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Synthesis, characterization and photoelectrochemical performance of a *tris*-heteroleptic ruthenium(II) complex having 4,7-dimethyl-1,10-phenanthroline

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ABSTRACT

The novel *cis*-[Ru(Me_2-phen)($dcbH_2$)$(NCS)_2$] complex was prepared using a one-pot route and characterized based on ^{1}H NMR, FTIR, absorption and emission spectra. The properties of this complex were compared with those of *cis*-[Ru(R_2-phen)($dcbH_2$)$(NCS)_2$], where R = Ph or H, to establish a relationship between the donor/acceptor character of the R substituent and the observed behavior of these compounds. Computational methods were also employed to gain a comprehensive understanding of this relationship. By using electron-donating/accepting substituents, it was possible to tune both the ground and excited states of the *cis*-[Ru(R_2-phen)($dcbH_2$)$(NCS)_2$] complexes. This compound is capable of sensitizing the TiO_2 surface and efficiently converting the sunlight into electricity. In comparison to *cis*-[Ru(Ph_2-phen)($dcbH_2$)$(NCS)_2$] it is observed that the presence of phenyl groups provide higher efficiency. The conversion efficiency was improved in comparison to *cis*-[Ru(phen)($dcbH_2$)$(NCS)_2$]. This increase in efficiency is attributed to an increase in electron density, thus favoring electron transfer to TiO_2.

1. Introduction

tris-Heteroleptic ruthenium compounds, such as *cis*-[Ru(L)(L′)$(X)_2$], where L ≠ L′, are very interesting because their properties, in both the ground and excited states, can be modulated by the choice of the ligands. The preparation of these compounds is not simple, and several routes can be used to obtain the desired compound. These routes can start from $Ru(DMSO)_4(Cl)_2$ [1] or polymeric $[Ru(CO)_2(Cl)_2]_n$ [2]. In early 2000s, a one-pot route using a dichloro(*p*-cymene)ruthenium(II) dimer was used to prepare a series of *tris*-heteroleptic ruthenium dye sensitizers, *cis*-[Ru(dRbpy)($dcbH_2$)$(NCS)_2$] (bpy = 2,2′-bipyridine derivatives, R = methyl, nonyl, hexyl or tridecyl substituents) [3], and since this time, several similar compounds, *cis*-[Ru(L)($dcbH_2$)$(NCS)_2$], L = 2,2′-bipyridine derivatives, have been prepared and investigated as sensitizers for use in dye-sensitized solar cells, DSSCs [4]. Among these complexes, the C101 complex [5], which has a thiophene derivative as the bipyridine substituents, exhibited better performance than *cis*-[Ru$(dcbH_2)_2(NCS)_2$], also known as N3, and its *bis*-deprotonated analogue, N719, which are considered standards for these investigations. Density functional theory (DFT) has been successfully employed to describe the electronic properties of these compounds and to establish a relationship with their behavior as dye-sensitizers in DSSCs [6–14]. Few compounds have been prepared using other ligands similar to 2,2′-bipyridine, such as 1,10-phenanthroline.

Some *cis*-[Ru(L)($dcbH_2$)$(NCS)_2$] compounds where L = 1,10-phenanthroline or its derivatives were prepared and evaluated as dye-sensitizers for DSSCs. Ligands including phen, dppz [15], 5,6-dimethyl-phen [16], Ph_2-phen [17] have been evaluated previously and, especially the complex having the Ph_2-phen ligand, exhibit a better performance than N719. However, there has been no investigation of the relationship between the electron donor or acceptor character of the ligand substituent and the properties of the ground and excited states of the complexes.

In this work, *cis*-[Ru(R_2-phen)($dcbH_2$)$(NCS)_2$] complexes where R = Me, H or Ph, Fig. 1, were synthesized and characterized. The relationship between the R group and the donor or acceptor characteristics was evaluated based on their electronic properties determined by quantum chemistry as well as their FTIR, ^{1}H NMR, absorption and emission spectra. Their performances as dye-sensitizers for solar cells are also compared and discussed in terms of the phenanthroline substituents.

