ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 145 (2001) 117–122

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

New Ru(II) phenanthroline complex photosensitizers having different number of carboxyl groups for dye-sensitized solar cells

Kohjiro Hara, Hideki Sugihara, Lok Prapap Singh, Ashlaful Islam, Ryuzi Katoh,
Masatoshi Yanagida, Kazuhiro Sayama, Shigeo Murata, Hironori Arakawa*

National Institute of Advanced Industrial Science and Technology (AIST), Photoreaction Control Research Center (PCRC),
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received 27 April 2001; received in revised form 22 June 2001; accepted 24 July 2001

Abstract

We have prepared and characterized four carboxylated Ru(II) phenanthroline complexes with different number of carboxyl groups, *cis*-dithiocyanato bis(4,7-dicarboxy-1,10-phenanthroline) ruthenium(II) [Ru(dcphen)$_2$(NCS)$_2$, DCP2], *cis*-dithiocyanato bis(4-monocarboxy-1,10-phenanthroline) ruthenium(II) [Ru(mcphen)$_2$(NCS)$_2$, MCP2], *cis*-dithiocyanato (4,7-dicarboxy-1,10-phenanthroline) (1,10-phenanthroline) ruthenium(II) [Ru(dcphen)(phen)(NCS)$_2$, DCPP], and *cis*-dithiocyanato (4-monocarboxy-1,10-phenanthroline)(1,10-phenanthroline) ruthenium(II) [Ru(mcphen)(phen)(NCS)$_2$, MCPP], as photosensitizers for nanocrystalline dye-sensitized solar cells. All complexes exhibit a broad MLCT absorption band around 500 nm in ethanol and an emission band around 700 nm in ethanol–methanol (4:1) at 77 K. The excited state lifetime of these complexes at 77 K was 1.5–2.9 μs and the oxidation potential, 0.90–1.12 V vs. NHE, was obtained by cyclic voltammetry in solution. The best solar-energy-to-electric conversion efficiency under AM 1.5 irradiation was obtained for DCPP which has two carboxyl groups on one phenanthroline ligand. The performance of photosensitizer of MCPP which has only one carboxyl group is lower than that for the other complexes, indicating that the number of carboxyl groups as anchor is very important for efficient solar cell performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ru(II) phenanthroline complex; Photosensitizers; Solar cells

1. Introduction

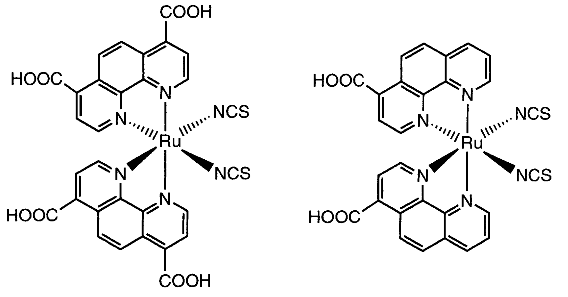
The quest for new materials that efficiently harvest solar light continues to be an important goal [1–4]. Grätzel and co-workers [5,6] have reported a 10% solar-to-electric energy conversion efficiency using *cis*-dithiocyanato bis (4,4′-dicarboxy-2,2′-bipyridine) ruthenium(II) [Ru(dcbpy)$_2$ (NCS)$_2$] anchored on porous nanocrystalline TiO$_2$ electrode. The efficiency of sensitization is critically dependent on electron injection from a photoexcited state of the dye into the conduction band of the semiconductor. However, parameters which control these kinetics are poorly characterized. Electron injection takes place via carboxylic group that binds the dye molecules to the semiconductor surface. Shklover et al. [7,8] on the basis of the crystal structure data of the sensitizer, Ru(dcbpy)$_2$(NCS)$_2$, and the TiO$_2$ surface proposed a thermodynamically favorable model. According to them, the anchoring geometry of Ru(dcbpy)$_2$(NCS)$_2$ complex attached to the TiO$_2$ surface with two carboxyl groups is thermodynamically favorable. However, the necessity of the number of carboxylic groups attached on TiO$_2$ for effective electron injection is not yet clear. Aranyos et al. [9] have prepared new Ru bipyridine complexes having new malonate anchoring groups and measured their photoelectrochemical properties of dye–TiO$_2$ solar cells. They discussed the effect of the number of anchoring groups on the photoelectrochemical properties of the solar cells.

