

Preparation and application of new ruthenium(II) polypyridyl complexes as sensitizers for nanocrystalline TiO₂

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Abstract

A series of Ru(II) polypyridyl complexes, containing carboxylic- and sulphonic ‘anchor’ groups, were synthesized as sensitizers for nanocrystalline TiO₂. Depending on number and type of ligands the sensitizers are divided into three classes: tris-homoleptic complexes **1a–d**, tris-heteroleptic complexes **2a–d** and bis-complexes **3a–f**. The compounds were characterized and the photophysical and electrochemical properties were examined. These studies proved the suitability of **1a–3f** as sensitizers for TiO₂-based photoelectrochemical ‘Graetzel’-type solar cells. A comparison of the performance of the complexes **1a–3f** in the cell relative to Ru(dcbpy)₂(NCS)₂ **3d** as internal standard for mean efficiency η is presented, whereby Ru(dcphen)₂(NCS)₂ **3f** is shown to have an efficiency of $\eta_{\text{rel.}}=62.3\%$ relative to **3d**. A possible reason for the particular efficiency of **3d** as sensitizer is discussed. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Ru-polypyridyl complexes; Graetzel cell; Nanocrystalline TiO₂; Solar cell

1. Introduction

Since the discovery of the ‘ferroin-reaction’ by Blau [1] more than a century ago, polypyridyl transition metal complexes have been investigated extensively and have found many applications besides analytical and preparative chemistry [2]. In the last three decades interest focused on the redox and photophysical properties of such coordination compounds, mainly because of coordinative stability in the oxidation states [3–6]. Especially dye sensitizers of the Ru(II)-polypyridyl type are playing an important role in the study of photoinduced electron transfer processes mimicking the processes in the photosynthetic reaction center [7–13]. Ru(II) sensitizers have been employed for solar energy conversion into chemical storage products, e.g. for splitting of water in hydrogen [5,10,14–18] and oxygen [19–21] or reduction of CO₂ to methane [9,11,22,23], or for conversion of light into electricity using photoelectrochemical cells [24–26]. Although the basic mechanisms of dye sensitized cells were already understood in the 1970s [27], a significant progress regarding efficiency and stability was achieved only in 1991, when a photoelectrochemical solar cell was introduced by Graetzel and O’Brian [28] based on polycrystalline TiO₂ and ruthenium-polypyridine antenna complexes — described for the first time by

Scandola et al. [29] — reaching even economical interest. A further improvement was made by employing *cis*-dithiocyanato-*N,N'*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)-ruthenium(II) **3d** as sensitizer [30]. Until today it shows outstanding efficiencies in the conversion of light into electricity ($\eta_{\text{AM1.5}} \approx 7\text{--}10\%$).

The expertise we have acquired during the past 15 years led us to reinvestigate the Graetzel cell in our laboratory to have an internal standard for the study of modified and new Ru based polypyridine complexes as dopants and thus sensitizers in photoelectrochemical TiO₂ solar cells.

In this paper we describe (1) the synthesis and characterization of mononuclear ruthenium(II)-bipyridine, — phenanthroline and — bipyridazine complexes and (2) the study of the performance of these photosensitizers in Graetzel-type solar cells using the Graetzel cell and its dye as an internal standard.

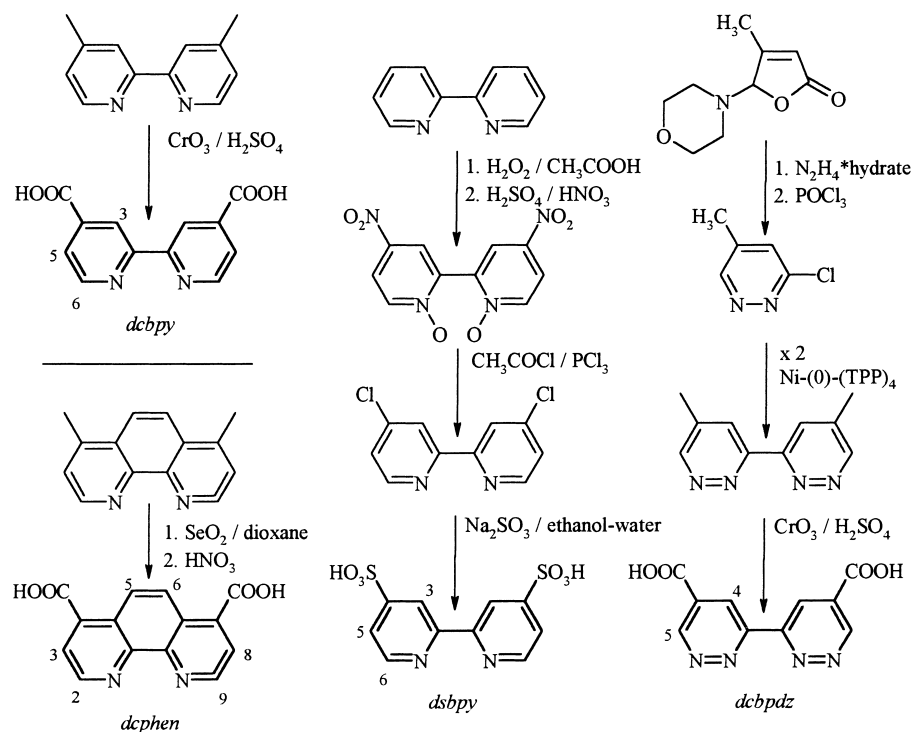
2. Experimental details

2.1. Synthesis of the ligands dcbpy, dsbpy, dcphen, dcbpdz and the ruthenium complexes 1–3

2.1.1. Ligands

The key step in the synthesis of the ligands is the introduction of anchor groups, an important requirement for

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Scheme 1. Synthesis of the 'anchor'-ligands.

effective attachment of a ruthenium complex to the TiO_2 surface. Beside, the well established carboxylic group, we present in this paper sulphonic acid as anchor unit. The ligands for the Ru(II) complexes were prepared according to Scheme 1.

