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Synthesis, characterization and sensitization properties of two novel mono and bis carboxyl-dipyrido-phenazine ruthenium(II) charge transfer complexes

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Abstract

Two novel heteroleptic ruthenium complexes of the type *cis*-[Ru(dppz-COOH)$_2$(NCS)$_2$] (**1**) and *cis*-[Ru(dppz-COOH)(phen)(NCS)$_2$] (**2**), where dppz-COOH = 11-carboxyl-dipyrido[3,2-α:2′,3′-c]phenazine and phen = 1,10-phenanthroline, were synthesized and fully characterized by analytical and spectroscopic techniques. The complexes showed a broad and intense metal-to-ligand charge transfer (MLCT) transition band in the visible region, which is emissive both in MeOH at room temperature and in a MeOH–EtOH glass (77 K). Both complexes **1** and **2** were anchored to nanocrystalline TiO$_2$ film electrodes and the resulting photoelectrodes were successfully incorporated in dye-sensitized solar cells (DSSCs) using a solid state redox electrolyte [PEO/TiO$_2$/I$^-$/I$_3$$^-$ (PEO = polyethyleneoxide, $M_W = 2 \times 10^6$)]. The photovoltaic performance of the DSSCs was evaluated and compared with the cell prepared with *cis*-(NBu$_4$)$_2$[Ru(Hdcbpy)$_2$(NCS)$_2$], so-called N719 dye (dcbpyH$_2$ = 4,4′-dicarboxy-2,2′-bipyridine). Although the efficiency of the **2**-sensitized solar cell was 10% higher than the **1**-sensitized solar cell, neither was as efficient as the N719-sensitized solar cell. The results obtained in the present article are consistent with the photochemical properties of the corresponding Ru(II) dyes.

Keywords: Dye-sensitized solar cell; Ruthenium complex; dppz; Nanocrystalline TiO$_2$; Emission spectra; Solid state electrolyte

1. Introduction

Over the past decades, the dye-sensitized solar cells (DSSC) have attracted a widespread interest for the conversion of sunlight into electricity because of their low cost and high efficiency [1–4]. The two outstanding sensitizers for DSSC reported so far in the literature are *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) [5], so-called N719 and tri(thiocyanato-2,2′,2″-terpyridyl-4,4′,4″-tricarboxylate)ruthenium(II) [6], so-called black dye. The highest efficiencies reported for N719 and the black dye are 10 and 10.4%, respectively, which are comparable to the conventional silicon-based solar cell [5,6]. In particular, N719 due to its high efficiency and high photo- and chemical stability, is used as a standard dye to compare and select other new sensitizers for DSSC.

On the other hand, ruthenium compounds based on the dppz ligand, dipyrido[3,2-α:2′,3′-c]phenazine, have been widely used as luminescent probes since the first report of their novel photophysical properties [7]. dppz is a heterocyclic aromatic ligand whose complexes have received much attention in recent years, primarily because the planarity and extended aromatic nature of dppz permits its intercalation with DNA [8]. In the last years, many research groups have focused on the design and preparation of new ruthenium complexes owning dppz ligands [9,10] for anchoring them to nanocrystalline TiO$_2$. The main goal of this is to enhance the spectrum response over a wide wavelength region and maintain a sufficient thermodynamic driving force for

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electron injection from a sensitizer to TiO_2 and electron transfer from I^- to the oxidized sensitizer [3–5]. This can been achieved since it is believed [11] that $RuL_2(dppz)^{2+}$, where L = bpy is made up of two “electronically independent” units, a $RuL_3{}^{2+}$-like chromophore and a phenazine-like electron acceptor. The last assumption is substantiated by the existence in dppz ligand, of both a 1,10-phenanthroline and a quinoxaline moiety. Moreover, compounds such as $Ru(bpy)_2(dppz)^{2+}$ are nonemissive in aqueous solution but have long-lived photoluminescent excited states in non-protic environments. Barton and co-workers [8] have also demonstrated that these compounds become highly emissive when phenazine nitrogens of dppz ligands are shielded from water, giving rise to the ‘light switch’ effect.

