



Versatile ruthenium(II) dye towards blue-light emitter and dye-sensitizer for solar cells[☆]

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ABSTRACT

A versatile Ru(II) complex bearing an anthracene moiety was synthesized in our search for suitable compounds towards efficient molecular devices. The new engineered dye, *cis*-[Ru(dcbH₂)(NCS)₂(mbpy-anth)] (dcbH₂ = 2,2'-bipyridyl-4,4'-dicarboxylic acid, mbpy-anth = 4-[*N*-(2-anthryl)carbamoyl]-4'-methyl-2,2'-bipyridine), exhibits a blueish emission in a vibronically structured spectrum ascribed to the fluorescence of a ¹LC_{Anth} (ligand centered) excited state in the anthracene and has a potential to be exploited in the fields of smart lighting and displays. This complex was also employed in dye-sensitized solar cells with fairly efficient solar energy conversion with the use of self-assembled TiO₂ compact layers beneath the TiO₂ mesoporous film to prevent meso-TiO₂/dye back reactions. Further photoelectrochemical investigations through incident photon-to-current efficiency and electrochemical impedance spectra showed that the all-nano-TiO₂ compact layer acts as contact layers that increase the electron harvesting in the external circuit, enhancing efficiencies up to 50%.

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1. Introduction

Polypyridyl ruthenium(II) complexes have been extensively investigated due to their rich photo- and electrochemical properties which can be conveniently exploited in electron and/or energy transfer processes towards the development of efficient molecular devices [1–3].

These compounds usually exhibit an intense metal-to-ligand charge transfer (¹MLCT) absorption that, after relaxation to the ³MLCT counterpart, can lead to luminescence at room temperature, being the subject of extensive research over the last 60 years [3,4]. Their emission is generally restricted to the orange-red spectral region and exhibits fairly efficient quantum yields [5], as exemplified by the well-known [Ru(bpy)₃]²⁺ complex, extensively investigated and used as an emission standard in inorganic photophysics and photochemistry [6–9]. These photophysical features are employed in light emitting devices such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) [10–16].

Also, their intense ¹MLCT absorption in the visible spectrum is highly employed in dye-sensitized solar cells (DSCs), artificial photosynthesis, chemical and biological sensing [17–22]. In special, the molecular engineering of new DSC-sensitizers has focused on improving

light harvesting, mostly relying on Ru-based chromophores with broad high extinction coefficient MLCT bands [23–26]. For example, the N719 dye (*cis*-[Ru(dcbH₂)(NCS)₂][TBA]₂, dcbH = 2,2'-bipyridyl-4,4'-dicarboxylate, TBA = tetrabutylammonium) is a standard DSC sensitizer that leads to conversion efficiencies exceeding 11% [27,28].

This work describes the synthesis, characterization and use of the *cis*-[Ru(dcbH₂)(NCS)₂(mbpy-anth)] complex (dcbH₂ = 2,2'-bipyridyl-4,4'-dicarboxylic acid, mbpy-anth = 4-[*N*-(2-anthryl)carbamoyl]-4'-methyl-2,2'-bipyridine), consisted of Ru (bpy) moieties and an anthracene fragment, Chart 1. Its photophysical properties are investigated aiming for insights of its unusual blueish emission. The synthesized complex is also employed in stable, fairly efficient DSCs, with electron transfer processes investigated based on comparisons with the standard N719 sensitizer.

2. Experimental Section

2.1. General Procedures

Other chemicals and solvents for synthesis were purchased from Sigma-Aldrich or Synth, and used as supplied. 4-[*N*-(2-anthryl)carbamoyl]-4'-methyl-2,2'-bipyridine was prepared following a procedure previously described [29].

¹H NMR spectra were recorded using a 300 MHz Bruker Avance spectrometer (AC-300) using D₂O as internal standard.

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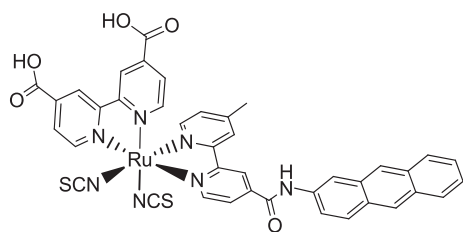


Chart 1. Chemical structure of *cis*-[Ru(dcbH₂)(NCS)₂(mbpy-anth)] (**RuAnth**).

UV-visible spectra were recorded with a Hewlett-Packard spectrophotometer model 8453 using 1.000 cm optical path quartz cuvettes.

2.2. Synthesis of *cis*-[Ru(dcbH₂)(NCS)₂(mbpy-anth)] (**RuAnth**)

RuCl₃·3H₂O (0.305 g, 1.17 mmol), 2,2'-bipyridine-4,4'-dicarboxylic acid (0.283 g, 1.17 mmol), 4-[N-(2-anthryl)carbamoyl]-4'-methyl-2,2'-bipyridine (0.454 g, 1.17 mmol) and LiCl (0.347 g, 8.26 mmol) were refluxed for 8 h in DMF (50 mL). The reaction mixture was allowed to cool to room temperature and filtered, then washed with acetone and dried under vacuum, to yield 0.798 g (84.9%) of the precursor complex, *cis*-[Ru(dcbH₂)(mbpy-Anth)Cl₂].

