

# A Ru(II) molecular antenna bearing a novel bipyridine–acrylonitrile ligand: Synthesis and application in dye solar cells



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## ABSTRACT

A new molecular photosensitizer (**DK108**) was synthesized from the reaction of *cis*-[Ru(H<sub>2</sub>dc bpy)<sub>2</sub>Cl<sub>2</sub>] with the novel bipyridine–acrylonitrile ligand **5**. **DK108** was completely characterized by a variety of spectroscopic techniques (one- and two-dimensional NMR, UV–Vis, FTIR, HRMS, Raman, and cyclic voltammetry), its photo-electrochemical properties were thoroughly investigated, and was utilized in nano-crystalline dye-sensitized solar cells. Liquid electrolyte dye solar cells incorporating **DK108**-sensitized TiO<sub>2</sub> photoelectrodes afford overall power conversion efficiencies of 1.3%. Despite the relatively low power conversion efficiencies of **DK108**-sensitized TiO<sub>2</sub> films, their fully transparent nature above 600 nm render **DK108** suitable for building integration applications and the investigation of fundamental issues related to the sensitization mechanism.

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## 1. Introduction

The increasing demand for energy along with fossil fuels depletion and concerns over global environment preservation render the development of non-polluting renewable power resources a need of utmost importance [1]. The photovoltaic technology is one of the most promising strategies dealing with this problem by harvesting sunlight and transforming it into clean and affordable electricity [2]. Solid-state photovoltaic cells, based on heterojunctions of inorganic semiconductors, have proven to achieve this goal; however, their relatively high production cost and the necessary use of toxic chemicals during their construction, imposes limitations on their mass utilization [3].

Over the last decades, solar cells based on nanocrystalline titania films sensitized by molecular dyes have attracted great attention as alternatives to classical photovoltaic devices, mainly due to their high conversion efficiency, easy fabrication, and low production cost [4]. The so-called dye-sensitized solar cells (DSCs) comprise of an active photoanode (consisting of a molecular sensitizer chemisorbed on the surface of a large band-gap

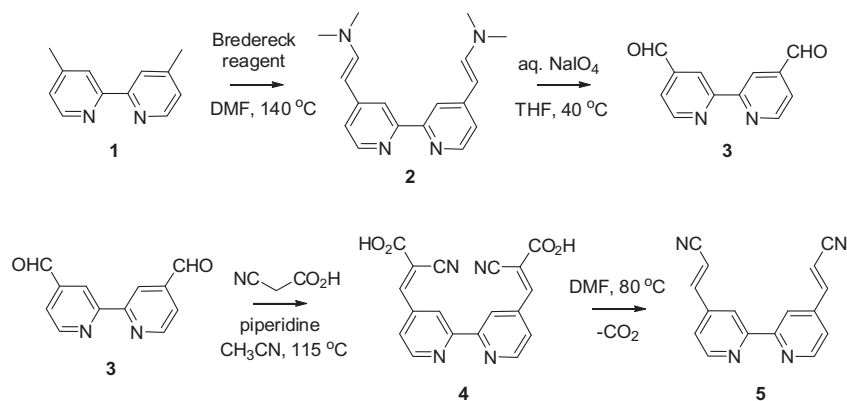
semiconductor) and a Pt counter electrode sandwiching an electrolyte containing the redox couple [5]. The development of this type of third generation photovoltaic solar cells is based on the optimization of several factors including: (i) the preparation of nanostructured, rough, and large surface area TiO<sub>2</sub> thin film electrodes; (ii) the design and synthesis of efficient light capturing antennas; and (iii) the use of competent redox couples in the appropriate medium.

The key element of this kind of solar cells is the photosensitizer [6]. Ruthenium(II) polypyridine complexes bearing suitable anchoring groups, in which carboxylic or phosphonic acid moieties are utilized, are the most successful known sensitizers. Among them, the most well-studied are the *cis*-[Ru(dcbpyH<sub>2</sub>)(NCS)<sub>2</sub>](NBu<sub>4</sub>)<sub>2</sub> (**N719**) (dcbpyH<sub>2</sub> = 2,2′-pyridine-4,4′-dicarboxylic acid) [7], [Ru(H<sub>3</sub>tcterpy)(NCS)<sub>3</sub>], known as the “black dye” (H<sub>3</sub>tcterpy = 2,2′:6,2″-terpyridine-4,4′,4″-tricarboxylic acid) [8], and the hydrophobic *cis*-[Ru(dcbpyH<sub>2</sub>)(4,4′-di-nonyl-2′-bipyridyl)(NCS)<sub>2</sub>](NBu<sub>4</sub>)<sub>2</sub> (**Z907**) [9].

In the context of our ongoing work on the development of novel tailor-designed ligands and ruthenium functional complexes [10], we herein describe the synthesis and complete characterization of a new bipyridine-type ligand (**4**, Scheme 1) bearing two cyanoacrylic acid anchoring groups. Amongst others, cyanoacrylic binding moieties have been successfully utilized in coumarin- [11], indoline- [12], and squaraine-type [13] organic DSC