Motivated by the forgone discussion, we proceeded in this work to the synthesis and full characterization of two new ruthenium(II) complexes, namely *cis*-$[Ru(dppz\text{-}COOH)_2(NCS)_2]$ (**1**) and *cis*-$[Ru(dppz\text{-}COOH)(phen)(NCS)_2]$ (**2**), where dppz-COOH = dipyrido[3,2-α:2′,3′-c]phenazine-11-carboxylic acid and phen = 1,10-phenanthroline (Fig. 1). In these complexes, the bidentate planar ligand contains a carboxylic acid group, dipyrido[3,2-α:2′,3′-c]phenazine-11-carboxylic acid, dppz(COOH), which is necessary for efficient chemisorption onto the TiO_2 surface, probably via formation of an ester-like chemical bond [12]. As a matter of fact, both complexes **1** and **2** have been anchored to nanocrystalline TiO_2 film electrodes, and the photovoltaic properties of the resulting dye-sensitized solar cells (DSSC) have been characterized and compared with the properties of the DSSCs prepared with *cis*-$(NBu_4)_2[Ru(Hdcbpy)_2(NCS)_2]$ (N719) and other similar Ru(II) dyes. Emphasis is drawn to in the solid state nature of the cells using a solid state redox electrolyte, $PEO/TiO_2/I^-/I_3{}^-$, in order to eliminate the drawbacks of the traditionally used liquid electrolytes.

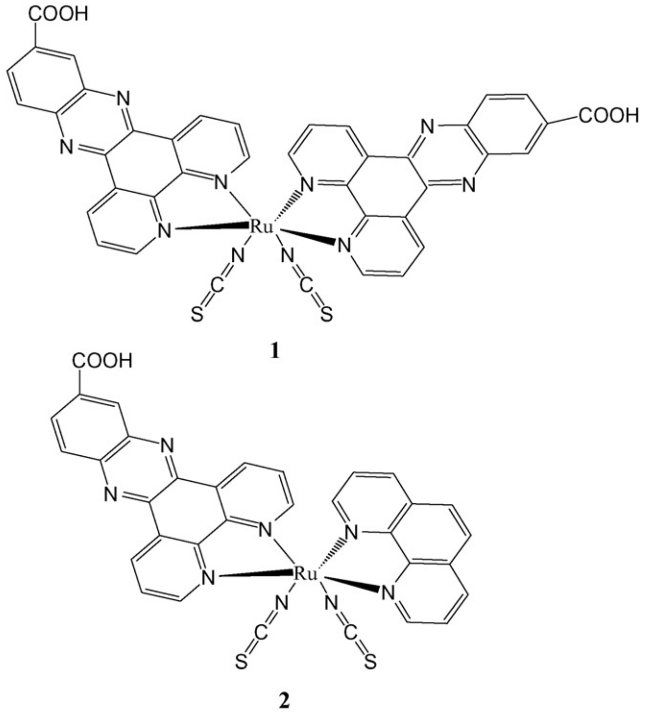


Fig. 1. Ruthenium complexes *cis*-$[Ru(dppz\text{-}COOH)_2(NCS)_2]$ (**1**) and *cis*-$[Ru(dppz\text{-}COOH)(phen)(NCS)_2]$ (**2**).

2. Experimental

2.1. Materials

All chemicals were reagent grade and used as received from Sigma–Aldrich unless otherwise specified. The solvents used in UV–vis studies were purified to spectroscopic quality by standard methods [13]. The deuterated solvents, which were utilized in NMR experiments, were purchased from Aldrich and were of 99.99% purity. Literature procedure was used to prepare the precursor $RuCl_2(DMSO)_4$ [14]. The 11-carboxyl-dipyrido[3,2-α:2′,3′-c]phenazine (dppz-COOH) and the $RuCl_2(dppz\text{-}COOH)_2$ precursor were synthesized with modified literature procedure [15]. The *cis*-$(NBu_4)_2[Ru(Hdcbpy)_2(NCS)_2]$ (N719) was purchased from Solaronix S.A. (Lausanne, Switzerland).

2.1.1. Synthesis of metal complexes

All metal complexes were synthesized by established literature techniques with minor variations [15,16].

2.1.1.1. Synthesis of cis-$RuCl_2(dppz\text{-}COOH)_2$. A suspension of $RuCl_3{\cdot}2H_2O$ (0.07 g, 0.34 mmol) and dppz-COOH (0.20 g, 0.61 mmol) in DMF (15 mL) was stirred and refluxed under N_2 for 8 h. After that time, the solution was concentrated to half, was cooled to 25 °C and diethylether was added to precipitate a dark red solid. The red product was filtered off, washed twice with ether (2× 5 mL) and then dried under vacuum. The resulting solid was almost insoluble in different solvents and no further purification was attempted. Yield 0.19 g (70%). Anal. calcd. for $RuC_{38}H_{20}N_8O_4Cl_2$—calculated: C 55.29%, H 2.43%, N 13.58%. Found: C 55.67%, H 2.39%, N 13.68%.