Recently we have synthesized 4,7-dicarboxy-1,10-phenanthroline ligand and explored its Ru(II) complex, *cis*-dithiocyanato bis(4,7-dicarboxy-1,10-phenanthroline) ruthenium (II) [Ru(dcphen)$_2$(NCS)$_2$] for sensitization on TiO$_2$ and achieved remarkable light-to-electric conversion efficiency of 6.1% (Fig. 1) [10,11]. Schwarz et al. [12] have also studied the dye-sensitized nanocrystalline TiO$_2$ solar cell using a Ru phenanthroline complex photosensitizer. In continuation on our work on Ru(II) phenanthroline complexes here, we present the synthesis of Ru(II) carboxylated phenanthroline complexes having different number of carboxylic groups and their photophysical properties and performance

---

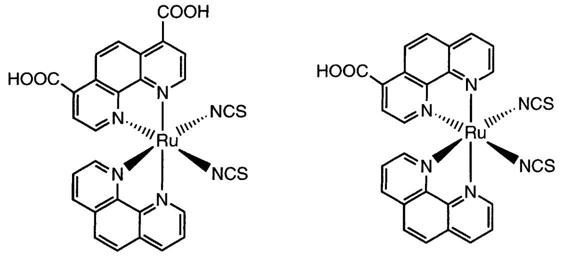
* Corresponding author. Tel./fax: +81-298-54-4750.
E-mail addresses: k-hara@aist.go.jp (K. Hara), h.arakawa@aist.go.jp (H. Arakawa).

1010-6030/01/$ – see front matter
PII: S1010-6030(01)00570-6



DCP2
Ru(dcphen)$_2$(NCS)$_2$

MCP2
Ru(mcphen)$_2$(NCS)$_2$



DCPP
Ru(dcphen)(phen)(NCS)$_2$

MCPP
Ru(mcphen)(phen)(NCS)$_2$

Fig. 1. Molecular structure of Ru(II) phenanthroline complexes with different number of carboxyl groups (Fig. 1) as anchor.

as photosensitizer for nanocrystalline dye-sensitized solar cells.

2. Experimental

2.1. Materials

2.1.1. Ligands [13]

All materials were reagent grade and used as received. Solvents for reactions and electrochemistry were pre-dried carefully and all reactions were carried out in an Ar atmosphere. 4-Methyl-1,10-phenanthroline (1 g) was refluxed for 2 h with selenium oxide (2.5 g) in dioxane containing 4% water and filtered through Celite 521 while hot. These were recrystallized from THF as pale-white crystals (yield 70%). The aldehyde obtained was oxidized with HNO_3 (70%) to give 4-carboxy-1,10-phenanthroline (mcphen) (70%). The m.p. 227°C, ^{1}H NMR, δ: 8.98 (d, $J = 4.6$ Hz, 3–1H), 8.79 (dd, $J = 4.6$ Hz, 9–1H), 8.02 (dd, $J = 8.2$ Hz, 2–1H), 7.88 (d, $J = 9.3$ Hz, 5–1H), 7.72 (d, $J = 4.3$ Hz, 7–1H), 7.54 (d, $J = 9.3$ Hz, 6–1H), 7.47 (dd, $J = 4.3$ Hz, 8–1H). MS (EIMS): m/z: 224.8 $(M{+}H)^+$. Anal. calc. for $C_{13}H_8N_2O_2Na$ (H_2O): C, 59.10; H, 3.43; N, 10.60. Found: C, 58.95; H, 3.57; N, 10.73.

4,7-Dicarboxy-1,10-phenanthroline (dcphen) was prepared in a similar manner using 4,7-dimethyl-1,10-phenanthroline in place of 4-methyl-1,10-phenanthroline (yield 70%). The m.p. > 300°C, ^{1}H NMR, δ: 9.08 (d, $J = 4.2$ Hz, 2H, 2,9H), 8.17 (s, 2H, 5,6H), 7.78 (d, $J = 4.2$ Hz, 2H, 3,8H). MS (EIMS): m/z: 269.0 $(M + H)^+$. Anal. calc. for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.01; N, 10.45. Found: C, 62.56; H, 2.92; N, 10.36.

