

Artificial photosynthesis based on dye-sensitized nanocrystalline TiO₂ solar cells

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Dedicated to Professor Michael Grätzel.

Abstract

A new series of amphiphilic heteroleptic ruthenium(II) sensitizers [Ru(H₂dcbpy)(dhbpy)(NCS)₂] (**C1**), [Ru(H₂dcbpy)(bccbpy)(NCS)₂] (**C2**), [Ru(H₂dcbpy)(mpubpy)(NCS)₂] (**C3**), [Ru(H₂dcbpy)(bhcbpy)(NCS)₂] (**C4**) have been synthesized and fully characterized by UV–Vis, emission, NMR and cyclic voltammetric studies (where dhbpy = 4,4'-dihexyl-2,2'-bipyridine, bccbpy = 4,4'-bis(cholesteroxycarbonyl)-2,2'-bipyridine, mpubpy = 4-methyl-4'-perfluoro-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-undecyl-2,2'-bipyridine, bhcbpy = 4,4'-Bis(hexylcarboxamido)-2,2'-bipyridine). The amphiphilic amide heteroleptic ruthenium(II) sensitizers, self-assembled on TiO₂ surface from ethanol solution, reveal efficient sensitization in the visible window range yielding ≈80% incident photon-to-current efficiencies (IPCE). Under standard AM 1.5 sunlight, the **C4** sensitizer gave 15 mA/cm² short circuit photocurrent density, 0.66 fill factor and an open circuit voltage of 0.75 V, corresponding to an overall conversion efficiency of 7.4%.

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1. Introduction

The forecasts for the next 50 years predict that human energy needs are likely to double while fossil energy reserves are shrinking. At the same time, on earth, per year, plants and bacteria capture and convert light into a quantity of biological material greater than 100 times the food needed for mankind [1]. To face future energy demand, a solution would be to copy one of the plants or bacteria mechanisms [2,3] to develop environmental friendly energy production systems having low technology manufacturing and low cost. The numerous publications during the last decade on the design of new solar cells and especially on dye-sensitized solar cells [4–7] (DSSC) explain the big interest for new systems. In these cells a homoleptic complex

cis-dithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II), known as **N3** is used. The **N3** sensitized cells exhibited 85% incident photon to current efficiency (IPCE), and under standard AM 1.5 solar conditions the total power conversion efficiency reached more than 10% [8]. To improve further the efficiency of the dye-sensitized solar cells, considerable efforts were focused on new ruthenium polypyridyl complexes [9–11]. Recently, we have reported a new promising class of hydrophobic heteroleptic complexes, which improved considerably the efficiency and the lifetime of dye-sensitized solar cells. The hydrophobicity parameter in dyes reveals to be crucial in DSSC for improving long-term stability [12] and performances [13]. The hydrophobic factor, is analogous to the one found in natural photosynthetic centers, which also plays a crucial role through hydrophobic pockets.

James Barber and his colleagues published [14,15] numerous papers, on X-ray structures, describing at the

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molecular level the composition and the spatial positioning of molecules and proteins in natural photosynthetic systems. Three similarities are always observed whatever the species are. The first one is the existence of a specific arrangement of proteins surrounding the photosynthetic center that tune, through their hydrogen bonding, the electronic properties of the electron donor and acceptor molecules.

The second similarity is the existence of a high organization level between subunits forming the photosynthetic complex. Kühlbrandt et al. [16] have reported that in the plant photosystem II reaction center, the arrangement of the constituting 23 trans-membrane helices is remarkably similar to that found in purple bacteria or plant photosystem I. Their similar arrangement combined with a maximum light conversion efficiency achievement after centuries of natural selection demonstrated the correlation between maximum conversion efficiency and a unique molecular positioning. The third similarity is the existence of hydrophobic zones surrounding the photosynthetic centers. The possible roles of these hydrophobic areas are to facilitate and direct a primary charge separation (across a lipidic membrane) and to avoid, by steric hindrance, non desired side reactions (back electron transfers and chemical reactions).