^1H NMR (DMSO-d_6, δ in ppm, spectra is not well resolved): 7.9 (dd, 4H, $phen_{dppz}$), 8.10 (dd, 4H, C_6H_3), 8.4 (q, 2H, C_6H_3), 9.2 (m, 4H, $phen_{dppz}$), 9.7 (m, 4H, $phen_{dppz}$).

*2.1.1.2. Synthesis of cis-$[Ru(SCN)_2(dppz\text{-}COOH)_2]{\cdot}H_2O$ (**1**).* $RuCl_2(dppz\text{-}COOH)_2$ (0.05 g, 0.06 mmol) was suspended in water. A NaOH 1 M solution was added dropwise under stirred conditions to maintain pH 7. The dark red solution was concentrated to half of its original volume and 10 mL MeOH was added. Consequently, a NH_4SCN solution (0.3 g) in methanol: water (5 mL:2 mL) was added, which had previously been boiled so that the *in situ* produced NH_3 be evaporated. The mixed solution was then refluxed under argon for 3 h in dark. The solvent was removed, the resulting solid was dissolved in distilled water and the desired complex was precipitated in pH 2 by adding 1 M HCl. The resulting dark red precipitate was filtered off, recrystallized in acetontrile/diethylether and vacuum dried. Yield 0.04 g (80%). Microanalytical data of the complex **1** are as follows: ESI–MS (*m*/*z*) 871.1 ($M + H^+$). Anal. calcd. for $RuC_{40}H_{22}N_{10}S_2O_5$—calculated: C 54.11%, H 2.50%, N 15.78%. Found: C 54.30%, H 2.70%, N 15.75%.

^{1}H NMR (acetone-d_6, δ in ppm): 7.88 (m, 2H, phen$_{\mathrm{dppz}}$), 7.92 (m, 2H, phen$_{\mathrm{dppz}}$), 8.25 (d, $J = 8.30$ Hz, 2H, C_6H_3), 8.38 (d, $J = 8.40$ Hz, 2H, C_6H_3), 8.42 (s, 1H, C_6H_3), 8.45 (s, 1H, C_6H_3), 8.95 (m, 2H, phen$_{\mathrm{dppz}}$), 9.10 (m, 2H, phen$_{\mathrm{dppz}}$), 9.23 (m, 2H, phen$_{\mathrm{dppz}}$), 9.5 (m, 2H, phen$_{\mathrm{dppz}}$).

*2.1.1.3. Synthesis of Ru(dppz-COOH)(phen)(SCN)$_2$·H$_2$O (**2**).* All solvents were degassed before use and the synthesis took place under standard Schlenk techniques in dark. To a solution of $RuCl_2(DMSO)_4$ (195 mg, 0.402 mmol) in DMF was added dppz-COOH (143 mg, 0.44 mmol) and stirred for 10 min. To the resulting mixture, phen (79 mg, 0.44 mmol) and 5 mL of aqueous solution of NH_4SCN (304 mg, 4 mmol) were added, and the suspension was stirred and heated at reflux for 5 h. After being cooled to room temperature, the non-reacted precursors were filtered. The solution was concentrated on the rotary evaporator. Ten microlitres of distilled water and 1 mL of NaOH 0.05 M were added to the latter and the resulting solution turned to a deep orange-red color. After filtration, pH was adjusted to 3 with HNO_3 0.5 M. The resulting solution was let stand in the fridge (−2 °C) for 12 h before being filtered. The resulting crystalline solid was respectively washed with aqueous solution of nitric acid (pH 3) and was dried in vacuo and preserved in dark. The precipitation was purified by column chromatography on Sephadex LH-20 (MeOH/ether), yielding the product as a red powder (278 mg, 85%). The same red product was received when the crude product was purified by chromatography on silica gel using THF as eluent. ESI–MS (*m/z*): 743.9 ($M + H^+$). Anal. calcd. for $RuC_{33}H_{18}N_8S_2O_2$: C 54.77%, H 2.51%, N 15.48%. Found: C 54.45%, H 2.72%, N 15.17%.

