Polyhedron 67 (2014) 381–387

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis of a novel dinuclear ruthenium polypyridine dye for dye-sensitized solar cells application

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ARTICLE INFO

Article history:
Received 8 June 2013
Accepted 3 September 2013
Available online 2 October 2013

Keywords:
Ruthenium dye
Polypyridine complexes
Dye-sensitized solar cells
TiO_2 sensitization

ABSTRACT

A new dinuclear ruthenium(II) polypyridine complex has been successfully synthesized. The new compound has been characterized by spectroscopic and electrochemical methods. Its potential application as a sensitizing dye in dye-sensitized solar cells has been checked under AM 1.5 G irradiation conditions (100 mW cm^{-2}) and its performance was compared to that of a commercially available mononuclear analogous dye. The overall light-to-electricity conversion efficiency of the photovoltaic device sensitized by the new dinuclear dye has been found to be over 2.5 times lower than that sensitized by the commercial analogue, despite a much higher extinction coefficient of the former dye. The probable reasons for the lower photovoltaic activity are discussed.

1. Introduction

Growing energy demand along with fossil fuel depletion and the need for global environment protection has made the development of non-polluting renewable energy technologies of a highest priority in science and technology [1]. Solar technologies, especially photovoltaics, are the most promising ones. The last 35 years have brought an explosion of popularity of silicone solar cells. The demand for solar energy has grown rapidly, with growth rates between 20% and 25% per every year [2]. Today the standard efficiency of a commercial silicone solar cell is between 15% and 20%. However, silicone solar cells still account for less than 0.1% of the total world energy production. The relatively high production costs of silicone photovoltaics and the fact that their production process needs ultraclean materials and toxic chemicals are the main reasons preventing their widespread use [2–4]. A low cost alternative for silicon solar cells appeared when O'Regan and Grätzel developed a highly efficient solar cell based on dye-sensitized titania [5]. The photoconversion efficiency of this device was 7.1–7.9%. The use of commercially available materials and chemicals without any specific treatment and purification, together with the relatively high efficiency (at that time) made dye-sensitized solar cells (DSSCs) an interesting alternative to the conventional silicon devices. Enormous interest in DSSCs may be illustrated by the fact that over the 20 years since the first announcement by O'Regan and Grätzel, more than 10,000 original works in this area were published by scientific groups all over the world. Nowadays, everyday a few new research articles on the subject are published [6].

In short, the DSSC device is made of two conductive glass electrodes [1,3,4,6–10]. The first electrode is a transparent photoanode, which consists of a tin conducting oxide glass (TCO) substrate coated with a thin mesoporous layer of a nanocrystalline semiconducting oxide with a wide band gap (mostly TiO_2). The surface of the semiconductor is modified with a monolayer of chemisorbed dye molecules. The second electrode, the counter electrode, is made of TCO coated with an ultrathin layer of platinum. The electrolyte containing redox medium (usually the I^-/I_3^- couple) is injected between these two electrodes to transfer charges between them. There are different opinions about which part of the DSSC device, the semiconductor [7] or the dye [1,11], plays the main role in the photoelectric process taking place in the cell upon its illumination. There is no doubt, however, that the whole operating process starts when the dye molecule absorbs a photon of visible light. After this process the electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye molecule, which leads to generation of the excited state of the dye. The excited electron is consequently injected from the LUMO orbitals of the dye to the conduction band of the semiconductor and in consequence the dye undergoes oxidation. The oxidized dye is regenerated through the electron transferred from the reduced form of redox mediator present in the electrolyte and simultaneously the oxidized form of the redox mediator is formed. At the same time, the photoinjected electron is transported through the nanoparticle network of the semicon-

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http://dx.doi.org/10.1016/j.poly.2013.09.023

ductor to reach the TCO substrate. The electrons collected on TCO are transported through the external circuit, give electric power, and finally get into the counter electrode, where they regenerate the reduced form of the redox mediator via reducing the oxidized form and close the circuit. In an ideal system the whole operation process takes place without consumption nor permanent transformation of any chemical species and theoretically it can occur until illumination is present.