Under protection of light, this precursor (0.100 g, 0.197 mmol) and NaSCN (0.100 g, 1.24 mmol) were refluxed for 8 h in 30 mL of ethanol/water (1:1). The resulting solution was concentrated by rotary evaporation. Addition of acetone precipitated a purple powder that was filtered and successively washed with acetone and diethyl ether. The crude product was purified by column chromatography (Sephadex LH-20), using methanol as an eluent to yield 0.056 g (54.90%) of **RuAnth**, Chart 1. RMN ¹H data in D₂O (δ/ppm): 2.50 (3H, s), 7.46 (1H, d), 7.49 (1H, d), 7.63 (2H, t), 7.76 (1H, d), 7.78 (2H, d), 8.13 (1H, s), 8.11 (1H, s), 8.16 (3H, d), 8.73 (1H, s), 8.87 (1H, s) 8.88 (3H, s), 8.92 (1H, d), 9.50 (3H, d).

2.3. Photophysical Characterization

Emission spectra were recorded in a PC1 photon-counting spectrofluorimeter (ISS) with a photomultiplier based, photon-counting detector with detector sensitivity correction. The absorbance at the excitation wavelength of sample solutions were set between 0.1 and 0.2 in four-polished-face quartz cuvettes with a 1.000 cm optical path length. Solutions were deoxygenated with argon for at least 10 min prior to measurement. Emission lifetimes were obtained using an ISS-PC1 photon-counting spectrofluorometer and an ISS laser (λ_{exc} = 378 nm, frequency = 20 kHz). For 77 K experiments, samples were prepared in a 5:5:2 (v/v) mixture of ether, isopentane, and ethanol (EPA) in cylindrical quartz tubes, 0.4 cm radius, and were inserted into a Dewar flask containing liquid N₂.

The emission quantum yield (φ) in methanol at 298 K was calculated by the relative method [30,31] using Eq. (1). A solution of [Ru(bpy)₃]Cl₂ in the same solvent (φ = 0.045 [32], λ_{ex} = 400 nm, with a 420 nm long pass filter) was employed as the emission standard.

$$\phi_{\text{RuAnth}} = \phi_{\text{ref}} \frac{P_{\text{RuAnth}}}{P_{\text{ref}}} \frac{A_{\text{ref}}}{A_{\text{RuAnth}}} \quad (1)$$

φ_{RuAnth} = Emission quantum yield for the sample; φ_{ref} = Emission quantum yield for the reference in the same solvent; A_{RuAnth} = Absorbance of the sample at the excitation wavelength; A_{ref} = Absorbance of the reference at the excitation wavelength; P_{RuAnth} = Integral of the sample's emission spectrum; P_{ref} = Integral of the reference's emission spectrum.

The x and y CIE coordinates were calculated by Eqs. (2a) and (2b) from their X, Y and Z tristimulus, Eqs. (3a) to (3c), using

photoluminescence spectral data in methanol at 298 K [31,33,34]. The numerical values of the CIE standard $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, are available as free-access tables [35].

$$x = \frac{X}{X + Y + Z} \quad (2a)$$

$$y = \frac{Y}{X + Y + Z} \quad (2b)$$

$$X = \int_{380}^{780} I(\lambda) \bar{x}(\lambda) d\lambda \quad (3a)$$

$$Y = \int_{380}^{780} I(\lambda) \bar{y}(\lambda) d\lambda \quad (3b)$$

$$Z = \int_{380}^{780} I(\lambda) \bar{z}(\lambda) d\lambda \quad (3c)$$

2.4. DSC Assemblage

A meso-TiO₂ paste (Dyesol) was deposited (area ~ 0.2 cm²) by painting over FTO substrates (Pilkington, TEC-15, 15 Ω/□) and sintered at 500 °C for 30 min. Some of the samples had TiO₂ compact layers on the FTO underneath the meso-TiO₂ film, assembled by layer-by-layer, as previously described [36–39], by immersing a pre-cleaned FTO substrate alternately in nonautoclaved suspensions of TiO₂(ac) (25 mg mL⁻¹, pH 2) and TiO₂(bas) (5 mg mL⁻¹, pH ~ 10), until it reached 20 bilayers of the compact film.

The sensitization of meso-TiO₂ films was achieved by overnight immersion in saturated solutions of **RuAnth** in methanol or N719 (Dyesol) in ethanol. Photoanodes were assembled in a sandwich-type arrangement using Pt-covered FTO as counterelectrodes, having a hole previously drilled using a Comco inc AccuFlo® micro-abrasive blaster for insertion of I₂/I₃⁻ electrolyte. Cells were sealed with Surlyn® (DuPont) using a hot press homemade machine consisted of a Watlow EZ-ZONE® temperature controller and a Watlow Ultramic ceramic heater.

2.5. DSC Photoelectrochemical Characterization

Photocurrent-photovoltage curves (J-V curves) and electrochemical impedance (EI) spectra were recorded by a Gamry Interface 1000

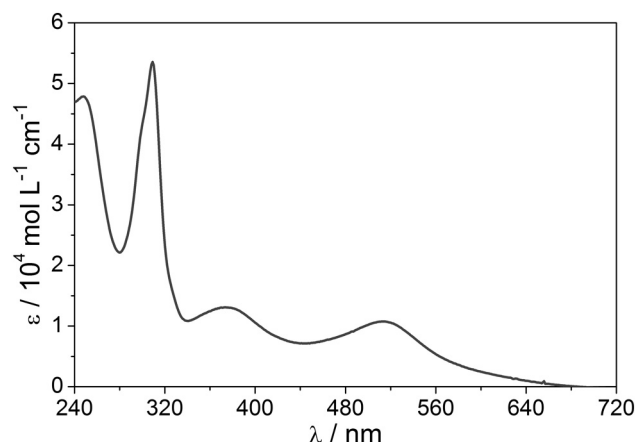


Fig. 1. Absorption spectrum of **RuAnth** in methanol at 298 K.

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