^{1}H NMR (acetone-d_6, δ in ppm): 7.1 (m, 1H, C_6H_3), 7.3 (m, 1H, phen$_{\mathrm{dppz}}$), 7.65 (dd, 2H, phen), 7.75 (m, 1H, phen$_{\mathrm{dppz}}$), 8.30 (d, $J = 8.40$ Hz, 1H, C_6H_3), 8.42 (s, 1H, phen$_{\mathrm{dppz}}$), 8.95–9.01 (m, 1H, phen$_{\mathrm{dppz}}$), 9.05 (s, 1H, C_6H_3), 9.10 (m, 1H, phen$_{\mathrm{dppz}}$), 9.2–9.32 (m, 4H, phen), 9.6 (m, 2H, phen), 9.72–9.82 (d, $J = 0.9$ Hz, 2H, phen), 10.72 (d, $J = 6.5$ Hz, 1H, phen$_{\mathrm{dppz}}$).

2.2. Methods

Photolysis experiment was carried out with a 1000 W Xe lamp in an Oriel, mod 68820, Universal Arc lamp source selected with appropriate interference filter (Corning). FT-IR spectra in solution and in KBr pellets were recorded on a Nicolet Magna IR 560 spectrophotometer having 1.0 cm^{-1} resolution. Electronic absorption spectra were recorded on a Varian Cary 300 spectrometer, having a circulating thermostat. The solute concentration was $\approx 10^{-5}$ M and the samples were prepared just before the measurements. ^{1}H NMR measurements were performed using a Varian Unity Plus 300 NMR spectrometer. Chemical shifts were reported relative to residual solvent signals. Elemental analyses were performed with a Euro Vector EA 3000 analyzer. ESI–MS were recorded on Fisons VG Quattro instrument with a VG Biotech Electrospray source, having an hexapole lens, using parameters as published before [17]. Emission measurements of complexes **1** and **2** were performed in methanol solution at room temperature and in a MeOH–EtOH glass at 70 K, using an Edinburgh Instruments FS-900 apparatus. Emission spectra were registered with a Xe lamp as the excitation source. Lifetime measurements were performed in single photon counting mode, with a nanosecond flash lamp as excitation source.

2.2.1. TiO_2 electrode preparation and dye-sensitized solar cell fabrication

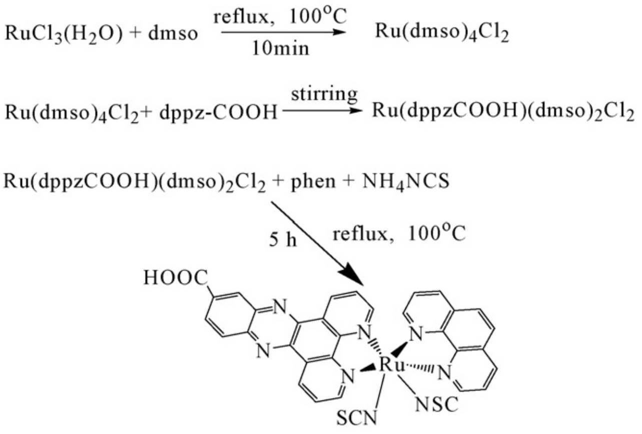
Using doctor blade technique, nanoporous TiO_2 thin films (15 μm thick) on conducting glass substrates TEC 15 (purchased from Hartford Glass Co. Inc.) were prepared, as previously reported [18]. An adhesive tape strip on the conductive glass was used to determine the film thickness. These films were sintered in air at 450 °C at a rate of 20 °C/min for 30 min and were stored in a vacuum desiccator in the dark till the time they were used. Finally, the electrodes were heated at 450 °C for 30 min and allowed to cool to about 80 °C before the sensitization process. The titania films were dipped into a dye solution of ca. 2.5×10^{-4} M in dimethylformamide (DMF) for 15–20 h. The dye-coated electrodes were taken out of the solution, rinsed thoroughly with ethanol to remove any physisorbed dye (excess), shortly dried under a stream of argon and used as such for photovoltaic cell fabrication. The sensitized TiO_2 thin films were incorporated in a sandwich-type solar cell employing a solid composite electrolyte ($PEO/TiO_2/I^-/I_3^-$) [19] and using a platinized TEC 8 counter electrode. An adhesive tape was placed between the electrodes to avoid short-circuiting, and the two electrodes were firmly pressed. The *cis*-$[Ru(dcbpyH)_2(NCS)_2](NBu_4)_2$ (N719 dye, purchased from Solaronix; $dcbpyH_2$ = 4,4′-dicarboxy-2,2′-bipyridine) was used as a reference to compare the new sensitizers.

I–V measurements were performed by illuminating the cell through the active photoelectrode (illuminated surface of 0.16 cm^2) under solar simulated light from a 300 W Xe lamp operating in conjunction with an AM 1.5 filter to give a flux of 1000 W/m^2 at the surface of the test cell. A more detailed fabrication procedure for the nanocrystalline titania electrodes, the cell assembly and the photoelectrochemical characterization has been described elsewhere [20].