Therefore, we took into account these three observations in our design strategy of new ligands and synthesized a series of ligands, by inserting on 4,4' position of the bipyridine, which are able to self organize through amide bonds, fluorinated or hydrogenated alkyl chains. The corresponding heteroleptic ruthenium sensitizers were synthesized by incorporating one 4,4'-dicarboxy-2,2'-bipyridine as an anchoring ligand, one newly designed ligand and with two NCS groups to tune metal HOMO levels. In this paper we describe, the syntheses of four novel ligands and the photophysical and photovoltaic properties of their heteroleptic ruthenium complexes **C1**, **C2**, **C3**, **C4**.

2. Experimental

All solvents and reagents, purchased from Fluka, were of analytical grade. Anhydrous toluene and THF, were used after distillation under argon from molten sodium. Solvent water content was measured before use by Karl-Fisher automatic titration using a Metrohm 684 KF coulometer for water content, which is typically below 20 ppm. 4,4'-Dimethyl-2,2'-bipyridine was sublimated under vacuum at 9 mbars. 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decyl iodide was purchased from Aldrich (Ref. 370525) and used without purification.

2.1. UV-Vis, fluorescence measurements

UV-Vis and fluorescence spectra were recorded in a 1 cm pathlength quartz cell on a Cary 5 spectrophotometer (Cary, <http://www.varianinc.com>) and Spex Fluorolog 112

Spectrofluorometer (Fluorolog series, <http://www.jobinyvon.com>), respectively.

2.2. NMR and mass spectroscopy measurements

NMR spectra were measured with a Bruker ACP-200 spectrometer (<http://www.bruker-biospin.de>) at 200 MHz for ^1H and 50.3 MHz for ^{13}C nucleus. The reported chemical shifts are given with respect to TMS signal. FAB-MS spectra were obtained at the University of Lausanne from a 4-nitrobenzyl alcohol matrix.

2.3. Electrochemical measurements

A Princeton Applied Research potentiostat, model 273 A, was used (<http://www.princetonappliedresearch.com>). The cyclic voltammograms were obtained at room temperature in degassed DMF solution. Tetrabutylammonium perchlorate (TBAP) 0.1 M was used as supporting electrolyte in DMF. A glassy carbon electrode, a Ag/AgCl/ KCl_{sat} and a platinum wire were used as a working, a reference and a counter electrode, respectively. In addition ferrocene was added to each sample solution at the end of the experiment and the ferrocenium/ferrocene couple was used as an internal electrochemical reference.

Doubled-layer TiO_2 electrodes were prepared and characterized according to the literature [17] method. The layer thickness was determined using a Alpha-Step IQ surface profiler (Tencor Instruments, <http://www.kla-tencor.com>). The final thickness for the transparent layer is 12 nm and 4 nm for the scattering layer. The porosity and average pore size of the transparent layer were measured with a Gemini 2327 nitrogen adsorption apparatus (Micromeritics Instruments Corp.) to be 63% and 22 nm, respectively. The screen-printed double layer was heated to 500 °C under oxygen and let for sintering. After the temperature reached 50 °C, the double layer was dipped in an ethanol solution of the dye (5 mM) at 20–22 °C for 8–10 h. After dipping, the surface was dried under vacuum and the TiO_2 electrode was covered with an electrolyte and assembled with a platinized conducting glass electrode.

2.4. Photoelectrochemical measurements

The light source was made with a 450 W xenon Osram lamp housed in an Oriel Research Arc lamp housing designed for 450–1000 W arc lamps (Oriel, <http://www.oriel.com>). This light source gave an irradiance of 100 mW cm^{-2} equivalent of one sun at AM 1.5. The spectral output of the lamp was matched in the region 350–750 nm with a Schott K series Tempax sunlight filter (Präzisions Glas & Optik GmbH, <http://www.pgo-online.com>) in order to reduce the mismatch between the simulated and the true solar spectra to less than 2%. Light intensities were regulated with neutral wire mesh attenuators. The current–voltage characteristics of the cell under these conditions were obtained by applying external potential

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