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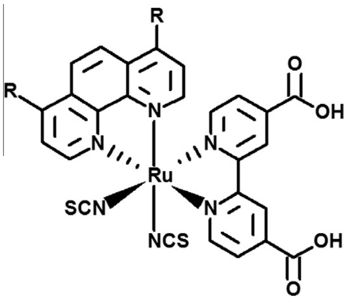

Fig. 1. Structure of the prepared compounds; R = Me, H or Ph.

2. Experimental details

4,4′-dimethyl-2,2′-bipyridine (Aldrich, 99%), H_2SO_4 (Sigma–Aldrich, 97%), [Ru(*p*-cymene)Cl_2]$_2$ (Aldrich), 1,10-phenanthroline, phen (Synth), 4,7-dimethyl-1,10-phenanthroline, Me_2-phen (Alfa Aesar, 98%), 4,7-diphenyl-1,10-phenanthroline, Ph_2-phen (Aldrich, 98%), a methanolic solution of tetrabutylammonium hydroxide (Acros Organics), Sephadex LH20 (Aldrich), N,N′-dimethylformamide-D_7, (Aldrich), NaNCS (Merck), $Na_2Cr_2O_7$ (Synth), HCl (Fluka), HNO_3 (Sigma–Aldrich), methanol (Synth), ethanol (Synth), isopropanol (Synth), N,N′-dimethylformamide, DMF (Synth), H_2PtCl_6 (Acros), fluorine-doped tin oxide (FTO – 8 ohm square^{-1}, Aldrich), the low temperature sealant – Surlyn (30 µm – Dyesol), acetonitrile (Lichrosolv – Merck), valeronitrile (HPLC – Aldrich), iodine (Sigma–Aldrich), guanidinium thiocyanate (Sigma–Aldrich) 4-*tert*-butylpyridine (Aldrich) and 1-butyl-3-methylimidazolium iodide (Aldrich) were used as received.

2.1. Synthesis of 2,2′-bipyridine-4,4′-dicarboxylic acid (dcbH_2)

The compound 2,2′-bipyridine-4,4′-dicarboxylic acid (dcbH_2) was synthesized as described in the literature [18]. Briefly, 1.60 g (8.6 mmol) of 4,4′-dimethyl-2,2′-bipyridine was added to a solution of 6.28 g (19.4 mmol) of $Na_2Cr_2O_7$ dissolved in 21 mL of concentrated H_2SO_4, and the mixture was stirred for 30 min. The resulting solution was added to 220 mL of cold water, and the solid was removed and dissolved in 10% NaOH. The final product was precipitated by the addition of HCl to the solution until it reached pH 2, and the white solid was collected. Yield: 70–80%. *Anal.* Calc. for $C_{12}H_{10}N_2O_5$: C, 57.60; H, 3.49; N, 11.20. Found: C, 57.84; H, 3.34; N, 11.27%.

2.2. Synthesis of cis-[Ru(R_2-phen)(dcbH_2)$(NCS)_2$]

The *tris*-heteroleptic complexes were synthesized using the procedure reported in the literature with slight modifications [15,17]. In general, the ruthenium *p*-cymene dimer, [Ru(*p*-cymene)Cl_2]$_2$, was added to N,N′-dimethylformamide (DMF) and 2 equivalents of (R_2-phen) was added. The mixture was kept at 80 °C for 2 h under an inert atmosphere. After this period, 2 equivalents of dcbH_2 was added to the mixture, and the temperature was increased to 160 °C. The mixture was kept at this temperature for 4 h. Finally, NaNCS was added to the mixture in a 10-fold excess, and the reaction was kept under these conditions for 4 h to allow the reaction to proceed to completion. All the reactions were monitored by UV–Vis spectrophotometry and thin layer chromatography (silica gel, 60 Å, as the stationary phase and methanol saturated with NaCl as the eluent). To obtain pure compounds, the complexes were deprotonated using a methanolic solution of tetrabutylammonium hydroxide (1 mol L^{-1}), centrifuged to remove any residual particulates and applied to a liquid chromatography column containing Sephadex LH-20 as the stationary phase. Methanol was used as the eluent. The pure fraction was concentrated, precipitated by the addition of HNO_3 and filtered, and the solid was dried in a desiccator.