3. Results and discussion

$RuCl_2(dppz\text{-}COOH)_2$ was synthesized by a method analogues to the synthesis of $RuCl_2(bpy)_2$ and involved the preparation and isolation of the free dppz-COOH ligand [15] and subsequent reaction with $RuCl_3 \cdot H_2O$. The resulting deep red solid was slightly dissolved in most used solvents and was used with no further purification.

The synthesis of the metal precursor $RuCl_2(DMSO)_4$ and complex **2** was carried out by following the route shown in Scheme 1. The first step was the coordination of the DMSO ligand, followed by its partial substitution of the dppz-COOH ligand, to obtain the intermediary complex, Ru(dppz-COOH)$(DMSO)_2Cl_2$. The next step was the coordination of both the phen and the –NCS ligands. A similar procedure was followed for the synthesis of complex **1**, but this time no phen was added. Actually, this is a one pot reaction since all the reagents, namely



Scheme 1.

dppz-COOH, phen and NH_4SCN, are added in the solution at the same time, yielding the desired complex. No isolation of any intermediary compound is required.

3.1. Infrared spectra

In the IR spectra of the complexes we observe the classical C=C and C=N bond signals (cm^{-1}) while the typical pattern of every specific dipyridine, namely dppz-COOH and phen, is also present. The intense signals at 1708 and 1698 cm^{-1} for complexes **1** and **2**, respectively, can be assigned to ν(CO) from carboxylic acid group. The blue shift of the aforementioned band (**2** versus **1**) implies the most extensive π-back donation from the $Ru(SCN)_2$ moeity to the dppz-COOH ligand, when only one of the latter is present in the complex. The high resolution spectra of **1** and **2** exhibit two bands centered at 2102/1993 cm^{-1} and 2099/1985 cm^{-1}, respectively, which are characteristic of the *cis*-configuration of the two thiocyanate ligands [5]. Furthermore, the aforementioned intense absorption is due to the *N*-coordinated ν(CN). This band is approximately three times more intense than the band at around 770 cm^{-1}, due to ν(CS). Actually, the *N*-coordination of the thiocyanate group is confirmed by the presence of the ν(C=S) resonance at 775 cm^{-1} for **1** (or at 755 cm^{-1} for **2**). If the thiocyanate groups were coordinated to ruthenium through their sulphur atoms, a weak ν(C=S) vibrational band around 700 cm^{-1} would have appeared [21].

3.2. ^{1}H NMR spectra

The ^{1}H NMR spectrum data for both complexes are given in Section 2.1.1. The spectra of the **1** and **2** complexes measured in acetone-d_6 are consistent with the structure (Fig. 1) and with data from the literature [22]. The complex **1** in solution shows (10) multipeaks in the aromatic region corresponding to two different pyridyl and phenazine protons in which two pyridine rings are trans to the NCS ligands and the remaining two are *trans* to each other. A similar pattern is indicated for the complex **2** in ^{1}H NMR spectrum, but now there are (13) proton peaks. The phenathroline protons are more dishielded after complexation with Ru^{2+} moiety, whereas dppz shifts are more shielded than the ones of the free ligands. This is due to the more extensive back donation on dppz ring than the phen ring.

3.3. UV–vis spectra

The solution electronic spectra were recorded in 200–800 nm range in MeOH. The data are listed in Table 1. The absorption spectra of both **1** and **2** sensitizers are dominated by metal-to-ligand charge transfer transitions (MLCT). This broad MLCT band appears between 400 and 600 nm centered at 455 nm with a shoulder at 507 nm for **1** and at 447 nm with a shoulder at 487 nm for **2**, in MeOH. This band is solvent dependent indicating blue shift in polar solvents (Table 1; Fig. 2).

The lowest energy MLCT of **2** is blue shifted 8 nm while the molar extinction coefficient increased by three-fold when compared to the complex **1**. This is due to the substitution of one dppz-COOH ligand by the phen ligand at **2** (compared to **1**), resulting to a most effective back donation to the remaining dppz-COOH. Both complexes display intense band in the UV region (380 nm for **1** and 362/379 nm for **2**), which has been assigned as intraligand π → π* transitions from dppz-COOH and phen [23]. The standard N719 sensitizer's lowest energy MLCT band is red shifted almost 30 nm while the molar extinction coefficient decreased by 50% when compared to the sensitizers **1** and **2** [24]. Inspecting the absorption spectra of **2** (Fig. 2), one may conclude that some impurities are present. Thus, to verify that the results of spectrochemical experiments were not affected by impurities that remained undetected with the used purification methods, reverse-phase HPLC (0.1 M triethylammonium acetate/CH_3CN eluent) was employed to obtain