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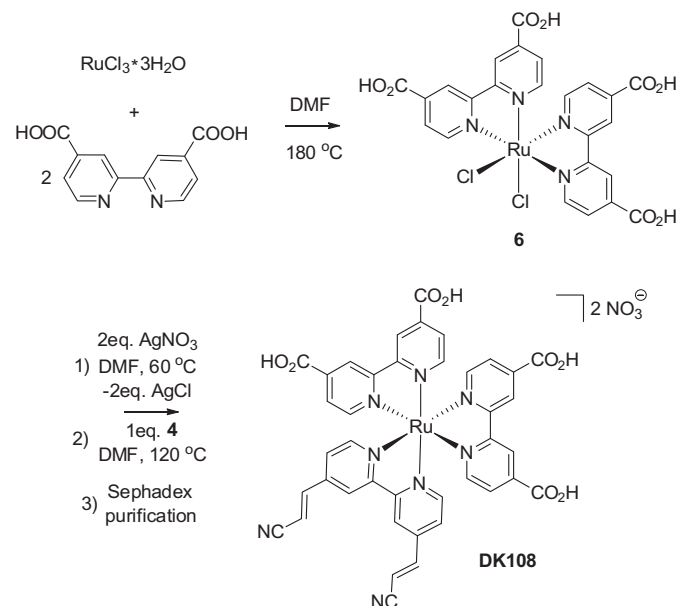
**Scheme 1.** The synthetic procedure followed for the preparation of the novel ligands **4** and **5**.

photosensitizers, but, to the best of our knowledge, have not been employed in ruthenium complexes thus far. Ligand **4** was designed in order to be utilized in the synthesis of the corresponding ruthenium sensitizers, which, due to the electron-poor nature of the cyanoacrylic moieties, were anticipated to be characterized by enhanced electron flow directionality towards the semiconductor. This was in turn expected to lead to improved charge separation and sensitizing ability. Interestingly, while trying to react ligand **4** with the appropriate Ru(II) precursor, we observed that the ligand readily undergoes decarboxylation at temperatures above 80 °C to afford the corresponding decarboxylated ligand **5** (Scheme 1). This ligand was utilized in the preparation of the novel Ru(II) complex **DK108** (Scheme 2), which was extensively characterized and utilized as a light harvesting molecular antenna in DSCs.

## 2. Experimental

### 2.1. General remarks

C, H, N Elemental Analyses were carried out on a Perkin Elmer 2400 CHN elemental analyzer. Infrared spectra (FTIR) in the powder form were obtained using a FTIR Nicolet 6700 spectrometer.



**Scheme 2.** The synthetic route followed for the preparation of the novel Ru(II) photosensitizer **DK108**.

Data for FTIR spectra are reported as follows: frequency ( $\text{cm}^{-1}$ ) and strength ( $s = \text{strong}$ ;  $m = \text{medium}$ ;  $w = \text{weak}$ ). Micro-Raman studies were performed with a Renishaw Invia-Reflex spectrometer. An  $\text{Ar}^+$  ion laser, emitting at the wavelength of 514.5 nm and a diode laser, at 785 nm, were used as excitation sources. The spectrometer has two diffraction gratings: one with 1800 and the other with 1200 grooves/mm, used for analysis in the visible and infrared region of the electromagnetic spectrum, respectively. The Raman signals were obtained from a high sensitivity CCD detector. The power of the laser was focused on 1  $\mu\text{m}$  spots and kept at very low intensities (0.01–0.1 mW) to avoid decomposition of the dye due to local heating. Absorption spectra were recorded on a Hitachi U-4001 spectrophotometer, using quartz cells with 1 cm optical path. The UV–Vis absorption spectra of the  $\text{TiO}_2$  films (sensitized or not) were obtained in the same spectrophotometer using an integrating sphere. High-resolution NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, and HSQC) were recorded at 298 K (Bruker Avance 500 MHz) in  $\text{DMSO-d}_6$ ,  $\text{MeOD-d}_4$ , or 0.05 M NaOD solutions in  $\text{D}_2\text{O}$ . Chemical shifts are reported in ppm downfield from  $\text{Me}_4\text{Si}$ , by using the residual solvent peak as internal standard. High Resolution Mass Spectra (HRMS) were recorded using a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer. Unless otherwise mentioned, column chromatography refers to flash chromatography carried out on  $\text{SiO}_2$  (63–200  $\mu\text{m}$ ). Dichloro (*p*-cymene) ruthenium(II) dimer (Alfa Aesar), 2,2'-bipyridine, and 2,2'-bipyridine-4,4'-dicarboxylic acid (Dyesol Australia), as well as all other reagents were used as received. Reagent-grade solvents were thoroughly degassed by bubbling argon for 15 min prior to their use. *cis*-[Ru(dcbpyH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] [14] and 2,2'-bipyridines **2** and **3** [15] were prepared according to synthetic procedures reported in the literature. During all synthetic procedures involving Ru(II) complexes, light exposure of the reaction mixtures was carefully avoided in order to prevent the *cis*-*trans* isomerization of *cis*-[Ru(dcbpyH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]. The progress of all reactions was monitored by thin layer chromatography (TLC), UV–Vis spectroscopy (by observing the absorption shift and intensity changes of the corresponding maxima), and/or  $^1\text{H}$  NMR spectroscopy.

### 2.2. Electrodes preparation and devices assembly-characterization

Titania films were prepared using the doctor-blade technique by depositing one transparent layer (7–8  $\mu\text{m}$ , measured with an AMBIOS XP-2 profilometer) of a commercial paste (DSL18NR-T, Dyesol) onto a pre-cleaned fluorine-doped tin oxide (FTO) conductive glass ( Pilkington Solar, 3.2 mm thickness). The DSL18NR-T paste solely consists of anatase particles and elongated nanorods with an average size of 17 nm, while its pore size distribution is wide, presenting a maximum at 30 nm. The films were then dried

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