The most important issue of DSSC research is to design effective sensitizing dyes. The main conditions an effective sensitizer should meet are as follows [12]:

- wide range of visible light adsorption spectra;
- strong anchoring on the semiconductor surface;
- efficient injection of the photoexcited electrons into the semiconductor conduction band;
- the energy of oxidation potential of excited state being higher than that of the conduction band edge of the semiconductor;
- high redox potential of the ground state;
- long term stability in the solar cell working conditions.

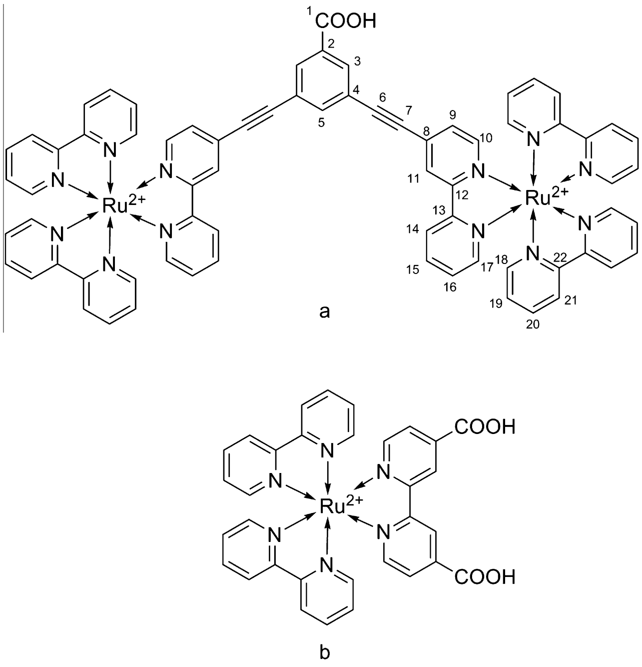
The ruthenium dyes cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II), its bis(tetrabutylammonium) salt and triisothiocyanato-(2,2′:6,6″-terpyridyl-4,4′,4″-tricarboxylato) ruthenium(II) tris(tetrabutylammonium), widely known as N3, N719 and “black dye”, respectively, meet all the above conditions and have become a benchmark for other sensitizers. The photon to current conversion efficiencies reached by the devices sensitized with these three dyes are 10.0%, 11.2% and 10.4% [13,14], respectively, though these are still not high enough as expected for commercial application in DSSCs. The mainstream research in ruthenium sensitizers is focused on structure modification of the ligands to improve light harvesting and electron injection efficiency and, in consequence, the efficiency of the DSSCs. The vast majority of work has concerned the modifications of ancillary ligands, which allowed a record efficiency of 12.3% for Z991 dye, which is an N3 analogue with an ancillary ligand substituted with bithiophene containing moieties [1,15]. Anchoring ligand modifications are rarely reported in the literature and most of the works have concerned the substitution of the carboxyl or phosphate groups with other ones capable of bonding the dye to the semiconductor surface [16]. A different approach to the anchoring ligand modifications has been presented by Funaki et al. [17], who have synthesized a “black dye” analogue with a π expanded ligand having a phenylene-ethynylene moiety. The modification led to an increase in the molar extinction coefficient, but unfortunately did not translate into better conversion efficiencies in the DSSCs.

In this work we present a new dinuclear dendritic-like ruthenium dye which consist of two trisbipyridyl ruthenium(II) derivatives clipped with an ethyl 3,5-diethynylbenzoate group (Scheme 1). Full spectroscopic and electrochemical characterization of the new compound is presented and the effects of DSSC sensitization in comparison with that achieved with a commercially available mononuclear analogue (Ruthenizer 455PF6, Solaronix; Scheme 1) are discussed.