Table 1
Spectroscopic data for complexes **1** and **2** in MeOH

Compound	λ_{abs} (nm)/ε ($\times 10^{-4}$ M^{-1} cm^{-1})		λ_{emit} (nm)	
	MLCT	π → π*	298 K[a] (τ, ns)	Glass 77 K[b]
1/MeOH	455(2.1)/507(1.9)	380 (8.3)	576 (190)	556, 599, 646
2/CH_3COCH_3	451/491	362/378		
2/CH_3CN	450/490	363/378		
2/MeOH	447(5.6)/487(5.3)	362(7.6)/379(7.2)	603 (230)	565, 612, 653
2/THF	469/522	362/379		
2/DMF	454/498	362/378		

[a] MeOH.
[b] Glass MeOH/EtOH.

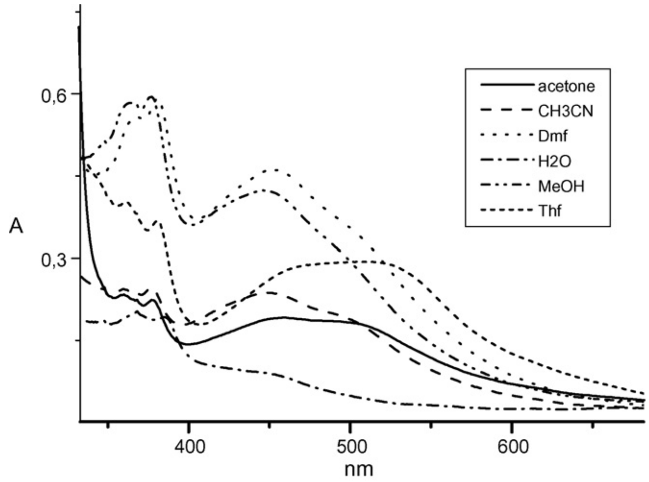


Fig. 2. Absorption spectra for **2** in different solvents. The solubility of **2** is different in the tested solvents. In some cases light heating is needed.

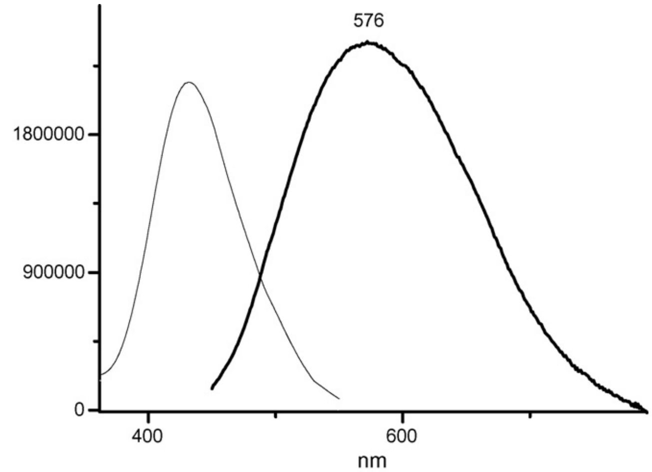


Fig. 3. Excitation and emission spectra of a 3.2×10^{-5} M solution of **1** in methanol. Excitation wavelength for the luminescence was 430 nm.

high-purity samples of complexes **1** or **2**. The material obtained from HPLC and the materials purified by recrystallization for **1** or column chromatography for **2** produced the same UV–vis spectra.

On the other hand, complex **2** differs from the analogue $Ru(bpy)_2(dppz)^{2+}$ complex. Complex **2** has two different chromophore ligands (namely dppz-COOH and phen) and the Ru(SCN) moeity. Thus, it probably has two almost nearby optical orbitals—one on the net phen ligand and one on the phen moiety of the dppz-COOH ligand. The existence of these two orbitals could affected the shape of the UV–vis spectra in the different solvents, since their polarazition would be different in each of the corresponding solvents (Fig. 2). This hypothesis could be proved by DFT calculations and such studies are underway. The almost indentical maxima of bands in water and methanol imply that short-range specific effects such as hydrogen bonds are present in both solvents.