2.1.2. 2,2'-Bipyridine-4,4'-dicarboxylic acid (dcbpy)

2,2'-Bipyridine-4,4'-dicarboxylic acid (dcbpy) was synthesized in >93% yield by oxidizing 4,4'-dimethyl-2,2'-bipyridine with stoichiometric amounts of CrO_3 in concentrated sulfuric acid at 40°C for 3 h, poured onto ice and left overnight (analogous to the oxidation of picoline [31]). The white crystals were filtered off and recrystallized from water. (mp > 300°C ; IR (KBr): $\nu = 3240, 3120, 1720, 1610, 1740, 1290 \text{ cm}^{-1}$; $^1\text{H NMR}$ (d_6 -DMSO): $\delta = 8.90$ (d, $^3J_{6,5} = 3.9 \text{ Hz}$, 2H, 6,6'-H), 8.83 (s, 2H, 3,3'-H), 7.90 (d, $^3J_{5,6} = 3.9 \text{ Hz}$, 2H, 5,5'-H) ppm.)

2.1.3. 2,2'-Bipyridine-4,4'-disulphonic acid (dsbpy)

2,2'-Bipyridine-4,4'-disulphonic acid (dsbpy) was first prepared by Seddon et al. [32] in a five step procedure starting from 2,2'-bipyridine. We managed to optimize this reaction by reducing the number of steps, avoiding also the use of $[\text{NH}_4]\text{VO}_3$. 2,2'-Bipyridine was oxidized with H_2O_2 in glacial ethanoic acid, followed by nitration in oleum-sulphuric/nitric acid to yield 4,4'-dinitro-2,2'-bipyridine-*N,N'*-dioxide, according to the procedures of Haginiwa [33] and Maerker and Case [34], respectively. The conversion into the dichloro compound and the reduction to 4,4'-dichloro-2,2'-bipyridine was per-

formed in one step — analogous to the monochloro derivative [35] — using acetyl chloride and phosphorus trichloride. Finally, 2,2'-bipyridine-4,4'-disulphonic acid (dsbpy) was obtained by refluxing 4,4'-dichloro-2,2'-bipyridine with a ten-fold excess of Na_2SO_3 in ethanol/water (1:1) for 60 h. The solution was concentrated and passed through a Dowex 50W-X8 cation-exchange column. The eluate was evaporated to dryness to give dsbpy in 95% yield. (mp > 300°C ; IR (KBr): $\nu = 3392, 1672, 1579, 1353, 1216, 1039, 848, 617 \text{ cm}^{-1}$; $^1\text{H NMR}$ (d_6 -DMSO): $\delta = 8.73$ (d, $^3J_{6,5} = 5.0 \text{ Hz}$, 2H, 6,6'-H), 8.58 (s, 2H, 3,3'-H), 7.67 (d, $^3J_{5,6} = 5.0 \text{ Hz}$, 2H, 5,5'-H) ppm.)

2.1.4. 1,10-Phenanthroline-4,7-dicarboxylic acid (dcphen)

1,10-Phenanthroline-4,7-dicarboxylic acid (dcphen) was prepared in a two step synthesis mainly according to an earlier approach [36]. 4,7-Dimethyl-1,10-phenanthroline was oxidized to give dicarboxyaldehyde using freshly prepared selenium dioxide in dioxan/water (95:5, v/v). The reaction mixture was refluxed for 4 h and filtered hot through a Celite layer. The filtrate was evaporated to 1/3, cooled to room temperature and the resulting precipitate filtered off. The dicarboxyaldehyde was directly refluxed with concentrated nitric acid (25 ml g^{-1}) for 3 h, poured onto ice and left overnight. The crystals were washed with methanol and recrystallized from water. The overall yield of dcphen was 35%. (mp > 300°C ; IR (KBr): $\nu = 3111, 2923, 1727, 1593, 1698, 1274, 1119, 839, \text{ cm}^{-1}$; $^1\text{H NMR}$ (d_6 -DMSO): $\delta = 9.39$ (d, $^3J_{2,3} = ^3J_{8,9} = 6.1 \text{ Hz}$, 2H, 2,9-H), 8.91 (s, 2H, 5,6-H), 8.45 (d, $^3J_{2,3} = ^3J_{8,9} = 6.1 \text{ Hz}$, 2H, 3,8-H) ppm.)

2.1.5. 3,3'-Bipyridazine-5,5'-dicarboxylic acid (dcbpdz)