2. Experimental

2.1. Synthesis

0.500 g of Ru(bpy)$_2$Cl$_2$ (0.96 mmol, as a dihydrate) and 0.230 g (0.48 mmol) of dinucleating ligand **1** (the synthetic procedure for ligand **1** has been published elsewhere [18] and for convenience also attached to this paper as Supplementary data) were dissolved in ethanol (200 mL) and refluxed under nitrogen over 10 h in the dark. Then the solvent was evaporated in vacuo. The obtained complex was dissolved in dry methanol (10 mL) and a concentrated solution of ammonium hexafluorophosphate (2 g in 4 mL of water) was added. The obtained dark red precipitate was filtered off, washed with water, methanol and diethyl ether and dried in vacuum to obtain 0.73 g of dye **B1** as a red amorphous powder (Scheme 2). Yield 81%. *Anal.* Calc. for $C_{71}H_{50}N_{12}O_2F_{24}P_4Ru_2$: C, 45.23; H, 2.67; N 8.92. Found: C, 45.41; H, 2.76; N, 8.78%. ESI-MS *m*/*z*: 326 $[M-4PF_6]^{4+}$. ^{1}H NMR ([^{2}H]$_3$-acetonitrile) δ: 7.41 (m, 8H; H-19); 7.43 (ddd, 2H; 7.4, 5.6, 1.3 Hz; H-16); 7.47 (dd, 2H; 5.9, 1.8 Hz; H-9); 7.72 (m; 6H; H-18); 7.75 (ddd, 2H; 5.6, 1.5, 0.8 Hz; H-17); 7.76 (dd, 2H; 5.9, 0.8 Hz; H-10); 7.80 (ddd, 2H; 5.6, 1.5, 0.8 Hz; H-18); 8.03 (t, 1H; 1.6 Hz; H-5); 8.07 (m, 8H; H-20); 8.09 (ddd, 2H; 8.3, 7.4, 1.5 Hz; H-15); 8.31 (d, 2H; 1.6 Hz; H-3); 8.51 (m, 8H; H-21); 8.54 (ddd, 2H; 8.3, 1.3, 0.8 Hz; H-14); 8.66 (dd, 2H; 1.8, 0.7 Hz; H-11); 11.0 (br, 1H; H-1). ^{13}C NMR ([^{2}H]$_3$-acetonitrile) δ: 87.91 (C-6); 96.12 (C-7); 123.61 (C-4); 125.39 (C-21); 125.55 (C-14); 127.13 (C-11); 128.68, 128.73 (C-19); 129.01 (C-9); 129.75 (C-16); 132.60 (C-8); 133.19 (C-2); 135.17 (C-3); 138.99 (C-15); 139.03 (C-20); 139.14 (C-5); 152.67 (C-17); 152.78 (C-10); 152.84, 152.86, 152.90 (C-18); 157.57 (C-13); 157.90, 157.99, 158.00 (C-22); 158.52 (C-12); 166.52 (C-1).



Scheme 1. The structures of the **B1** (a) and 455PF6 (b) dyes.

2.2. Electrochemical and photochemical studies

Cyclic voltammograms were collected using an Autolab electrochemical analyzer (Eco Chemie, B. V., Utrecht, The Netherlands). The working electrode was a Pt wire, the counter electrode was a Pt plate and the reference electrode was a saturated calomel electrode (SCE). 10^{-3} M solutions of the dyes in acetonitrile (Aldrich) with 0.1 M LiClO$_4$ (Fluka) as a supporting electrolyte were used. The experiments were carried out in an electrochemical cell under a pure Ar gas flow. UV–Vis absorbance spectra were measured on a Lambda 35 UV–Vis spectrometer (Perkin Elmer, Waltham MA, USA) and the amounts of adsorbed dye were determined on Cary 50 Probe UV–Vis spectrometer (Varian Inc., Palo Alto CA, USA). Photoluminescence spectra were recorded on a LS 55 fluorescence spectrometer (Perkin Elmer, Waltham MA, USA). In both cases, the