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Synthesis and photophysical properties of *trans*-dithiocyanato bis(4,4′-dicarboxylic acid-2,2′-bipyridine) ruthenium(II) charge transfer sensitizer

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Abstract

The ruthenium complexes *trans*-[Ru(dcbpyH$_2$)$_2$(Cl)$_2$] (**1**), *trans*-[Ru(dcbpyH$_2$)$_2$(NCS)$_2$] (**2**), were synthesized and characterized by UV–Vis absorption, emission, IR, and NMR spectroscopy. The absorption and emission maxima of the *trans* complexes are red-shifted when compared to the *cis* analogs. The low energy MLCT maximum of complex **2** shows at 582 nm and exhibits a luminescence consisting of a single band with a maximum at 870 nm, in DMF solution at 298 K. The red shift of the MLCT absorption of the *trans*-chloro complex **1** (662 nm) is even more pronounced than that of the *trans*-complex **2** and shows the onset of weak and broad emission signals above 900 nm. The proton NMR spectra of the *trans*-isomers show only three peaks corresponding to the two dcbpy ligands in which all the pyridine rings are equivalent. The ^{13}C NMR spectrum of the *trans*-isomer is characterized by a relatively simple pattern of resonances from the four equivalent pyridine rings. The enhanced red response of the *trans*-complex **2** renders it an attractive candidate as a panchromatic charge transfer sensitizer in mesoporous oxide solar cells. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium(II) complexes; Photophysical properties; Optical properties; Charge transfer sensitizer; Dithiocyanato complexes

1. Introduction

Photophysical and photochemical properties of ruthenium polypyridyl complexes have been studied extensively for many years [1,2] in part because of their possible applications in energy conversion processes [3,4]. The choice of ruthenium metal is attractive for its octahedral coordination geometry, where one can introduce specific ligands in a controlled manner to tune the photophysical, photochemical and the electrochemical properties. The majority of the ruthenium complexes, reported to date containing two bipyridyl and two monodentate ligands have a *cis*-configuration [5], although the synthesis and crystal structure of a few *trans*-complexes have been described [6]. A case of particular interest is that of the dithiocyanato complex Ru(II)(4,4′-dicarboxy-2,2′-bipyridine)$_2$(NCS)$_2$]. The *cis*-form of this complex is one of the most efficient heterogeneous charge transfer sensitizers known to date and is widely used in the nanocrystalline TiO$_2$ solar cell [4]. The present study reports on the synthesis and characterization of the *trans* isomer of this complex, which was found to exhibit very interesting optical properties.

2. Experimental

UV–Vis and fluorescence spectra were recorded in a 1 cm path length quartz cell on a Cary 5 spectrophotometer and Spex Fluorolog 112 Spectrofluorometer, respectively. The measured emission and excitation spectra were routinely corrected for the wavelength dependent features. The emission lifetimes were measured by exciting the sample with a pulse from an active modelocked Nd YAG laser, using the frequency doubled line at 532 nm. The emission decay was followed on a Tektronix DSA 7912 Digitising Signal Analyser, having used a Hamamatsu R928 photomultiplier to convert the light signal to a voltage signal. Proton and

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^{13}C NMR spectra were measured on a Bruker 200 MHz spectrometer. The reported chemical shifts are against TMS. Infrared spectra were obtained with a Perkin–Elmer Paragon 1000 FTIR spectrophotometer at a resolution of 5 cm^{-1} with the samples dispersed in compressed KBr pellets. The *cis*-[Ru(II)(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(Cl)$_2$] and *cis*-[Ru^{II}(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(NCS)$_2$] complexes were prepared by a literature procedure [4]. All other chemicals and solvents were reagent grade and used without further purification.