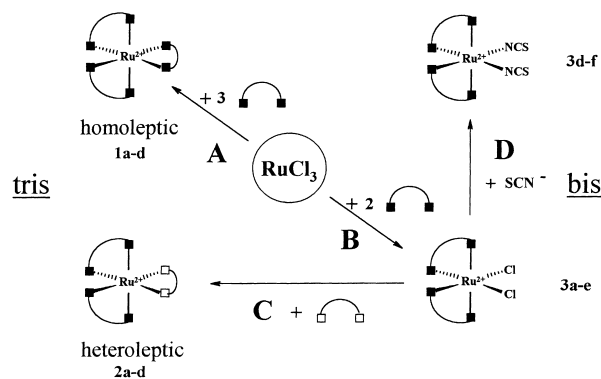
3,3'-Bipyridazine-5,5'-dicarboxylic acid (dcbpdz) was prepared in a four step synthesis starting from 5-morpholino-4-methyl-2-(5H)-furanone which was obtained from glyoxylic acid hydrate, morpholine and propanal (1:2:1, ethanol) according to literature procedure [37]. Treatment of the furanone (35.9 g, 0.2 mol) in 200 ml of ethanol with hydrazine hydrate (10.0 g, 0.2 mol) and refluxing for 6 h afforded 5-methyl-pyridazine-3-ol which was recrystallized from water to give white needles. (13.3 g; yield 61%; mp 151°C; IR (KBr): $\nu=3422, 2873, 1653, 1546, 1184, 933 \text{ cm}^{-1}$; $^1\text{H NMR}$ (d_6 -DMSO): $\delta=10.81$ (s, 1H, -OH), 7.65 (s, 1H, 6-H), 6.72 (s, 1H, 4-H), 2.24 (s, 3H, -CH₃) ppm.). For the conversion into 3-chloro-5-methyl-pyridazine, 5-methyl-pyridazine-3-ol (10.0 g, 0.09 mol) was dissolved in POCl₃ and heated to 90°C for 1 h. The excess POCl₃ was distilled off and the oily residue carefully poured onto crushed ice. Extraction with CH₂Cl₂ (3 ml × 50 ml), evaporating the combined solvent and sublimation of the brown residue (100°C, 1 torr) yielded 3-chloro-5-methyl-pyridazine as white-yellow crystals (4.3 g, 36.8%). (mp 138°C; IR (KBr): $\nu=3057, 1583, 1473, 1252, 899, 710 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl₃): $\delta=8.97$ (s, 1H, 6-H), 7.38 (s, 1H, 4-H), 2.41 (s, 3H, -CH₃) ppm.). 5,5a'-Dimethyl-3,3'-bipyridazine was prepared in 32% yield by coupling of 3-chloro-5-methyl-pyridazine with Ni(0)-(triphenyl-phosphine)₄, which was prepared 'in situ', applying literature procedure [38]. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂/MeOH (95:5–90:10)). (mp 164°C; IR (KBr): $\nu=3056, 2873, 1661, 1594, 1437, 1053, 884 \text{ cm}^{-1}$; $^1\text{H NMR}$ (d_6 -DMSO): $\delta=9.26$ (s, 2H, 6,6'-H), 8.57 (s, 1H, 4,4'-H), 2.50 (s, 3H, -CH₃) ppm.). 3,3'-Bipyridazine-5,5'-dicarboxylic acid (dcbpdz) was obtained by oxidation of the dimethyl derivative with CrO₃ (vide supra) (yield 73%; mp >300°C; IR (KBr): $\nu=3491, 3074, 1701, 1594, 1655, 1295, 1195, 999, 695 \text{ cm}^{-1}$; $^1\text{H NMR}$ (d_6 -DMSO): $\delta=9.73$ (s, 2H, 6,6'-H), 9.01 (s, 1H, 4,4'-H) ppm.).

2.1.6. Sensitizers

Three different types of Ru(II) complexes were synthesized by standard procedures according to Scheme 2. [30,39–41] The complexes were isolated and purified by column chromatography on Sephadex G15.

2.1.7. Tris-homoleptic complexes

Tris-homoleptic complexes **1a–d** (Route A): (Ru(II) (dcbpy)₃Cl₂ **1a**: yield 81%; Elemental Analysis for C₃₆H₂₄N₆O₁₂Cl₂Ru (calculated values in parentheses): C 47.02 (47.80), H 2.80 (2.67), N 9.25 (9.29); $^1\text{H NMR}$ (D₂O): $\delta=8.96$ (s, 6H, 3,3'-H), 7.96 (d, $^3J_{6,5}=5.5 \text{ Hz}$, 6H, 6,6'), 7.77 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 6H, 5,5'-H) ppm. Ru(II)(dsbpy)₃Cl₂ **1b**: yield 75%; Elemental Analysis for C₃₀H₂₄N₆O₁₈S₆Cl₂Ru: C 31.98 (32.15), H 2.30 (2.16), N 7.40 (7.50); $^1\text{H NMR}$ (D₂O): $\delta=9.04$ (s, 6H, 3,3'-H), 8.05 (d, $^3J_{6,5}=5.5 \text{ Hz}$,



Scheme 2. Schematic representation of four different synthetic approaches A–D to Ru(II)-complexes **1a–3f**.

6H, 6,6'-H), 7.85 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 6H, 5,5'-H) ppm. Ru(II)(dcphen)₃Cl₂ **1c**: yield 75%; Elemental Analysis for C₄₂H₂₄N₆O₁₂Cl₂Ru: C 51.44 (51.65), H 2.60 (2.48), N 8.64 (8.60); $^1\text{H NMR}$ (D₂O): $\delta=8.53$ (s, 6H, 5,6-H), 8.16 (d, $^3J_{2,3}=5.5 \text{ Hz}$, 6H, 2,9-H), 7.66 (d, $^3J_{3,2}=5.5 \text{ Hz}$, 6H, 3,8-H) ppm. Ru(II)(dcbpdz)₃Cl₂ **1d**: yield 75%; Elemental Analysis for C₃₀H₁₈N₁₂O₁₂Cl₂Ru: C 39.38 (39.57), H 2.01 (1.99), N 18.47 (18.46); $^1\text{H NMR}$ (D₂O): $\delta=8.51$ (s, 6H, 4,4'-H), 8.00 (s, 6H, 6,6'-H) ppm.).

