Efficient Photosensitization of Nanocrystalline TiO_2 Films by a New Class of Sensitizer: *cis*-Dithiocyanato bis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II)

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A new class of ruthenium(II) complexes containing carboxylated 1,10-phenanthroline were synthesized. Photosensitization of nanocrystalline TiO_2 electrode by bis(tetrabutylammonium)dihydronium *cis*-dithiocyanato bis(4,7-dicarboxy-1,10-phenanthroline)ruthenium(II) showed a high incident photon-to-current conversion efficiency (IPCE: 70% at 540 nm). The overall solar-to-electric power conversion efficincy of 6.1% was obtained at AM-1.5 (100 mW/cm^2).

Dye sensitized nanocrystalline TiO_2 solar cell technology (new generation of solar cells) is a subject of intense investigation because of its low cost and high performance.[1,2] Using a bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) complex as charge transfer sensitizer, solar to electric power conversion efficiency of 10% has been reported.[2] Since then, various other photosensitizers such as porphyrins,[3] bipyridine[4] and terpyridine complexes of ruthenium,[5] phthalocyanines,[6] Eosin,[7] and perylene derivatives[8] have been explored. However, ruthenium complexes containing anchoring phenanthroline ligands have never been tried as sensitizers till today. Here we report for the first time, synthesis and characterization of a new class of ruthenium complexes containing 4,7-dicarboxy-1,10-phenanthroline ligand and photosensitization of TiO_2 films by these complexes.

4,7-Dicarboxy-1,10-phenanthroline ($dcphenH_2$) was prepared from 4,7-dimethyl-1,10-phenanthroline via dialdehyde with slight modification of reported procedure.[9]

cis-Dichlorobis(4,7-dicarboxy-1,10-phenanthroline) ruthenium(II), $[Ru(dcphenH_2)_2Cl_2]$, **1** was synthesized by refluxing $RuCl_3(H_2O)_3$ (52 mg) and 4,7-dicarboxy-1,10-phenanthroline (103 mg) in DMF for 3 h. After cooling the reaction mixture was filtered and the solvent was evaporated completely. The resulting solid was washed with 1:4 acetone and diethyl ether mixture. Further, the solid was stirred for 2 h in a HCl solution (3 mol dm^{-3}) and was collected on a membrane filter. The yield was 120 mg, (86%). The complex **1** is soluble in most of the organic solvents and undergoes trans isomerisation under light.

cis-Dithiocyanato bis(4,7-dicarboxy-1,10-phenanthroline) ruthenium(II), $[Ru(dcphenH_2)_2(NCS)_2]$, **2** was synthesized from **1** by reacting with NH_4NCS in a water-DMF solution. Bis(tetrabutylammonium)dihydronium *cis*-dithiocyanato bis (4,7-dicarboxy-1,10-phenanthroline)ruthenium(II), $[Ru(dcphen TBA (H))_2(NCS)_2]$, **3** was synthesized by titrating complex **2** with a tetrabutylammonium hydroxide solution.[10] Complex 3 is a nonhygroscopic and air stable solid. Therefore, it is convenient to purify the complex and to deal with it.

The absorption properties of ruthenium complexes are shown in Table 1. The UV-vis absorption and emission spectra of complex **3** are shown in Figure 1(a) and 1(b), respectively. For comparison purpose, the absorption spectrum of *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) $[Ru(dcbpyH_2)_2(NCS)_2]$, **4** is also included in Figure 1(a). The absorption spectrum of complex **3**, in ethanol shows an intense broad band at 522 nm due to metal-to-ligand charge transfer transition, with a molar absorption coefficient of 1.8 x 10^5 dm^2 mol^{-1}. On the other hand the complex **4** shows two bands at 396 and 534 nm, with a molar absorption coefficient of 1.4 x 10^5 dm^2 mol^{-1}. Presence of single broad absorption band in complex **3**, indicate that the phenanthroline ligands around ruthenium are more symmetric compared to the bipyridine ligands.

Deprotonation of the carboxyl groups in complex **3** caused blue shift of the low energy MLCT band from 522 to 498 nm. The blue shift is due to an increase in the energy of the LUMO of the ligand causing the $\pi - \pi^*$ and $d - \pi^*$ transitions to occur at higher energy. When excited within the MLCT absorption band, **3** in ethanol solution at room temperature exhibits a luminescence band with a maximum at 790 nm. Cyclic voltammogram of complex **3** shows an irreversible oxidation wave at +0.8 V and reduction wave at -1.3 V vs SCE. They are due to the oxidation of Ru (II)/(III) and reduction of 4, 7-dicarboxy-1,10-phenanthroline, respectively. The irreversible oxidation wave could be due to the presence of thiocyanate groups whose oxidation potential is very close to the oxidation potential of complex **3**.