3.4. Emission spectra

Both complexes **1** and **2** luminesce at room temperature, their excited lifetimes in methanol being 190 and 230 ns, respectively (Table 1). The emission maximum of **1** is almost 30 nm blue shifted as compared to that of **2**. The emission and excitation spectra of **1** in methanol are displayed in Fig. 3. The luminescence maximum is located at 576 nm, and the broad MLCT band is centered at 500 nm (in fact, the two bands at 507 and 450 nm, as calculated by the first derivative of the absorption spectrum, are not separated and they form an almost wide band from 400 to 560 nm. The excitation spectrum is centered at 430 nm implying that probably only one of the two aforementioned states is emissive in room temperature). For complex **2**, the luminescence maximum is at 603 nm. Furthermore, both complexes **1** and **2** luminesce at glass methanol/ethanol (77 K), but this time the emission spectra provides a splitting of the main band at 556, 599 and 646 nm for **1** (Fig. 4) and at 565, 612 and 653 nm for **2** (Table 1). Complexes **1** and **2** display fluorescent maxima at lower energy than the free dppz-COOH ligand [25], suggesting that the presence of the metal ion affects the emission wavelength. Otherwise, the ruthenium complexes **1** and **2** show MLCT emissions.

3.5. Photovoltaic performance

Immersion of nanocrystalline titania photoelectrodes in a 2.5×10^{-4} M DMF solution of the dyes resulted in strong coloration (reddish color) of the films. Fig. 5 exhibits the photocurrent density–voltage (*I*–*V*) characteristics of a solar cell sensitized with **1** and **2** under direct irradiance of 1000 W/m^2 (spectra ‘a’ and ‘b’, respectively). The resulting performance characteristics of the ruthenium complexes **1** and **2** as sensitizers on nanocrystalline TiO_2 are summarized in Table 2.

Under standard global AM 1.5 solar illumination conditions, the cell of dyes **1** and **2** give a photocurrent density of ca. 0.8 mA/cm^2, a fill factor of 0.55 (0.58), an open circuit potential of 456 mV (420 mV) and yields a power conversion efficiency of 0.21% (0.19%), respectively, lower enough compared to the standard sensitizer N719. This can be primary attributed to the

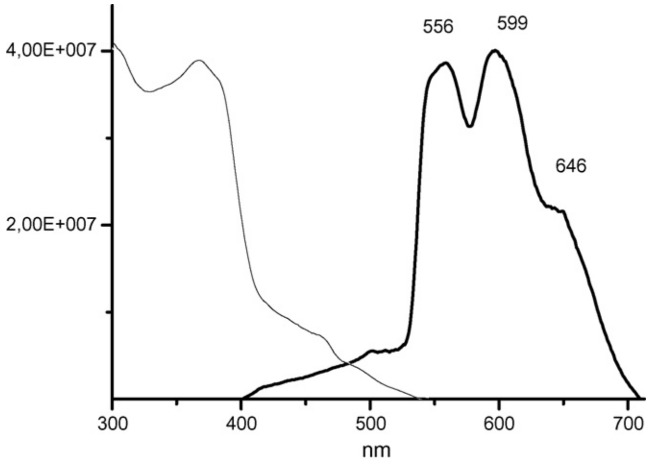


Fig. 4. Excitation and emission spectra of **1** in MeOH/EtOH glass (77 K). Excitation wavelength for the luminescence was 370 nm.