2.1.8. Tris-heteroleptic complexes

Tris-heteroleptic complexes **2a–d** (Route C): (Ru(II) (dmbpy)₂(dcbpy)Cl₂ **2a**: yield 68%; Elemental Analysis for C₃₆H₃₂N₆O₄Cl₂Ru (calculated values in parentheses): C 54.97 (55.11), H 4.29 (4.11), N 10.59 (10.71); $^1\text{H NMR}$ (D₂O): (dsbpy) $\delta=8.89$ (s, 2H, 3,3'-H), 7.91 (d, $^3J_{6,5}=5.5 \text{ Hz}$, 2H, 6,6'-H), 7.70 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 2H, 5,5'-H) ppm (dmbpy) $\delta=8.39$ (s, 2H, 3-H), 8.38 (s, 2H, 3'-H), 7.60 (d, $^3J_{6,5}=5.5 \text{ Hz}$, 2H, 6-H), 7.46 (d, $^3J_{6',5'}=5.5 \text{ Hz}$, 2H, 6'-H), 7.26 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 2H, 5-H), 7.20 (d, $^3J_{5',6'}=5.5 \text{ Hz}$, 2H, 5'-H), 2.56 (s, 6H, -CH₃), 2.54 (s, 6H, -CH₃) ppm. Ru(II)(dmbpy)₂(dsbpy)Cl₂ **2b**: yield 66%; Elemental Analysis for C₃₄H₃₂N₆O₆S₂Cl₂Ru: C 47.40 (47.66), H 3.88 (3.76), N 9.81 (9.66); $^1\text{H NMR}$ (D₂O): (dcbpy) $\delta=8.96$ (s, 2H, 3,3'-H), 8.04 (d, $^3J_{6,5}=5.5 \text{ Hz}$, 2H, 6,6'-H), 7.75 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 2H, 5,5'-H) ppm (dmbpy) $\delta=8.41$ (s, 2H, 3-H), 8.37 (s, 2H, 3'-H), 7.61 (d, $^3J_{6,5}=5.5 \text{ Hz}$, 2H, 6-H), 7.58 (d, $^3J_{6',5'}=5.5 \text{ Hz}$, 2H, 6'-H), 7.29 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 2H, 5-H), 7.25 (d, $^3J_{5',6'}=5.5 \text{ Hz}$, 2H, 5'-H), 2.55 (s, 12H, -CH₃) ppm. Ru(II)(dmbpy)₂(dcphen)Cl₂ **2c**: yield 64%; Elemental Analysis for C₃₆H₃₂N₆O₄Cl₂Ru: C 56.36 (56.44), H 4.17 (3.99), N 10.19 (10.39); $^1\text{H NMR}$ (D₂O): (dcphen) $\delta=8.45$ (s, 2H, 5,6-H), 8.24 (d, $^3J_{2,3}=5.5 \text{ Hz}$, 2H, 2,9-H), 7.76 (d, $^3J_{3,2}=5.5 \text{ Hz}$, 2H, 3,8-H) ppm (dmbpy) $\delta=8.44$ (s, 2H, 3-H), 8.31 (s, 2H, 3'-H), 7.74 (d, $^3J_{6,5}=5.5 \text{ Hz}$, 2H, 6-H), 7.43 (d, $^3J_{6',5'}=5.5 \text{ Hz}$, 2H, 6'-H), 7.29 (d, $^3J_{5,6}=5.5 \text{ Hz}$, 2H, 5-H), 7.08 (d, $^3J_{5',6'}=5.5 \text{ Hz}$, 2H, 5'-H), 2.59 (s, 6H, -CH₃), 2.52 (s, 6H, -CH₃) ppm. Ru(II)(dmbpy)₂(dcbpdz)Cl₂ **2d**: yield 63%; Elemental Analysis for C₃₄H₃₀N₈O₄Cl₂Ru: C 54.97

(51.69), H 3.94 (3.84), N 14.17 (14.24); ^1H NMR (D_2O): (dcbpdz) $\delta=8.89$ (s, 2H, 3,3'-H), 7.91 (d, $^3J_{6,5}=5.5$ Hz, 2H, 6,6'-H), 7.70 (d, $^3J_{5,6}=5.5$ Hz, 2H, 5,5'-H) ppm (dmbpy) $\delta=8.39$ (s, 2H, 3-H), 8.38 (s, 2H, 3'-H), 7.60 (d, $^3J_{6,5}=5.5$ Hz, 2H, 6-H), 7.46 (d, $^3J_{6',5'}=5.5$ Hz, 2H, 6'-H), 7.26 (d, $^3J_{5,6}=5.5$ Hz, 2H, 5-H), 7.20 (d, $^3J_{5',6'}=5.5$ Hz, 2H, 5'-H), 2.56 (s, 6H, $-\text{CH}_3$), 2.54 (s, 6H, $-\text{CH}_3$) ppm.).

2.1.9. *cis*-Dichloro-bis-complexes

cis-Dichloro-bis-complexes **3a–c** (Route B): (Ru(II) (dcbpy) $_2$ Cl $_2$ **3a**: yield 70%; Elemental Analysis for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_8\text{Cl}_2\text{Ru}$ (calculated values in parenthesis): C 43.35 (43.65), H 2.61 (2.44), N 8.19 (8.48); ^1H NMR (d_6 -DMSO): $\delta=8.91$ (s, 2H, 3-H), 8.71 (s, 2H, 3'-H), 9.45 (d, $^3J_{6,5}=5.7$ Hz, 2H, 6-H), 7.72 (d, $^3J_{6',5'}=5.7$ Hz, 2H, 6'-H), 8.15 (d, $^3J_{5,6}=5.7$ Hz, 2H, 5-H), 7.36 (d, $^3J_{5',6'}=5.7$ Hz, 2H, 5'-H) ppm. Ru(II)(dsbpy) $_2$ Cl $_2$ **3b**: yield 81%; Elemental Analysis for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_{12}\text{S}_4\text{Cl}_2\text{Ru}$: C 29.74 (29.86), H 2.18 (2.00), N 7.05 (6.96); ^1H NMR (d_6 -DMSO): $\delta=9.03$ (s, 2H, 3-H), 8.91 (s, 2H, 3'-H), 9.68 (d, $^3J_{6,5}=5.7$ Hz, 2H, 6-H), 7.74 (d, $^3J_{6',5'}=5.7$ Hz, 2H, 6'-H), 8.28 (d, $^3J_{5,6}=5.7$ Hz, 2H, 5-H), 7.90 (d, $^3J_{5',6'}=5.7$ Hz, 2H, 5'-H) ppm. Ru(II)(dcphen) $_2$ Cl $_2$ **3c**: yield 80%; Elemental Analysis for $\text{C}_{28}\text{H}_{16}\text{N}_4\text{O}_8\text{Cl}_2\text{Ru}$: C 47.35 (47.47), H 2.41 (2.28), N 8.09 (7.91); ^1H NMR (d_6 -DMSO): $\delta=10.43$ (d, $^3J_{2,3}=5.5$ Hz, 2H, 2-H), 8.61 (d, $^3J_{3,2}=5.5$ Hz, 2H, 3-H), 9.13 (d, $^3J_{5,6}=10.0$ Hz, 2H, 5-H), 9.01 (d, $^3J_{6,5}=10.0$ Hz, 2H, 6-H), 8.14 (d, $^3J_{8,9}=5.5$ Hz, 2H, 8-H), 7.68 (d, $^3J_{9,8}=5.5$ Hz, 2H, 9-H) ppm.).