2.1.2. Synthesis of cis-dichloro bis(4-carboxy-1,10-phenathroline) ruthenium(II), Ru(mcphen)$_2$Cl$_2$

$RuCl_3{\cdot}3H_2O$ (523 mg, 2 mmol) was dissolved in 50 ml of DMF under N_2. To this mcphen (862 mg, 3.85 mmol) was added and the mixture was refluxed for 3 h under dark. It was cooled to room temperature, filtered and DMF was evaporated in vacuo, and the resulting solid was washed with a mixture of 1:4 acetone and diethylether. The purple complex obtained was stirred with 100 ml of 2 mol HCl for 4 h and filtered through a membrane filter. ^{1}H NMR, δ: 8.60 (d, 2H), 8.48 (d, 2H), 8.24 (d, 2H), 8.12 (d, 4H), 7.62 (d, 4H). MS (EIMS): m/z: 308.5 $(M-2H)^{2-}$, 618.7 $(M-H)^-$. Anal. calc. for $C_{26}H_{16}N_4O_4Cl_2Ru$: C, 50.32; H, 2.58; N, 9.03. Found: C, 50.42; H, 2.57; N, 9.22.

2.1.3. Synthesis of cis-dithiocyanato bis(4-carboxy-1,10-phenanthroline) ruthenium(II) [Ru(mcphen)$_2$(NCS)$_2$, MCP2]

Three hundred and ten milligrams (0.5 mmol) of Ru(mcphen)$_2$Cl$_2$ was dissolved in 50 ml of DMF under reduced light. To this solution 10 ml of 0.1 M aqueous NaOH was added to deprotonate the carboxyl groups. NH_4NCS (380 mg, 5.0 mmol) was separately dissolved in 5 ml of H_2O and subsequently added to the above solution. The reaction mixture was heated to reflux under Ar atmosphere, while magnetic stirring was maintained. After 6 h, it was cooled, and the solvent was removed using a rotary evaporator. The resulting solid was dissolved in water and filtered through a membrane filter, pH of the filtrate was lowered to 2.5 by adding HNO_3 to give dense precipitate. It was placed in refrigerator for 12 h and after that the solid was collected on a membrane filter, washed well with H_2O/acetone–ether and air-dried (yield 320 mg, 85%). The complex was purified on a Sephadex LH20 column. ^{1}H NMR, δ: 9.85 (d, 2H), 8.92 (d, 1H), 8.75 (d, 2H), 8.40 (d, 1H), 8.35 (d, 1H), 8.22 (d, 2H), 8.10 (d, 1H), 7.80 (d, 2H), 7.55 (d, 1H), 7.35 (d, 1H). MS (EIMS): m/z: 331.7 $(M-2H)^{2-}$, 664.9 $(M-H)^-$. Anal. calc. for $C_{28}H_{16}N_6O_4S_2Ru$: C, 50.52; H, 2.41; N, 12.63. Found: C, 50.62; H, 2.37; N, 12.42. Any isomeric separation of MCP2 was not carried out, so MCP2 was an isomeric mixture of *cis* and *trans* complexes.

2.1.4. Synthesis of cis-dithiocyanato bis(4,7-dicarboxy-1,10-phenanthroline) ruthenium(II) [Ru(dcphen)$_2$(NCS)$_2$, DCP2]

The complex was synthesized in a similar manner as above or described elsewhere [10,11] using 4,7-dicarboxy-1,10-phenanthroline in place of 4-carboxy-1,10-phenanthroline. For Ru(dcphen)$_2$Cl$_2$, ^{1}H NMR, δ: 9.62 (d, $J = 5.5$ Hz, 2H, 2H), 8.55 (d, $J = 9.1$ Hz, 2H, 5H), 8.42 (d, $J = 9.3$ Hz, 2H, 6H), 8.18 (d, $J = 5.4$ Hz, 2H, 3H), 8.03 (d, $J = 5.6$ Hz, 2H, 8H), 7.39 (d, $J = 5.6$ Hz, 2H, 9H). MS (FAB): *m/z*: 673 $(M - Cl)^+$. Anal. calc. for $C_{28}H_{16}N_4O_8Cl_2Ru$: C, 47.47; H, 2.28; N, 7.91. Found: C, 47.24; H, 2.16; N, 7.69. For $Ru(dcphen)_2(NCS)_2$, ^{1}H NMR, δ: 9.83 (d, $J = 5.5$ Hz, 2H, 2H), 8.53 (d, $J = 9.1$ Hz, 2H, 5H), 8.41 (d, $J = 9.3$ Hz, 2H, 6H), 8.23 (d, $J = 5.5$ Hz, 2H, 3H), 7.90 (d, $J = 5.5$ Hz, 2H, 8H), 7.37 (d, $J = 5.5$ Hz, 2H, 9H). MS (FAB): *m/z*: 696 $(M - NCS)^+$. Anal. calc. for $C_{30}H_{16}N_6O_8S_2Ru$ (H_2O): C, 46.69; H, 2.33; N, 10.89.

