A Dye-sensitized Solar Cell Using a Red Ruthenium(II) Complex with 9,9-Bis(4-methoxyphenyl)-4,5-diazafluorene

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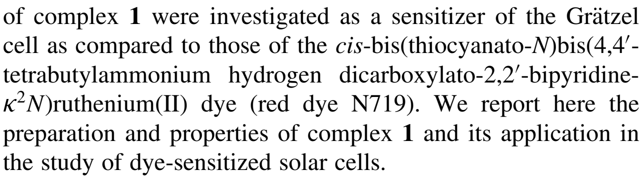
A ruthenium(II) complex containing a 4,5-diazafluorene moiety as a polypyridyl ligand was synthesized and its properties were investigated. A solar cell using the complex as a dye sensitizer showed a solar energy-to-electricity conversion efficiency of $\eta = 7.3\%$ under irradiation with AM 1.5 solar light; the value was slightly higher than that of red dye N719 ($\eta = 7.0\%$).

The study of dye-sensitized solar cells has attracted considerable attention since the device is expected to be fabricated at a low cost and to show superior performance.[1] Grätzel and co-workers reported high solar energy-to-electricity conversion efficiencies (η) above 10% using nanocrystalline TiO_2 technology.[2] Ruthenium(II) complexes with polypyridyl ligands, such as bipyridyl,[2,3] terpyridyl,[4] and 1,10-phenanthroline,[5] which have been widely investigated, are effective charge-transfer sensitizers. Recently, pure organic dyes have been also studied.[6] Although the performances of dye-sensitized solar cells are comparable to those of amorphous silicon devices, further modification of polypyridyl ligands in ruthenium complexes is required for the improvement of conversion efficiency. In this context, we have prepared a red ruthenium complex **1**, which has 9,9-bis(4-methoxyphenyl)-4,5-diazafluorene as a polypyridyl ligand (Chart 1). This ligand revealed a good performance as an electron-transporting material in the organic electroluminescent (EL) device due to the high electron affinity.[7] The properties of complex **1** were investigated as a sensitizer of the Grätzel cell as compared to those of the *cis*-bis(thiocyanato-*N*)bis(4,4′-tetrabutylammonium hydrogen dicarboxylato-2,2′-bipyridine-$\kappa^2 N$)ruthenium(II) dye (red dye N719). We report here the preparation and properties of complex **1** and its application in the study of dye-sensitized solar cells.

The synthesis of complex **1** was fundamentally performed according to the procedures reported by Grätzel et al.[3b] Complex **2** was obtained by the reaction of the diazafluorene ligand[7] with dichloro(*p*-cymene)ruthenium(II) dimer in refluxing ethanol. After chelating 2,2′-bipyridine-4,4′-dicarboxylic acid in DMF to afford **3**, complex **1** was prepared by the reaction of **3** with ammonium thiocyanate. The structure was identified by ^1H NMR, IR, and MALDI-TOF mass spectrometry (M^+, 842.1).[8] The ^1H NMR analysis indicated that complex **1** was a cis isomer since the signals assigned to the ligands were observed to be unsymmetrical. The complex was obtained as a dark red powder (decomp > 300 °C). The UV–vis spectrum of **1** in methanol is shown in Figure 1, and the spectrum is similar to that of N719. The metal-to-ligand charge-transfer (MLCT) band of complex **1** extends to 700 nm, and the maximum was observed at 525 and 396 nm. These values are slightly red-shifted from those of N719 (521 and 380 nm). N719 exhibited weak photoluminescence (PL) in the wavelength region between 650 and 800 nm, whereas PL emission from complex **1** was not observed due to the diazafluorene ligand.



1 X = NCS
3 X = Cl

N719

2

Chart 1.

The ionization potentials of complex **1** and N719 on TiO_2 electrodes were measured to be 5.40 and 5.45 eV in the photoelectron spectroscopy study, indicating that the HOMO energy level of complex **1** is slightly higher than that of N719. The increase in the HOMO energy level is due to the diazafluorene ligand and implies more effective electron transfer from I^- to the SOMO energy level of the oxidized dye after charge separation. The LUMO energy levels were calculated to be −3.72 eV for complex **1** and −3.77 eV for N719 according to the band edges of the absorption spectra (1.68 eV). These energy levels are able to interact effectively with the conduction band of TiO_2 electrode (−3.8 eV).

Nanocrystalline TiO_2 films with transparent and light-scattering layers (thickness; 7.8 and 7.8 µm) were formed on transparent conducting oxides (TCO; F-doped SnO_2) as previously described in the literature[9] and they were coated with the dyes by dipping in solutions of complex **1** (cell 1) and N719 (cell 2) in acetonitrile–*tert*-butanol (volume ratio; 1:1) for 3 days. Each dye-coated TiO_2 electrode was incorporated into a thin-layer sandwich-type cell with a Pt-sputtered TCO, the

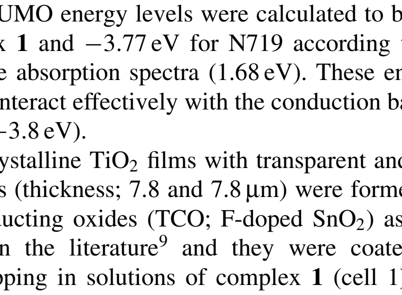


Figure 1. UV–vis absorption spectra of complex **1** and N719.