The performance of **3** as photosensitizer on nanocrystalline TiO_2 electrode has been studied. The photocurrent action spectra obtained with the TiO_2 film electrode coated with complex **3** is shown in Figure 2. A sandwich-type cell configuration was used to measure the spectrum. The preparation of the nanostructured TiO_2 films and experimental details for the measurements are given earlier.[2] The dye solutions were prepared in 1:1 v/v acetonitrile and *tert*-butanol solvent mixtures at a typical concentration of 5 x 10^{-4}

Table 1. Absorption properties of ruthenium complexes

complex	absorption (RT) max (nm) (ε(10^{-5} dm^2 mol))
$Ru(dcphenH_2)_2Cl_2$ **1**	534(0.76), 282(3.4)
$Ru(dcphenH_2)_2(NCS)_2$ **2**	529, 287
$Ru(dcphenTBA(H))_2(NCS)_2$ **3**	522(1.8), 311(4.1)
$Ru(dcbpyH_2)_2(NCS)_2$ **4**	534(1.4), 396(1.4), 313(3.1)

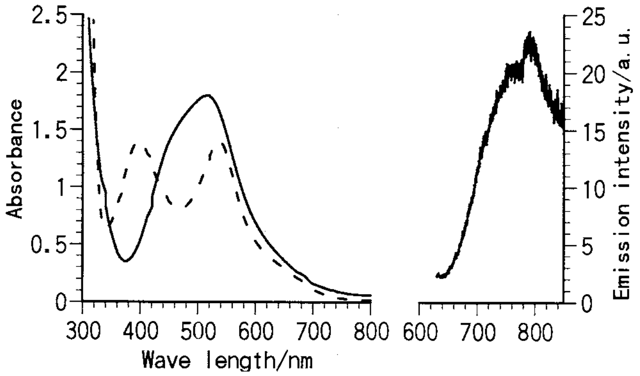

Figure 1. (a) Absorption spectra of complex **3**—— and **4**- - - , and (b) emission spectrum (excited at 522nm) of complex **3** in ethanol solution at room temperature.

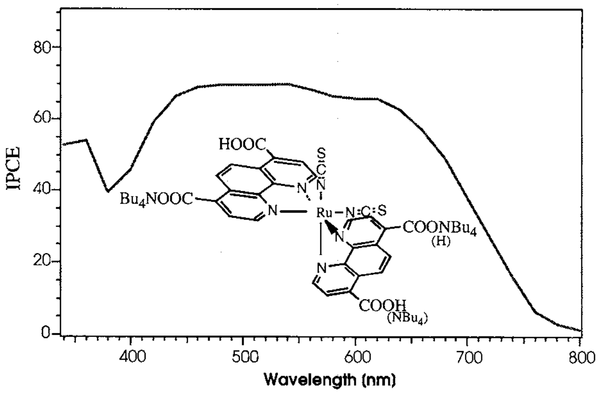

Figure 2. Photocurrent action spectrum of nanocrystalline TiO_2 film sensitized by complex **3**

mol dm^{-3}. The TiO_2 electrodes were heated at 400 °C for 20 min before dipping them into the dye solution. The electrodes were left in the solution for 12 - 15 h. The redox electrolyte consisted of a solution of 5 x 10^{-4} mol dm^{-3} dimethylpropylimidazolium iodide, 2 x 10^{-2} mol dm^{-3} I_2, 5 x 10^{-4} mol dm^{-3} tert-butyl pyridine, 4 x 10^{-2} mol dm^{-3} l LiI in methoxy acetonitrile.

The incident monochromatic photon-to-current conversion efficiency (IPCE) is plotted as a function of excitation wavelength. The photocurrent action spectra of photosensitizer **3** shows quite broad features covering a large part of visible spectrum where the IPCE shows 70%. The total current obtained using a 13 μm thick TiO_2 electrode under an illumination of AM 1.5 (100 mW/cm^2) is 13.6 mA/cm^2. The open circuit potential is 670 mV with an impressive fill factor of 67%, yielding solar to electric power conversion efficiency of 6.1%.

References and Notes

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10 **3**: ^1H NMR(300 MHz, D_2O): δ 9.85 (d, 2H, *J*=5.2 Hz), 8.59(d, 2H, *J*=9.3 Hz), 8.46(d, 2H, *J*=9.6 Hz), 8.27(d, 2H, *J*=5.5 Hz), 7.91(d, 2H, *J*=5.5 Hz), 7.41(d, 2H, *J*=5.5 Hz), 2.98(t, 16H, *J*=8.4 Hz), 1.47(m, 16H), 1.19(m, 16H), 0.82(t, 24H, *J*=7.3 Hz), MS (ESIMS): m/z 617.2 $(M)^{2-}$