0.275 \text{ mA/cm}^2 \), \( \eta = 0.101\% \). In this case, the high viscosity of the electrolyte limits the diffusion of the redox mediator and the dye regeneration is thus not as good as for the iodide/triiodide redox couple. This ultimately diminishes the solar cell performance [42], as is observed in our experiments.

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**Table 1**

| Solar cell | \( V_{OC} \) (mV) | \( J_{SC} \) (mA/cm\(^2\)) | FF | Efficiency, \( \eta \) (%) |
|------------|-------------------|-----------------------------|---|--------------------------|
| N719-EL1   | 568 ± 1           | 9.77 ± 0.05                 | 0.63 ± 0.03 | 8.8 ± 0.5 |
| C1-EL1     | 550 ± 1           | 0.444 ± 0.008               | 0.529 ± 0.011 | 0.324 ± 0.011 |
| C1-EL2     | 396 ± 1           | 0.378 ± 0.008               | 0.623 ± 0.013 | 0.233 ± 0.024 |
| C1-EL3     | 256 ± 1           | 0.275 ± 0.008               | 0.575 ± 0.015 | 0.101 ± 0.024 |
| C2-EL1     | 510 ± 1           | 0.306 ± 0.008               | 0.528 ± 0.006 | 0.206 ± 0.003 |
| C2-EL2     | 492 ± 1           | 0.397 ± 0.008               | 0.662 ± 0.015 | 0.324 ± 0.003 |
| C2-EL3     | 180 ± 1           | 0.122 ± 0.008               | 0.50 ± 0.04  | 0.028 ± 0.004 |