2.1.5. Synthesis of cis-dithiocyanato (4-carboxy-1,10-phenanthroline) (1,10-phenanthroline) ruthenium(II) [Ru(mcphen)(phen)(NCS)$_2$, MCPP]

To 10 ml of 1 N HCl 100 mg (0.38 mmol) of $RuCl_3 \cdot H_2O$ and 90 mg (0.45 mmol) of 1,10-phenanthroline were added. After stirring under dark for 30 min and maintaining argon atmosphere, the reaction was allowed to stand overnight. The product $(Ru(phen)Cl_4)$ was isolated by filtration, washed with water and dried in vacuo. MS (ESIMS): *m/z*: 424.1 $(M + H)^+$. A mixture of $Ru(phen)Cl_4$ (423 mg, 1 mmol) and mcphen (224 mg, 1 mmol) was then dissolved in 50 ml of DMF and refluxed under dark for 6 h, while maintaining nitrogen atmosphere. After cooling the reaction mixture was filtered, and solvent was evaporated and the solid mixture was washed with 1:4 acetone–ether mixture to give $Ru(mcphen)(phen)Cl_2$. MS (ESIMS): *m/z*: 541.4 $(M-Cl)^+$.

Finally $Ru(mcphen)(phen)(NCS)_2$ was prepared by refluxing a mixture of 576 mg (1 mmol) of Ru(mcphen)(phen) Cl_2 and 760 mg (10 mmol) of NH_4NCS in DMF. After 6 h, the reaction was stopped, cooled to room temperature, filtered and the solvent was removed using a rotary evaporator. The solid mixture was washed with water, acetone, and ether and dried. The complex was purified on a silica column (packed with hexane) using acetonitrile and methanol as eluent. Lastly, the complex was purified on a Sephadex LH20 column. ^{1}H NMR, δ: 10.15 (d, 1H), 9.75 (d, 1H), 9.54 (d, 1H), 8.65 (d, 1H), 8.50 (d, 1H), 8.32 (d, 1H), 8.05 (d, 1H), 7.82 (d, 1H), 7.75 (d, 1H), 7.30 (m, 4H), 6.90 (d, 2H). MS (ESIMS): *m/z*: 621.0 $(M - H)^-$. Anal. calc. for $C_{27}H_{16}N_6O_2S_2Ru$: C, 52.17; H, 2.59; N, 13.52. Found: C, 52.01; H, 2.57; N, 13.75. Any isomeric separation of MCPP was not carried out.

2.1.6. Synthesis of cis-dithiocyanato (4,7-dicarboxy-1,10-phenanthroline) (1,10-phenanthroline) ruthenium(II) [Ru(dcphen)(phen)(NCS)$_2$, DCPP]

The complex was prepared by slightly modifying the method described by Kimberly et al. [14]. A mixture of $RuCl_2$ $(DMSO)_4$ (484 mg, 1 mmol), dcphen (280 mg, 1.05 mmol), and phen (208 mg, 1.05 mmol) in DMF was heated for 30 min. A pale-orange complex was formed. To this reaction mixture, 760 mg (10 mmol) of NH_4NCS dissolved in 10 ml of H_2O was added, and the reaction was monitored by UV–Vis spectroscopy. After 5 h, the reaction was stopped, cooled and filtered. DMF was evaporated and the solid complex obtained was washed well with water, acetone and ether. The complex was purified on a silica column using methanol–acetonitrile as eluent and finally over a Sephadex LH20 column. ^{1}H NMR, δ: 9.75 (d, 1H), 9.70 (d, 1H), 8.73 (d, 1H), 8.64 (d, 1H), 8.60 (d, 1H), 8.24 (d, 1H), 8.16 (d, 1H), 8.10 (d, 1H), 8.07 (d, 1H), 7.97 (d, 1H), 7.68 (d, 1H), 7.65 (d, 1H), 7.36 (d, 1H), 7.29 (d, 1H). MS (ESIMS): *m/z*: 331.7 $(M - 2H)^{2-}$, 663.7 $(M - H)^-$. Anal. calc. for $C_{28}H_{16}N_6O_4S_2Ru$: C, 50.52; H, 2.42; N, 12.63. Found: C, 50.62; H, 2.42; N, 12.73.