Using this procedure, it was possible to prepare *cis*-[Ru(phen)(dcbH_2)$(NCS)_2$] (yield = 78%; *Anal.* Calc. for $C_{26}H_{21}N_6O_7RuS_2$: C, 44.83; H, 3.49; N, 12.31. Found: C, 44.95; H, 3.05; N, 12.10%), *cis*-[Ru(Ph_2-phen)(dcbH_2)$(NCS)_2$] (yield = 65%; *Anal.* Calc. for $C_{50}H_{44}N_8O_{11}RuS_2$: C, 57.49; H, 3.05; N, 10.59. Found: C, 57.18; H, 4.11; N, 9.63%) and *cis*-[Ru(Me_2-phen)(dcbH_2)$(NCS)_2$] (yield = 76%; *Anal.* Calc. for $C_{28}H_{26}N_6O_7RuS_2$: C, 46.38; H, 3.54; N, 11.53. Found: C, 46.47; H, 3.62; N, 11.6%).

2.3. Dye-sensitized solar cells

Dye-sensitized solar cells were prepared in a sandwich-type arrangement, as shown in Fig. 2. Nanocrystalline TiO_2 mesoporous films were prepared as described elsewhere [19] and deposited onto FTO conducting glasses to provide an active area of 0.16 cm^2 and sintered for 30 min at 450 °C. The films were sensitized by immersing the processed electrodes into an ethanolic solution of each prepared compound for a minimum duration of 12 h. The counter-electrodes have a thin film of platinum as a catalyst layer on their conductive sides. The solar cells were sealed using a film of sealant, and the mediator was placed between photoanode and counter-electrode through holes made on the counter-electrodes. The mediator was prepared by dissolving iodine (76 mg), guanidinium thiocyanate (118 mg), 4-*tert*-butylpyridine (0.76 mL) and 1-butyl-3-methylimidazolium iodide (1.60 g) in a mixture of acetonitrile:valeronitrile (85:15) to produce a solution with a final volume of 10 mL.

2.4. Methods

NMR spectra were recorded at 25.0 °C on a DRX-500 Bruker Avance spectrometer at 500.13 MHz using DMF-D_7 as the solvent.

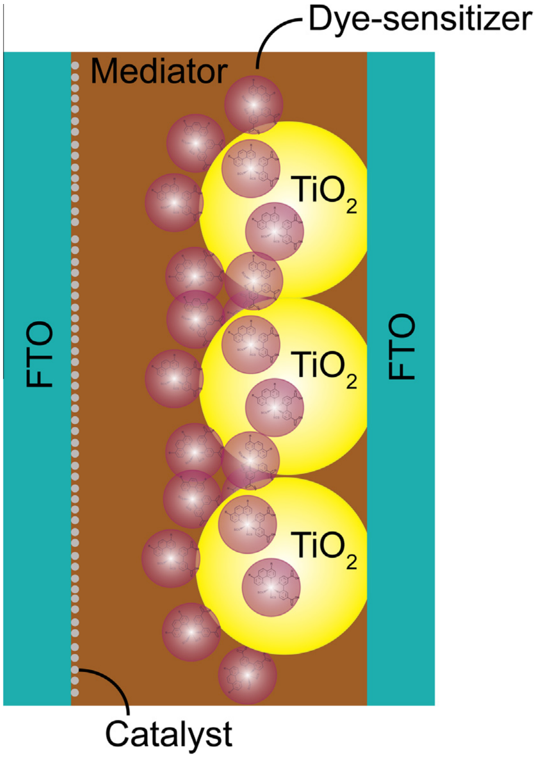

Fig. 2. Schematic representation of a dye-sensitized solar cell.