2.1.10. *cis*-Dithiocanato-bis-complexes

cis-Dithiocanato-bis-complexes **3d–f** (Route D): (Ru(II) (dcbpy) $_2$ (NCS) $_2$ **3d**: yield 59%; Elemental Analysis for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_8\text{Cl}_2\text{Ru}$ (calculated values in parenthesis): C 44.01 (44.26), H 2.46 (2.29), N 11.72 (11.91); ^1H NMR (d_6 -DMSO): $\delta=9.18$ (s, 2H, 3-H), 9.02 (s, 2H, 3'-H), 9.45 (d, $^3J_{6,5}=5.7$ Hz, 2H, 6-H), 7.80 (d, $^3J_{6',5'}=5.7$ Hz, 2H, 6'-H), 8.38 (d, $^3J_{5,6}=5.7$ Hz, 2H, 5-H), 7.60 (d, $^3J_{5',6'}=5.7$ Hz, 2H, 5'-H) ppm. Ru(II)(dsbpy) $_2$ (NCS) $_2$ **3e**: yield 67%; Elemental Analysis for $\text{C}_{22}\text{H}_{16}\text{N}_6\text{O}_{12}\text{S}_6\text{Ru}$: C 30.87 (31.09), H 2.02 (1.90), N 9.87 (9.89); ^1H NMR (d_6 -DMSO): $\delta=9.01$ (s, 2H, 3-H), 8.85 (s, 2H, 3'-H), 9.67 (d, $^3J_{6,5}=5.5$ Hz, 2H, 6-H), 7.95 (d, $^3J_{6',5'}=5.5$ Hz, 2H, 6'-H), 8.29 (d, $^3J_{5,6}=5.5$ Hz, 2H, 5-H), 7.61 (d, $^3J_{5',6'}=5.5$ Hz, 2H, 5'-H) ppm. Ru(II)(dcphen) $_2$ (NCS) $_2$ **3f**: yield 60%; Elemental Analysis for $\text{C}_{30}\text{H}_{16}\text{N}_6\text{O}_8\text{S}_2\text{Ru}$: C 47.55 (47.81), H 2.31 (2.14), N 11.00 (11.15); ^1H NMR (d_6 -DMSO): $\delta=9.87$ (d, $^3J_{2,3}=5.5$ Hz, 2H, 2-H), 8.79 (d, $^3J_{3,2}=5.5$ Hz, 2H, 3-H), 9.20 (d, $^3J_{5,6}=9.5$ Hz, 2H, 5-H), 9.07 (d, $^3J_{6,5}=9.5$ Hz, 2H, 6-H), 8.11 (d, $^3J_{8,9}=5.5$ Hz, 2H, 8-H), 7.82 (d, $^3J_{9,8}=5.5$ Hz, 2H, 9-H) ppm.).

In the case of dcbpdz the reaction did not stop at the stage of a bis-complex, resulting directly in the tris-complex.

2.2. Methods

^1H NMR spectra were recorded with a Bruker aspect 500 MHz spectrometer. Chemical shifts are given in ppm, relative to TMS. Infrared spectra were obtained with an Excalibur FTIR spectrometer. Absorption spectra were recorded on a HP 8542 diode array spectrophotometer. Emission spectra were taken using a Hitachi FI-3000 spectrometer in degassed solutions. Luminescence quantum yields ϕ_L were determined using $\text{Ru}(\text{bpy})_3^{2+}$ as a standard ($\phi_L=0.042$ (H_2O) and 0.052 (EtOH) [3]). The luminescence lifetimes were measured employing laser flash photolysis using ≈ 8 ns pulses (530 nm) from a Nd:YAG laser (for a detailed setup see [42]). Cyclic voltammetry was performed with a VA Scanner E 612 and Polarecord 626 (Metrohm). The working electrode was glassy carbon, the counter electrode platinum and the reference electrode Ag/AgCl (3 M KCl, double junction). All measurements were recorded in dry DMF solutions containing 0.1 mol l^{-1} $(\text{Bu})_4\text{NBF}_4$ as supporting electrolyte. Typically a scan rate of 100 mV/s was employed. $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ was used as a standard [3] and all potentials are given in DMF versus SCE. The AFM graph was recorded with a Nanoscope III (Digital Inst.). The light source for the determination of the performance characteristics of the photoelectrochemical cells was a 300-W Xenon AM 1.0 direct solar simulator (Oriol).

2.3. Studies of the photoelectrochemical solar cells

The photoanode of Graetzel's solar cell consists of a nanocrystalline TiO_2 membrane layer deposited on a transparent conducting glass covered by a ruthenium-bipyridine monolayer as sensitizer. An electrolyte solution containing the redox couple iodide/tri-iodide links the platinum covered conductive glass plate covered with the anode, thus constituting a photoelectrochemical cell. After light induced excitation of the sensitizer and transfer of an electron into the TiO_2 conduction band the oxidized dye is restored by the redox mediator, which is reduced at the platinum counter electrode closing the cycle of the processes involved (Fig. 1).