2.2. Characterization

The following instruments were used for routine spectroscopic works: Varian 300 BB spectrometer (300 MHz, in D_2O/NaOD solvent unless otherwise stated) for ^{1}H NMR spectroscopy; Shimadzu UV-3101PC for UV–Vis spectroscopy; Hitachi F-4500 spectrophotometer for emission spectroscopy; Nd-YAG laser (Continuum Surelite II) for emission lifetime. The oxidation potentials of the complexes in ethanol solution were estimated using a conventional three-compartment cell consisting of a carbon or a Au working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode in a saturated KCl solution. Measurement was carried out using an electrochemical measurement system BAS100B.

2.3. Photovoltaic measurement of solar cells

TiO_2 film electrodes were prepared by screen printing of organic paste containing TiO_2 nanoparticles prepared by the method as reported by Barbé et al. [15], onto a transparent conducting oxide (TCO, F-doped SnO_2) coated glass (Nippon Sheet Glass, 10 Ω/cm^2, transparency 80%) and then sintered at 500°C for 1 h. The thickness of the semiconductor films was 12 μm. The Ru phenanthroline complexes were dissolved in dehydrated ethanol (Wako Chemicals) at a concentration of 3×10^{-4} M. The semiconductor films were immersed into the dye solution and then kept at 25°C for over 18 h to fix the dye onto the semiconductor surface. A sandwich-type two electrode electrochemical cell for photovoltaic measurement consisted of the dye-coated semiconductor film electrode, a Pt film counter electrode, a polyethylene film spacer, and an organic electrolyte. Apparent size of the dye-sensitized TiO_2 electrode was 0.25 cm^2 (0.5 cm × 0.5 cm). The electrolyte solution was a mixture of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine (TBP) in methoxyacetonitrile. The photoelectrochemical performance of the solar cell was measured with a source meter (Keithley, model 2400 and Advantest, R6246). The light source was a standard AM 1.5 solar simulator with a 300 W Xe lamp (Wacom, WXS-80C-3). The incident light intensity was calibrated with a thermopile (The Eppley Lab., Newort, RI) and a standard solar cell for amorphous silicon solar

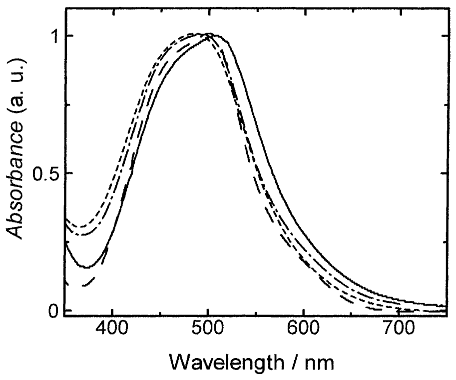


Fig. 2. Absorption spectra of carboxylated Ru(II) phenanthroline complexes in ethanol: (—) DCP2, (——) MCP2, (– – –) DCPP, (— -) MCPP.

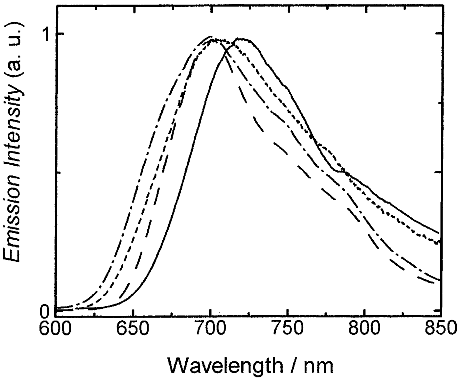


Fig. 3. Emission spectra of carboxylated Ru(II) phenanthroline complexes in ethanol–methanol (4:1) solution at 77 K: (—) DCP2, (——) MCP2, (– – –) DCPP, (— -) MCPP.

cell produced by Japan Quality Assurance Organization (JQA).