2.1. Synthesis of trans-[Ru^{II}(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(Cl)$_2$]·2H$_2$O (**1**)

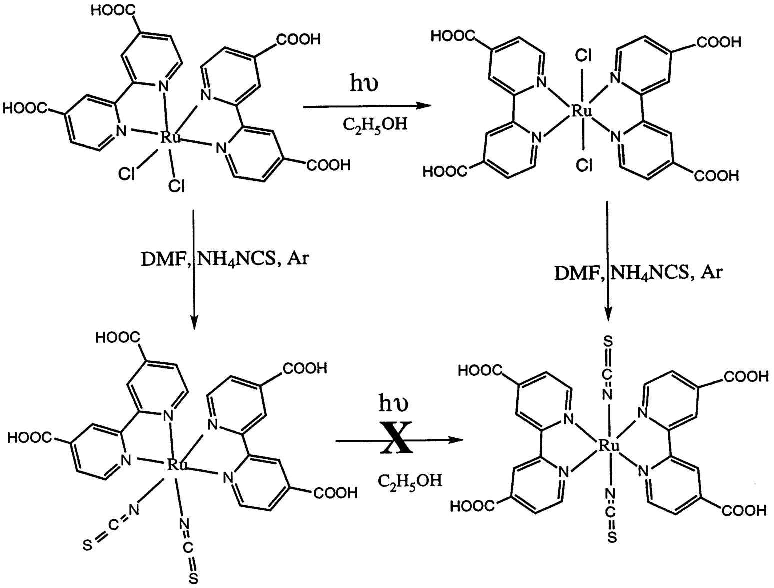
The *cis*-[Ru(II)(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$-(Cl)$_2$] complex was dissolved in ethanol (1×10^{-3} M) and filtered in order to remove insoluble by-products. The filtered solution was photolyzed with a 250-W sunlamp to induce *cis–trans* isomerization. The *trans* isomer precipates from the solution. After 3 h of irradiation precipitation appeared complete. The same precipitate was also obtained by leaving an ethanolic solution of *cis*-[Ru^{II}(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(Cl)$_2$] complex under room light for several days. The precipitate was filtered off, washed with ethanol followed by diethyl ether and dried under vacuum. Yield 90%. *Anal.* Calc. for $RuC_{24}H_{16}N_4Cl_2O_8$: C, 41.38; H, 2.87; N, 8.05; Cl, 10.20. Found: C, 41.52; H, 2.92; N, 8.17; Cl, 10.23%. ^1H NMR (D_2O/NaOD) δ ppm: 9.66 (4H, d), 8.87 (4H, s), 8.11 (4H, d). UV–Vis: λ max. 662, 584, 424 and 314 nm.

2.2. Synthesis of trans-[Ru^{II}(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(NCS)$_2$] (**2**)

This dithiocyanato complex was synthesized by heating under magnetic stirring a solution of *trans*-[Ru^{II}(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(Cl)$_2$] (50 mg) and ammonium thiocyanate (90 mg) in DMF (10 ml) for 3 h at 100°C in the dark under an argon atmosphere. The solvent DMF was evaporated completely on a rotary evaporator under vacuum. The resulting solid product was collected on a sintered glass crucible, washed with methanol and followed by diethyl ether. Yield 15%. ^1H NMR (D_2O/NaOD) δ ppm: 9.48 (4H, d), 8.83 (4H, s), 8.03 (4H, d). ^{13}C NMR (D_2O/NaOD) δ ppm: 172.46 (COOH), 160.43 (C-6), 157.46 (C-2), 155.27 (NCS), 146.20 (C-4), 124.55 (C-3) and 122.40 (C-5). UV–Vis: λ max. 582, 528, 402 and 314 nm.

3. Results and discussion

Scheme 1 shows the details of the strategy adopted for the synthesis of *trans*-complexes. The *trans*-dichloro complex **1** was obtained by photolyzing the *cis*-dichloro complex that gave the precipitate in ethanol solution. Heating the complex **1** in the presence of ammonium thiocyanate resulted in the formation of the *trans*-dithiocyanate complex **2**. The UV–Vis absorption spectrum of complex **2** in DMF shows three intense metal-to-ligand charge transfer (MLCT) bands at 402, 528 and 582 nm, with a molar extinction coefficient of



Scheme 1.