2.3.1. Cell materials

A viscous nanocrystalline TiO_2 paste was prepared by dropping 25 ml of titanium(IV)-isopropoxide in 6 ml

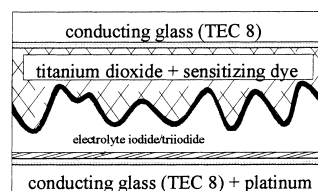


Fig. 1. Scheme of a dye-sensitized — TiO_2 based — photoelectrochemical solar cell ('Graetzel cell').

2-propanol to a stirred and cooled (0°C) solution of 50 ml glacial acetic acid and 160 ml of deionized water over a period of 30–45 min. The resulting mixture was heated at 80°C for 8 h and for 12 h at 230°C in an autoclave. Upon removal from the Teflon coated autoclave, the solution was sonicated for 15 min and concentrated to 200 g l⁻¹. To prevent aggregation of the particles and to produce almost crack free films, 5 g Carbowax 20000 were added. X-ray diffraction analysis established the particles to consist of pure anatase crystal structure with an average diameter of 20 nm.

The nanocrystalline TiO₂ films were prepared in a three step procedure. First a drop of 0.01 M titanium(IV)-isopropoxide in 2-propanol was spread uniformly on a FTO (fluorine-tin-oxide) coated glass plate (40 mm×10 mm×3 mm, TEC 8, Libby-Owens-Ford) and air dried. To control the thickness of the second TiO₂ layer, two edges of the glass substrate were covered with scotch tape and the viscous TiO₂ paste spread on top of the first film followed by heating in air for 30 min at 450°C. To increase the active surface area of the electrode a third TiO₂ layer was deposited by soaking the electrode overnight in a solution of 0.01 M titanium(IV)-isopropoxide in 2-propanol in a closed reaction chamber. The membranes were washed with water and calcinated again for 30 min at 450°C in air. While still hot (80°C) the films were dipped for at least 12 h in 5×10⁻⁴ M dye solutions in dry ethanol or methanol.

The counter electrode for the sandwich cells was an electrochemically platinized FTO glass substrate of the

same type as described above. The electrolyte between the two glass sheets was 0.5 M LiI, 0.5 mM I₂ and 100 mM 4-*tert*-butylpyridine in 3-methyl-2-oxazolidinone (NMO). All other chemicals were commercial samples of the highest possible purity and used without further treatment.

3. Results

Light absorption, emission and electrochemical properties of Ru-(II)-polypyridyl sensitizers **1a–3f** are listed in Table 1.

3.1. The UV spectra

The UV spectra for all coordination compounds **1a–3f** are typical for the different complex classes. The spectra of the tris-compounds **1a–2d** showed an intense MLCT band in the range of 458–488 nm. The MLCT absorption of the bis-complexes **3a–3f** was considerably red shifted, which is advantageous for solar light harvesting. Due to the different ligand strength, the lowest energy transition of the dichloro compounds **3a–3c** is located at 540–551 nm and for the dithiocyanato complexes **3d–3f** at 519–534 nm.

3.2. Luminescence spectra

Luminescence spectra of the Ru-polypyridine sensitizers **1a–3f** give rise to considerable Stokes shifts of 152–200 nm.

Table 1
Absorption, luminescence and electrochemical properties of the complexes **1a–3e**

Ru-(II)-complex	$\lambda_{\text{max abs}}$ [nm] (log ϵ)	$\lambda_{\text{max em}}$ [nm]		τ_L [μs]	ϕ_L	$E_{\text{Ru}^{2+*/3+}}$ [V] ^a
		298 K	77 K			
tris-homoleptic ^b						
Ru(dcbpy) ₃ Cl ₂ 1a	458 (4,21), 352 (4,18), 303 (4,93)	622	643, 594	0.71	0.032	~1.6 ^c
Ru(ds bpy) ₃ Cl ₂ 1b	458 (4,23), 330 (4,20), 297 (4,94)	623	646, 595	0.55	0.035	~1.2 ^c
Ru(dcphe n) ₃ Cl ₂ 1c	459 (4,25), 272 (5,03)	610	636, 592	1.77	0.017	~1.6 ^c
Ru(dcbpdz) ₃ Cl ₂ 1d	460 (4,04), 428 (4,05), 354 (3,98)	646	624	0.49	0.014	~1.8 ^c
tris-heteroleptic ^d (L=4,4'-Dimethyl-2,2'-bipyridine)						
RuL ₂ (dcbpy)Cl ₂ 2a	462 (4,18), 338 (4,03), 289 (4,80)	614	611	1.36	0.075	1.37
RuL ₂ (ds bpy)Cl ₂ 2b	463 (4,20), 287 (4,92)	646	623	0.74	0.026	1.28
RuL ₂ (dcphe n)Cl ₂ 2c	463 (4,19), 327 (4,02), 288 (4,83)	610	647, 604	1.85	0.070	1.38
RuL ₂ (dcbpdz)Cl ₂ 2d	488 (3,98), 412 (4,02), 283 (4,58)	712	698	0.24	0.002	1.47
bis ^d						
Ru(dcbpy) ₂ Cl ₂ 3a	540 (3,95), 380 (3,98), 304 (4,60)	~730 ^e	735	–	–	0.66
Ru(ds bpy) ₂ Cl ₂ 3b	551 (3,84), 379 (4,05), 296 (4,58)	~720	723	–	–	0.41
Ru(dcphe n) ₂ Cl ₂ 3c	550 (3,94), 287 (4,51)	~750	753	–	–	0.63
Ru(dcbpy) ₂ (NCS) ₂ 3d	534 (4,14), 398 (4,13), 314 (4,57)	~710	716	–	–	0.99
Ru(ds bpy) ₂ (NCS) ₂ 3e	523 (4,00), 367 (4,01), 303 (4,55)	~700	704	–	–	0.80
Ru(dcphe n) ₂ (NCS) ₂ 3f	519 (4,04), 279 (4,67)	~720	723	–	–	0.98

^a DMF versus SCE.