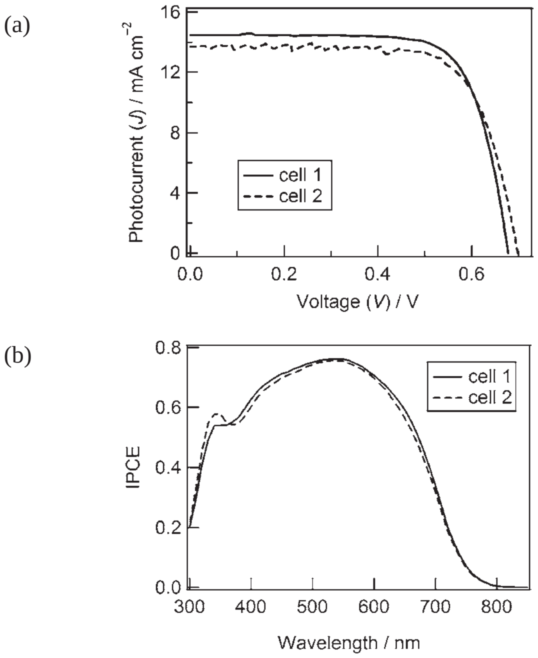


Figure 2. Solar cells using complex **1** (cell 1) and N719 (cell 2) as dyes. a) Photocurrent–voltage characteristics, b) photocurrent action spectra.

counter electrode, and an organic electrolyte solution. The electrolyte was a solution of 1,2-dimethyl-3-propylimidazolium iodide (DMPII, 0.6 M), lithium iodide (LiI, 0.1 M), iodine (I_2, 0.05 M), and 4-*tert*-butylpyridine (TBP, 0.5 M) in methoxyacetonitrile.[10] The performance of the solar cell was measured under irradiation with AM 1.5 solar light (100 mW cm^{-2}). The active cell area was 0.27 cm^2.

Figure 2a shows the photocurrent–voltage curves for solar cells 1 and 2. The conversion efficiency (η) of cell 1 was recorded to be 7.3% with a short-circuit photocurrent density (J_{sc}) of 14.5 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 0.68 V, and a fill factor of 0.74. On the other hand, an efficiency of $\eta = 7.0\%$ with $J_{sc} = 13.7$ mA cm^{-2}, $V_{oc} = 0.70$ V, and a fill factor of 0.73 was observed for cell 2. Thus, the conversion efficiency of cell 1 was slightly higher than that of cell 2; this result was due to the increase in the photocurrent density in cell 1. The diazafluorene ligand slightly improved inhibiting the recombination of charge carriers because of its electron-transporting ability and the increase of the HOMO energy level of complex **1**. The photocurrent action spectra of cells 1 and 2 are shown in Figure 2b, where incident photon-to-current conversion efficiencies (IPCE) are plotted as a function of the wavelength. The IPCE spectrum of cell 1 is slightly higher than that of cell 2 in the wavelength region between 400 and 700 nm.

In conclusion, we have synthesized a new type of red dye **1**, which is a ruthenium(II) complex containing 9,9-bis(4-methoxyphenyl)-4,5-diazafluorene as one of the polypyridyl ligands. Complex **1** on a TiO_2 electrode has slightly higher HOMO and LUMO energy levels as compared to those of N719. The solar cell using complex **1** as a dye sensitizer indicated the high performance of solar energy-to-electricity conversion efficiency ($\eta = 7.3\%$). The value is higher than that of N719 ($\eta = 7.0\%$). This result is attributed to the improvement of charge separation by the diazafluorene ligand. Further modification of the polypyridyl ligand is expected to afford a higher conversion efficiency.

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8 Complex **1**: mp > 300 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.76 (s, 3H), 3.79 (s, 3H), 6.84 (d, 4H, $J = 8.7$ Hz), 7.02 (d, 2H, $J = 8.7$ Hz), 7.07 (dd, 1H, $J = 7.8, 5.7$ Hz), 7.14 (d, 2H, $J = 8.7$ Hz), 7.15 (d, 1H, $J = 5.7$ Hz), 7.61 (d, 1H, $J = 7.8$ Hz), 7.65 (d, 1H, $J = 5.8$ Hz), 7.72 (dd, 1H, $J = 7.9, 5.3$ Hz), 7.92 (d, 1H, $J = 7.9$ Hz), 8.17 (m, 2H), 8.74 (s, 1H), 8.84 (s, 1H), 9.10 (d, 1H, $J = 5.3$ Hz), 9.81 (d, 1H, $J = 5.8$ Hz). IR (neat) 2091 (NCS), 1726 (CO_2H) cm^{-1}. MALDI-TOF Mass *m/z*: 842.1 (M^+), 784.1 ($M^+ -$ NCS).

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