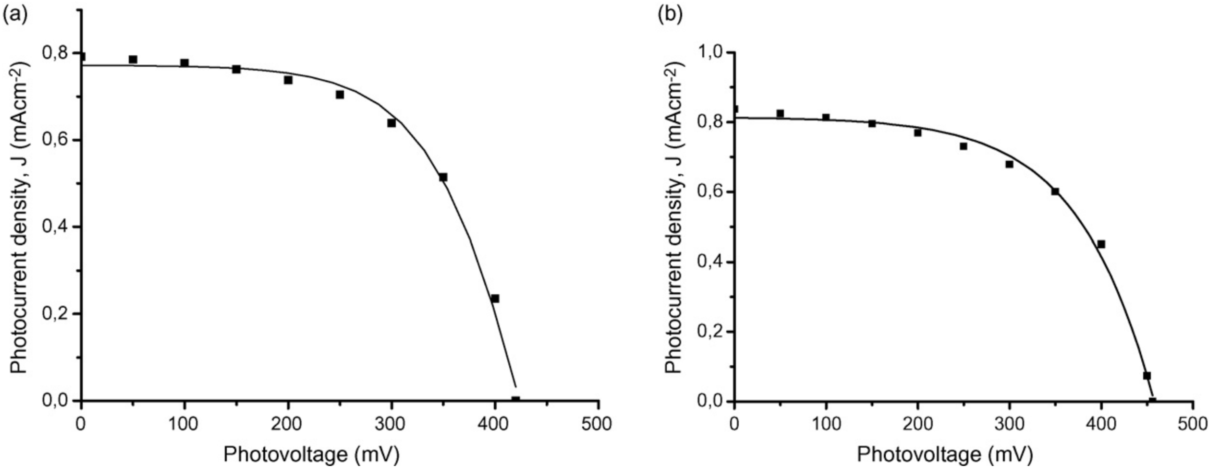


Fig. 5. Photocurrent density–photovoltage characteristics of DSSCs using Ru(II) dyes **1** (a) and **2** (b), under AM 1.5 simulated light.

blue shift of the MLCT bands of **1** and **2** compared to the one of N719. The best data obtained for **2** are directed us to replace the phen ligand with electron donating groups. However, besides a slight superiority of the dye **2** [the photovoltage (V_{oc}) of the cell with complex **2** is 36 mV higher than that of dye **1**], the two new sensitizers behave in an almost similar way. The relatively low current density values for dyes **1**, **2** are in good agreement with literature results. In fact, it has been reported that for the ruthenium(II) complexes Ru(TAPNB)$_2$(NCS)$_2$ (TAPNB = 4-(1H-1,3,7,8-tetraaza-cyclopenta[1]phenanthren-2-yl)-benzoic acid) and [Ru(TAPNB)(bipy)$_2$](PF$_6$)$_2$ with similar molecular structures, the short circuit currents were of the same order (J_{sc} = 0.09 and 0.22 mA/cm^2, respectively) [26]. This behaviour is attributed to the small amount of dyes chemisorbed on the TiO$_2$ surface and/or to the absence of strong absorption in the visible, at longer wavelengths. In addition, taking into account that in our case the films are strongly colored (which means that the amount of chemisorbed dye is significant) and the fact that the new dyes present strong luminescence at room temperature, a fast recombination of the injected electron [from the excited dye state (D*)] with the oxidized dye (D$^+$) cannot be excluded. Such a decay pathway competitive with the electron injection from the dye to the semiconductor (TiO$_2$) could be probably responsible for the rather low efficiency of these dyes as compared to N719 [27]. Moreover, the new complexes **1** and **2** merit high interest and value, as in this work a solid state photovoltaic cell is constructed using the composite redox polymer electrolyte.

Table 2
Photovoltaic performance characteristics of the solid state DSSCs using the Ru(II) dyes **1** and **2**

Complexes	J_{sc} (mA/cm^2)	V_{oc} (mV)	ff	η (%)
1	0.79	420	0.58	0.19
2	0.84	456	0.55	0.21
N719	9.29	583	0.53	2.87

Corresponding parameters using the N719 dye are also given.

4. Conclusion

Two novel ruthenium complexes, namely *cis*-[Ru(dppz-COOH)$_2$(NCS)$_2$] (**1**) and *cis*-[Ru(dppz-COOH)(phen)(NCS)$_2$] (**2**), where dppz-COOH = 11-carboxyl-dipyrido[3,2-α:2′,3-c]phenazine and phen = 1,10-phenanthroline, have been synthesized and their spectroscopic properties were studied. Both complexes **1** and **2** have been anchored to nanocrystalline TiO$_2$ film electrodes, and the photovoltaic properties of the resulting dye-sensitized solar cells have been characterized and compared with the properties of the one prepared with *cis*-(NBu$_4$)[Ru(Hdcbpy)$_2$(NCS)$_2$] (N719). Although the efficiency of the **2**-sensitized solar cell is 10% higher than the **1**-sensitized solar cell, neither is as efficient as the N719-sensitized solar cell. This is mainly attributed to differences in the absorption and emission spectra of all the aforementioned dyes. The complexes **1** and **2** have indicated a broad and intense metal-to-ligand charge transfer (MLCT) transition band in the visible region, which is blue shifted compared to the MLCT band of N719. This band luminesces both at room temperature and in a MeOH–EtOH glass (77 K). The superiority of complexes **2** versus **1** has been attributed to the existence of the phen ligand and the more extensive π-back donation on the single dppz-COOH ligand. Contrary to these results, photosensitizers **1** and **2** are of substantial interest since in the present work, a solid state electrolyte, namely PEO/TiO$_2$/I$^-$/I$_3{}^-$ has been used with its observed efficiencies being comparable to others reported in the literature for a liquid electrolyte. Thus, further modification/substitution of the phen ligand is in progress.

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