^b H₂O.

^c Calculated using the approach of A.B.P. Lever [43].

^d EtOH.

^e Very broad and weak.

The emission bands of the dsbpy and dcbbpdz tris-complexes **1b**, **2b** and **1d**, **2d** were strongly red shifted and thus of low emission energy, resulting in small quantum yields and relatively short luminescence lifetimes. The bis-complexes **3a–3f** showed at room temperature only weak and broad emission signals at 700–750 nm, which did not allow for quantum yield or lifetime measurements.

3.3. Luminescence lifetime studies

Luminescence lifetime studies were carried out with a ns LASER equipment [42]. Besides the dcbbpdz based sensitizers **1d** and **2d**, all tris-complexes show similar or larger lifetimes compared to $\text{Ru}(\text{bpy})_3^{2+}$ ($\tau_L=0.65 \mu\text{s}$ [3]). Especially, the dcphen tris-complexes **1c** and **2c** exhibited lifetimes 2–3 times larger than $\text{Ru}(\text{bpy})_3^{2+}$ which renders them promising candidates for biomolecular photochemical reactions.

3.4. Electrochemical studies

Electrochemical studies show the ability of **1a–3f** for electron injection from the excited state into the TiO_2 conduction band (see Table 1). The driving force for electron injection $\Delta G^\circ \approx E(\text{Ru}^{2+*}/\text{Ru}^{3+}) - E(\text{conduction band } \text{TiO}_2)$ increased in the following order: **1a–d** < **2a–d** < **3a–f**.

3.5. The TiO_2 films

The TiO_2 films were characterized by AFM microscopy. Fig. 2 shows an AFM micrograph of a TiO_2 layer, prepared according to the procedure described above. The film consisted of spherical TiO_2 nanocrystallites with approximately 25–50 nm diameter. The effective surface of the membrane

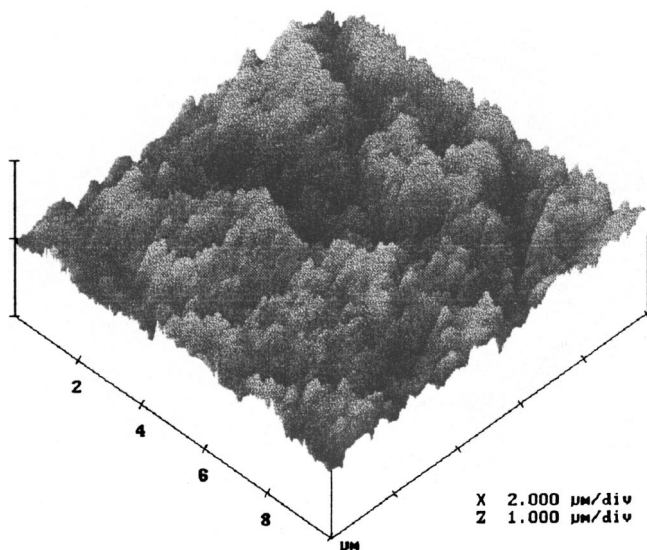


Fig. 2. AFM graph of a nanocrystalline TiO_2 layer prepared according to the described three step procedure.

prepared employing the described three-step procedure was determined to be 650 times greater than that of a smooth membrane.

We have first repeated Graetzel's work on his solar cell in our laboratories to have an internal standard for the mean efficiency η . No special optimizations were made to reach the η value published by Graetzel. Thus we were able to build a solar cell employing $\text{Ru}(\text{dcbbpy})_2\text{NCS}_2$ **3d** with an efficiency of $\eta_{\text{AM}1.0} \approx 6.1\%$. This lower efficiency compared to reported values of $\eta_{\text{AM}1.5} \approx 10.4\%$ [30] is most probably due to (a) the spectral mismatch between the sensitizer and the AM 1.0 solar simulator with a high output of near UV radiation, and (b) the poor transmission of the conducting glass (65–70% in the visible range), (c) the 'large' dimensions of the prepared cells resulting in higher ohmic losses and (d) the mass transfer limitations of the photocurrent imposed by the high viscosity of the solvent NMO compared to acetonitrile or NMO/acetonitrile mixtures. For the same reasons the fill factor were low (around 0.40). Conditions (c and d) were chosen with respect to practical use.

The complexes **1a–3f** were tested as sensitizers for nanocrystalline TiO_2 . Current-voltage characteristics and over-all energy conversion efficiencies of the solar cell assemblies obtained under illumination with simulated AM 1.0 direct solar light are given in Table 2. The reported values are not corrected for light losses due to reflection or absorption by the supporting electrode. All data presented are the average of three cells measured. The relative η values for the different cell assemblies compared to **3d** (100%) are presented in Fig. 3.

The three classes of sensitizers showed significant differences. The cell assemblies with tris-homoleptic (**1a–d**) and tris-heteroleptic (**2a–d**) complexes exhibited open circuit currents (I_{oc}) and voltages (U_{oc}) of 1.0–1.4 mA cm^{-2} and 510–550 mV, respectively, and over-all efficiencies η around 1%. In the case of tris-heteroleptic complexes **2** the values obtained were in general slightly higher compared to the tris-homoleptic compounds **1**. The dcbbpdz complexes **1d** and **2d** gave the poorest results, most probably due to their relatively positive oxidation potentials (small ΔG° -value) and their preference for non-radiative reaction pathways (small ϕ_L -value). The best data were obtained for the bis-complexes **3a–f**. Compared to the standard **3d** the new dcphen sensitizer **3f** was only slightly inferior, reaching considerable energy conversion of $\eta=3.8\%$ (62.3% relative to **3d**). The dsbpy complexes **3b** and **3e** gave only small energy conversion efficiencies, indicating weak adsorption properties of the sulphonic group on TiO_2 . Additionally, it is remarkable that the dichloro complex **3b** yielded higher values than dithiocyanato **3e**, in contrast to the dcbbpy and dcphen bis-complexes **3a,c** and **3d,f**.