3. Results and discussion

3.1. Characterization

UV–Vis absorption spectra of all the complexes, DCP2, MCP2, DCPP, and MCPP in ethanol at room temperature, are shown in Fig. 2 and summarized in Table 1. The strong absorption bands due to the π–π^* intraligand transitions are observed around 250–300 nm (not shown) in the UV region. A broad and intense absorption band around 500 nm are due to metal to ligand charge transfer (MLCT) transition for each complex with a molar absorption coefficient of $1.2–1.8 \times 10^4\,M^{-1}\,cm^{-1}$. The maximum of MLCT absorption of the complexes shifts slightly to the blue with decreasing number of carboxyl groups as shown in Fig. 2.

Emission spectra of these complexes shown in Fig. 3 were obtained at 77 K in a degassed ethanol–methanol glass matrix. On excitation within the charge transfer absorption band, all the complexes exhibited luminescence around 700–720 nm. The maximum of emission spectra of the complexes also shifts to the blue with decreasing number of carboxyl groups. From the threshold wavelength of the emission spectra, the 0–0 transition energy was determined to be 1.9–2.0 eV for all the complexes. The excited state lifetimes of these complexes measured at 77 K were in the range of 1.5–2.9 μs, while they were observed to be 20–80 ns at 298 K. The short-lived excited states in fluid solution may be attributed to the efficient non-radiative decay.

Cyclic voltammetries of the complexes were carried out in acetonitrile or methanol and the data are presented in Table 1. The oxidation potentials of DCP2, MCP2, DCPP, and MCPP were determined to be 1.12, 0.96, 1.09, and 0.90 V vs. NHE, respectively, which were derived from oxidation of Ru(II) to Ru(III). Irreversible oxidation waves can be ascribed to the presence of thiocyanato ligands whose oxidation potential is close to that of Ru(II)/Ru(III). The oxidation potentials of these Ru phenanthroline complexes are sufficiently positive than the I^-/I_3^- redox potential. Fig. 4 shows the HOMO–LUMO energy levels of the four Ru phenanthroline complexes vs. the conduction band level of TiO_2 and the redox potential of I^-/I_3^-. The LUMO levels of these complexes estimated from the oxidation potential and the 0–0 energy gap are sufficiently negative to inject electrons into the conduction band of TiO_2.

3.2. Photovoltaic performance of the solar cells

The photovoltaic performance of nanocrystalline TiO_2 solar cells sensitized by the four Ru phenanthroline complexes under the standard AM 1.5 irradiation are shown in Table 2. Electrolyte solution composed of 0.6 M DMPImI, 0.1 M LiI, 0.05 M I_2, and 0.5 M TBP in methoxyacetonitrile

Table 1
Absorption, luminescence, and electrochemical properties of carboxyl Ru(II) phenanthroline complexes

Complex	MLCT maximum[a] (nm)	Abs. coeff. ($\times 10^4\,M^{-1}\,cm^{-1}$)	Emission maximum[b] (nm)		Emission lifetime (ns)		E_{ox} (V) vs. NHE
			77 K	298 K	77 K	298 K	
DCP2	508	1.8	719	800	1500	20	1.12
MCP2	500	1.5	702	770	2000	60	0.96
DCPP	485	1.3	705	750	2900	80	1.09
MCPP	493	1.2	700	770	2300	60	0.90

[a] Absorption spectra were measured in ethanol solution.

[b] Emission spectra were measured in ethanol–methanol (4:1) solution at 77 K.

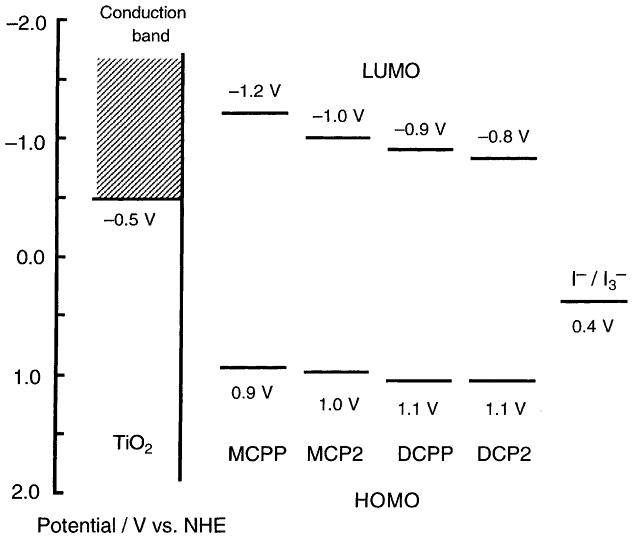


Fig. 4. HOMO–LUMO energy levels of four Ru phenanthroline complexes vs. the conduction band level of TiO_2 and the redox potential of I^-/I_3^-.