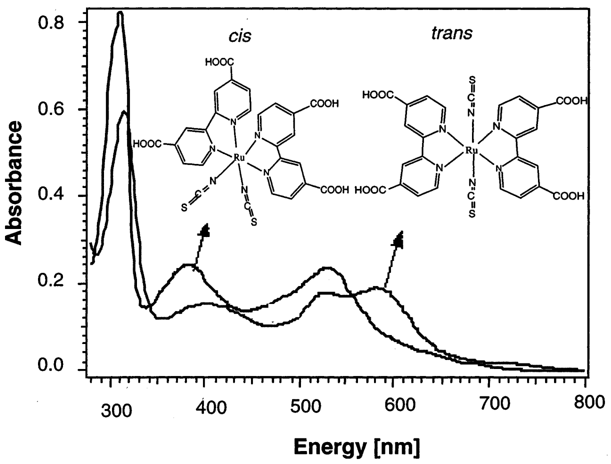


Fig. 1. UV–Vis absorption spectra of *cis*- and *trans*-dithiocyanato-bis(2,2′-bipyridine-4,4′-dicarboxylic acid) ruthenium(II) complexes, 1.5×10^{-5} M in DMF solution, 1-cm cell.

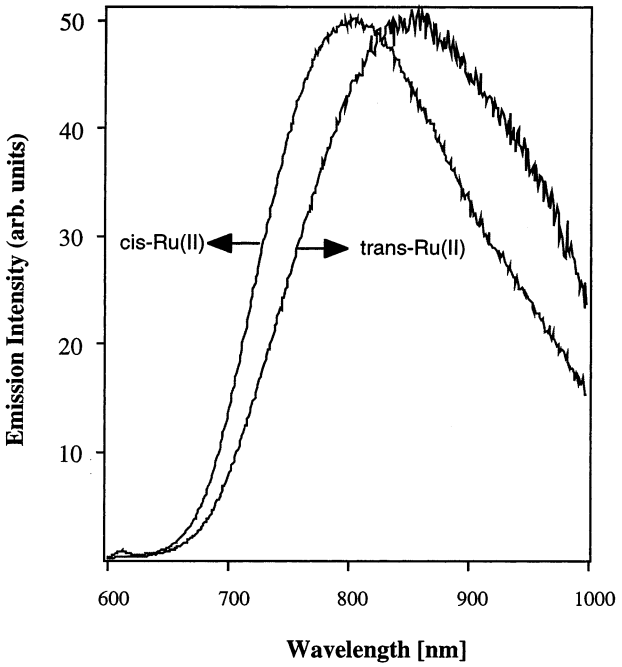


Fig. 2. Emission spectra of *cis*- and *trans*-dithiocyanatobis(2,2′-bipyridine-4,4′-dicarboxylic acid) ruthenium(II) complexes measured at 298 K under aerobic conditions in DMF solution.

12500 M^{-1} cm^{-1} for the lowest energy band. The band at 314 nm is assigned to the intra ligand π–π^* transition of dcbpy ligand. There is a striking difference in the visible absorption spectra of the *trans*- and *cis*-isomer (Fig. 1). The lowest energy MLCT maximum shifts from 538 to 582 nm upon *cis*-to-*trans* isomerization. This is a significantly larger red shift than for any of the Ru(II) bis-bipyridyl complex reported to date in the literature [7].

The bathochromic shift in the *trans*-complex **2** compared to its *cis*-analog is attributed to a destabilization of the ruthenium t_{2g} orbital due to electron donation from the two anionic NCS ligands to ruthenium center. The red shift of the MLCT absorption of the *trans*-chloro complex **1** (662 nm) is even more pronounced than that of the *trans*-complex **2**. This is expected as the Cl^- ligand is a stronger donor than NCS^-.