Important reasons for the differences in sensitizing power for **1a–3f** are obviously the varying MLCT absorption maxima and oxidation potentials, being less favorable for tris-complexes **1a–2d**. Nevertheless, this does not explain the outstanding properties of **3d** or the differences between

Table 2

Performance characteristics of photoelectrochemical TiO₂ solar cells treated with sensitizers **1a–3f**. (radiant power: 27 mW/cm² (AM 1.0 direct); RedOx electrolyte NMO, LiI (0.5 M), I₂ (0.5 mM) and 4-*tert*-butylpyridine (100 mM))

Cell+cpx	U_{oc} [mV]	I_{oc} [mA cm ⁻²]	FF	$\eta_{AM\ 1.0}$ [%]	$\eta_{rel.}$ [%] ($\eta_{rel.}(\mathbf{3d})=100\%$)
tris-homoleptic					
1a	520	1.0	0.37	0.7	11.5
1b	520	1.4	0.34	0.9	14.8
1c	510	1.1	0.37	0.8	13.1
1d	120	0.2	0.30	0.03	0.5
tris-heteroleptic					
2a	540	1.2	0.39	1.0	16.4
2b	530	1.3	0.37	0.9	14.8
2c	550	1.3	0.45	1.2	19.7
2d	460	0.4	0.30	0.2	3.3
bis					
3a	570	2.6	0.38	2.1	34.4
3b	510	1.3	0.42	1.1	18.0
3c	550	2.0	0.42	1.7	27.9
3d	610	6.4	0.42	6.1	100
3e	520	0.5	0.36	0.4	6.6
3f	600	3.9	0.43	3.8	62.3

the three classes of sensitizers (e.g. the bis-dichloro complexes **3a–c** show smaller energy conversion efficiencies η than the bis-dithiocyanato compounds **3d–f**, although they exhibit less positive oxidation potentials and more bathochromically shifted MLCT absorption bands). According to our studies in case of Ru(II)-polypyridine complexes outstanding properties of a sensitizer for the application in photoelectrochemical solar cells seem to depend strongly on the absorption properties of the particularly doped TiO₂-photoanode. In Fig. 4 the absorption spectra of sensitized TiO₂-layers are depicted, doped from 5×10^{-4} M alcoholic solutions of the Ru(II)-dyes employing identical conditions in each case.

As expected the films incorporating Ru(II)-tris-complexes **1c** and **2b** showed only efficient light absorption up to 500 nm due to the MLCT maxima of the complexes, but only **3d** out of all other Ru(II)-bis-complexes **3a–c, e, f** covered the largest part of the visible spectrum, combined with

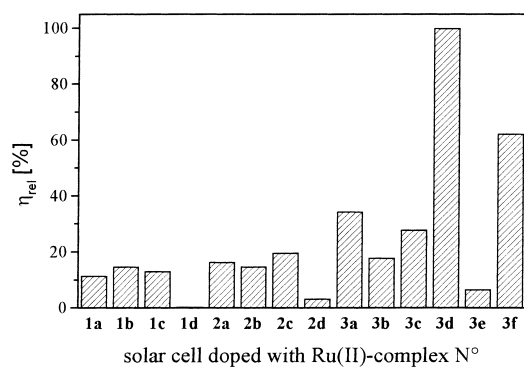


Fig. 3. Relative over-all energy conversion efficiencies η_{rel} of photoelectrochemical solar cells, sensitized with **1a–3f**, compared to **3d** ($\eta_{rel.}(\mathbf{3d})=100\%$).

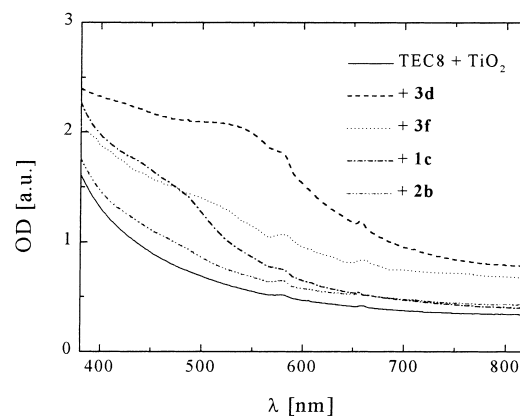


Fig. 4. Absorption spectra of sensitized and undoped TiO₂ films.

intense absorption, despite the nearly similar absorption properties of **3a–f** in solution. This efficient light harvesting behavior is obviously one of the main reasons for the particular properties of **3d** as sensitizer for the photoelectrochemical solar cell.

4. Conclusions

In this paper, we describe the synthesis and characterization of mostly new Ru(II) polypyridyl complexes. The compounds were especially designed towards their suitability for sensitizing TiO₂. For this purpose nanocrystalline TiO₂ films were prepared and characterized by AFM technique. We reproduced Graetzel's procedure for building photoelectrochemical solar cells employing Ru(dcbpy)₂NCS₂ **3d** as an internal standard. All sensitizers **1a–3f** were successfully tested in the solar cell assembly whereby

Ru(dcphe)₂(NCS)₂ **3f** showed a remarkable energy conversion of $\eta=62.3\%$, compared to the internal standard, which renders **3f** one of the most promising candidates for further studies in the photoelectrochemical cell. The still outstanding properties of sensitizer **3d** are most likely due to the very efficient light harvesting since **3d** covers a wide part of the visible spectrum.

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