solvent. DCP2–2TBA in which two protons of the four carboxyl groups of DCP2 are replaced by two tetrabutylammonium cations (TBA) showed good performance as photosensitizer for TiO_2 solar cell producing 6.1% solar-energy conversion efficiency, η [10,11]. In this study, the η value of 5.8% was obtained for a DCP2–2TBA/TiO_2 solar cell with a short-circuit photocurrent density, J_{sc} of $12.2\,mA\,cm^{-2}$, an open-circuit photovoltage, V_{oc} of 0.70 V, and a fill factor, ff of 0.68, as shown in Table 2. Substitution of protons by TBA cations on the carboxyl groups improves V_{oc} especially by suppressing the positive shift of the conduction band level of TiO_2 due to protonation of the TiO_2 surface.

A solar cell using DCPP, which has two carboxyl groups on one phenanthroline ligand, showed the best η of 3.7% ($J_{sc} = 8.8\,mA\,cm^{-2}$, $V_{oc} = 0.61\,V$, and ff $= 0.68$). DCP2 having four carboxyl groups produced the best J_{sc} of $9.5\,mA\,cm^{-2}$. The performance of MCPP, which has only one carboxyl group, is the lowest among four complexes, with J_{sc} of $4.5\,mA\,cm^{-2}$ and V_{oc} of 0.55 V. Our results showed that the number of carboxyl groups as anchor influences the solar cell performance significantly and the performance decreased with decreasing number of carboxyl groups from two to one. The absorption intensity of MCPP on the TiO_2 film is lower than that of DCP2, indicating that MCPP is less efficiently adsorbed on the TiO_2 surface than DCP2. Thus the lower performance of the MCPP/TiO_2 solar cell is due at least partly to the inefficient adsorption of the dye.

Table 2
Photovoltaic performance of nanocrystalline TiO_2 solar cells sensitized by Ru(II) phenanthroline complexes[a]

Complex	J_{sc} ($mA\,cm^{-2}$)	V_{oc} (V)	Fill factor	η (%)
DCP2	9.5	0.55	0.57	3.0
MCP2	6.1	0.56	0.71	2.4
DCPP	8.8	0.61	0.68	3.7
MCPP	4.5	0.55	0.65	1.6
DCP2–2TBA	12.2	0.70	0.68	5.8

[a] Conditions: light source, a AM 1.5 solar simulator ($100\,mW\,cm^{-2}$); TiO_2 electrode, $0.25\,cm^2$ and $13\,\mu m$ thick; electrolyte, mixture of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, 0.5 M *tert*-butylpyridine in methoxyacetonitrile.

In addition to the inefficient adsorption of MCPP, we considered that different anchoring geometry due to different number of carboxyl groups also influences electron injection. Aranyos et al. [9] have prepared new Ru bipyridine complexes having new anchoring functionality malonate and measured their photoelectrochemical properties of dye–TiO_2 solar cells. They reported that the J_{sc} and IPCE values obtained for the complex having one carboxyl group as anchor was inferior to those for the complex which contains malonate anchoring group (i.e. two carboxyl groups). They considered that the differences in the J_{sc} and IPCE are most likely due to differences in the efficiency of the electron injection from excited dye to the TiO_2, and should be related to the number of carboxylates involved in the binding [9]. The electron injection from excited molecules adsorbed on the semiconductor surface to the conduction band is one of the most important primary processes for the solar cell. The rate constant for the electron injection, k_{inj}, can be expressed as [16,17]:

$$k_{inj} = \left(\frac{4\pi^2}{h}\right)|V|^2\rho(E) \qquad (1)$$

where V is the electronic coupling between the excited molecule and the semiconductor and $\rho(E)$ the density of states of the conduction band. It has been reported that the k_{inj} from the excited $Ru(dcbpy)_2(NCS)_2$ complex, which has four carboxyl groups, to the TiO_2 film is very large [18]. The complex having more than two carboxyl groups has been expected to be attached to the surface with two carboxyl groups. This anchoring geometry has been confirmed through X-ray diffraction studies [7,8]. This indicates that the anchoring geometry with two carboxyl groups is favorable for the electron injection, namely, the electronic coupling V is considerably large. On the contrary, the complex having just one carboxyl group such as MCPP does not have the same geometry as that of the complex having more than two carboxyl groups. It is known that the electronic coupling V is sensitive to the relative configuration between the excited molecule and the semiconductor surface. Therefore, we consider that the low efficiency of MCPP/TiO_2 solar cell is due to unfavorable anchoring geometry for the electron injection process. Detailed studies of the electron injection process by transient absorption spectroscopy are in progress in our laboratory.

4. Conclusions

Four carboxylated Ru(II) phenanthroline complexes with different number of carboxyl groups, $Ru(dcphen)_2(NCS)_2$

[DCP2], Ru(mcphen)$_2$(NCS)$_2$ [MCP2], Ru(dcphen)(phen)(NCS)$_2$ [DCPP], and Ru(mcphen)(phen)(NCS)$_2$ [MCPP], showed similar broad MLCT absorption bands around 500 nm in ethanol and showed emission maxima at 700–720 nm in ethanol–methanol (4:1) at 77 K. The excited state lifetime of these complexes at 77 K ranged from 1.5 to 2.9 μs. The photovoltaic performance of nanocrystalline TiO$_2$ solar cells sensitized by the phenanthroline complexes depends remarkably on the number of carboxyl groups. The performance of MCPP as a photosensitizer, which has only one carboxyl group, is lower than that of the other complexes, indicating that the number of carboxyl groups as anchor influences the efficient solar cell performance.

Acknowledgements

This work was supported by Science and Technology Agency, Center of Excellence Development Project (COE project), Japan.

References

[1] A. Kay, M. Grätzel, J. Phys. Chem. 117 (1993) 6272.

[2] Md.K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, B.A. Murrer, Chem. Commun. (1998) 719.

[3] K. Sayama, M. Sugino, H. Sugihara, Y. Abe, H. Arakawa, Chem. Lett. (1998) 753.

[4] S. Ferrere, A. Zaban, B.A. Gregg, J. Phys. Chem. B 101 (1997) 4490.

[5] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.

[6] Md.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.

[7] V. Shklover, Md.K. Nazeeruddin, S.M. Zakeeruddin, C. Barbe, A. Kay, T. Haibach, W. Steurer, R. Hermann, H.-U. Nissen, M. Grätzel, Chem. Mater. 9 (1997) 430.

[8] V. Shklover, Yu.E. Ovchinnkov, L.S. Braginsky, S.M. Zakeeruddin, M. Grätzel, Chem. Mater. 10 (1998) 2533.

[9] V. Aranyos, H. Grennberg, S. Tingry, S.-E. Lindquist, A. Hagfeldt, Solar Energy Mater. Solar Cells 64 (2000) 97.

[10] H. Sugihara, L.P. Singh, K. Sayama, H. Arakawa, Md.K. Nazeeruddin, M. Grätzel, Chem. Lett. (1998) 1005.

[11] M. Yanagida, L.P. Singh, K. Sayama, K. Hara, R. Katoh, A. Islam, H. Sugihara, H. Arakawa, Md.K. Nazeeruddin, M. Grätzel, J. Chem. Soc., Dalton Trans. (2000) 2817.

[12] O. Schwarz, D. van Loyen, S. Joskusch, N.J. Turro, H. Dürr, J. Photochem. Photobiol. A 132 (2000) 91.

[13] C.J. Chandler, L.W. Deady, A.J. Reiss, J. Heterocycl. Chem. 18 (1981) 599.

[14] A.M. Kimberly, M. Sykora, J.M. DeSimone, T.J. Meyer, Inorg. Chem. 39 (2000) 71.

[15] C.J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, J. Am. Ceram. Soc. 80 (1997) 3157.

[16] R.J.D. Miller, G.L. McLendon, A.J. Nozik, W. Schmickler, F. Willig, Surface Electron Transfer Processes, VCH, New York, 1995 (Chapter 5).

[17] J.-E. Moser, M. Grätzel, Chimia 52 (1998) 160.

[18] Y. Tachibana, J.E. Moser, M. Grätzel, D.R. Klug, J.R. Durrant, J. Phys. Chem. 100 (1996) 20056.