When excited at the lowest energy MLCT absorption band, the *trans*- and *cis*-NCS isomers in DMF solution at 298 K exhibit a luminescence consisting of a single band with a maximum at 870 and 780 nm, respectively (Fig. 2). Excitation of these complexes at different wavelengths within the manifold of the MLCT bands gave the same emission maxima. This phenomenon shows that exciting the complex between 380 and 650 nm leads to population of the same luminescent state. The excited state lifetimes of *trans*- and *cis*-isomer, measured at 298 K under aerobic conditions, are 12 and 24 (± 5) ns, respectively. We could not observe any detectable emission up to 900 nm for complex **1**, in DMF solution at room temperature. However, complex **1** showed at room temperature onset of a weak and broad emission signals above 900 nm that did not allow for lifetime measurements. Hence, the emission from the *trans*-complex **1** is expected to be in the 900 to 1100 nm region, beyond the detector response of our equipment.

The *trans* configurations of the complexes **1** and **2** also have been confirmed by the proton and ^{13}C NMR spectra. The *cis*-isomer in a $D_2O + NaOD$ solution shows six peaks in the aromatic region corresponding to two different pyridine ring protons (Fig. 3(a)). In the *trans*-isomer, two dcbpy ligands are equivalent in which all the pyridine rings are *trans* to each other and show only three peaks (Fig. 3(b)). For the complex **2**, no evidence was found for the substitution of thiocyanate ligand or the isomerization to *cis* during several days under room light in DMF solution.

The carbon 13 NMR spectroscopy proved to be the most valuable tool for determining the geometric configuration of the ruthenium complex and the linkage

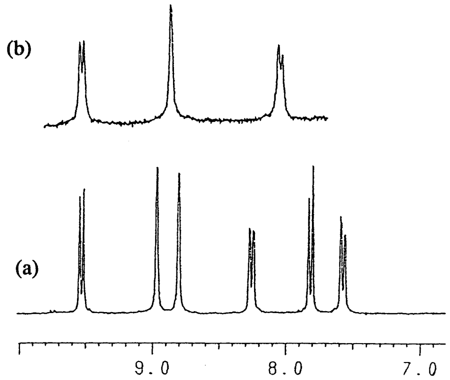


Fig. 3. Proton NMR spectra of (a) *cis*- and (b) *trans*-dithiocyanato-bis(2,2′-bipyridine-4,4′-dicarboxylic acid) ruthenium(II) complexes measured in $D_2O + NaOD$ solution.

properties of the NCS ligand. Since, the NCS ligand is an ambidentate ligand it can coordinate to the metal through N or S end. The proton decoupled carbon 13 NMR spectra of *cis*- and *trans*-isomers show different carbon resonances that were identified by comparing with known bipyridine complexes [8]. Carbon 13 NMR spectrum of the *cis*-isomer shows 12 resonance peaks consisting of six sets due to two different dcbpy ligands. The single resonance peak at 132.84 ppm we assign to the carbon of N-coordinated NCS. The two downfield resonances at 172.59 and 172.24 are assigned to the carboxylate carbons.

The ^{13}C NMR spectrum of the *trans*-isomer is characterized by a relatively simple pattern of resonances from the four equivalent pyridine rings. The pattern consists of six single resonance peaks coming from the pyridine carbons and one resonance peak at 155.27 ppm that was assigned to the *trans* NCS ligands. There is a noteworthy difference between the *cis* NCS carbon resonance (132 ppm) and the *trans* NCS (155.27 ppm), which could be due to the *trans* NCS carbons being more deshielded than the *cis* analog. In an axial position, both the thiocyanate ligands have less π back bonding from the ruthenium center compared to *cis* NCS. Our observation is consistent with a known ruthenium complex that contains *trans* NCS ligands [9].

A perfect *trans*-symmetry with two NCS ligands *trans* to each other is expected to give rise to a single ν(NC) stretch [10]. The IR spectrum of *trans*-complex **2** shows an intense single band at 2106 ν(NC) and 782 ν(CS) cm^{-1} due to N-coordinated NCS ligand. The band at 1721 ± 2 cm^{-1} is due to the carboxyl groups.

The enhanced red response of the *trans*-complex **2** renders it an attractive candidate for substituting the *cis* analog as a panchromatic charge transfer sensitizer in mesoporous oxide solar cells. Initial experiments confirm efficient photoinduced electron injection into nanocrystalline TiO_2 films derivatized with this sensitizer.

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