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New Class of Thiocyanate-free Ruthenium(II) Complex as a Near-IR Sensitizer for Dye-sensitized Solar Cells

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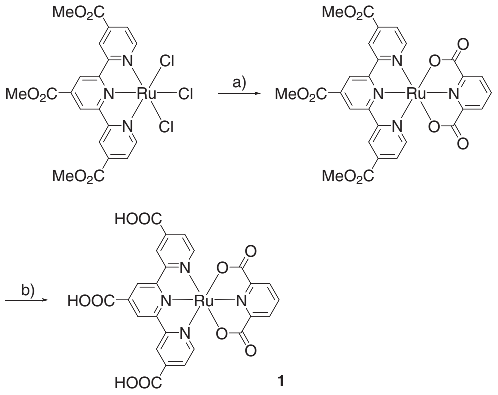
A new class of thiocyanate-free ruthenium(II) complex containing a 2,6-pyridinedicarboxylate ligand was designed and synthesized as a near-IR sensitizer for dye-sensitized solar cells, and its photophysical and photochemical properties were characterized. The solar cell sensitized with this complex exhibited efficient panchromatic sensitization over the entire visible wavelength region extending into the near-IR region. An overall conversion efficiency of 6.5% was attained under standard AM 1.5 irradiation ($100\,\mathrm{mW\,cm^{-2}}$).

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 films have been intensively investigated over the past decades.[1] Since the sensitizers used in DSSCs are critical to the cell's photovoltaic performance, extensive efforts have been focused on the synthesis of new, highly efficient sensitizers. Among the numerous sensitizers, ruthenium(II)–polypyridyl complexes have received significant attention owing to their superior performance in DSSCs. $[Ru(dcbpy)_2(NCS)_2]$ (dcbpy: 4,4′-dicarboxy-2,2′-bipyridine) (N3)[2] and $[Ru(tctpy)(NCS)_3](TBA)_3$ (tctpy: 4,4′,4′′-tricarboxy-2,2′:6′,2′′-terpyridine, TBA: tetra-*n*-butylammonium) (N749)[3] are two of the most successful sensitizers, and the DSSCs sensitized with these complexes achieve 11% conversion efficiency from solar light to electricity.[2b,4]

In these ruthenium(II) complexes, NCS ligands tune the spectral and redox properties of the complexes by destabilizing the metal t_{2g} orbital. Although the NCS ligand is a good donor, it is believed to provide the weakest bonding in the complexes. The NCS ligand can undergo a photosubstitution or photodegradation reaction, which decreases not only the long-term stability of the complexes but also the photovoltaic performance of DSSCs.[5] Several researchers have attempted to replace NCS ligands with bidentate or tridentate donor ligands.[6] Although the initial examinations gave only limited success, it has been reported that $[Ru(dcbpy)_2(2,4\text{-difluorophenylpyridinato})]^+$ and [Ru(tctpy)(2,6-bis(5-pyrazolyl)pyridine)] exhibit a conversion efficiency up to 10%.[6e,6i] However, most thiocyanate-free ruthenium(II) complexes show insufficient light-harvesting efficiency above 800 nm. The improvement of the light-harvesting efficiency in the longer wavelength region is important because the solar spectrum has a large photon flux in the near-IR region above 800 nm. To create robust ruthenium(II) complexes as near-IR sensitizers, a new molecular design of the donor ligand is required.

The absorption properties of ruthenium(II) complexes can be tuned by careful consideration of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels.[7] The absorption band can be extended into a longer-wavelength region by introducing a ligand with a low-lying π^*-level molecular orbital and/or by destabilizing the metal t_{2g} orbital using a strong donor ligand. It was reported that ruthenium(II)–terpyridyl complexes exhibit better photoresponse in the longer-wavelength region than ruthenium(II)–bipyridyl complexes.[3] Therefore, ruthenium(II) terpyridyl complexes with strong donor ligand are suitable for the purpose of the expansion of the absorption band in the longer-wavelength region.[6m] An advantage of multidentate donor ligand is that the electron-donating ability can be changed by introducing a substituent on the ligand.[8]

Here we report a new class of thiocyanate-free ruthenium(II) complex **1** as a near-IR sensitizer for DSSCs. This is the first example of a ruthenium(II) complex sensitizer containing a 2,6-pyridinedicarboxylate as a donor ligand. As shown in Scheme 1, **1** was synthesized by a slight modification of the procedures reported in the literature.[9] The structure of the resulting complex was identified by nuclear magnetic resonance (NMR) spectroscopy and electrospray-ionization mass spectrometry (ESI-MS) analyses (see Supporting Information).[15] To gain insight into the photophysical properties of **1**, we performed a semi-empirical calculation (ZINDO/1).[10] A schematic representation of the frontier orbitals for **1** is shown in Figure 1. The HOMO is localized on the metal center with the carboxy groups of the 2,6-pyridinedicarboxylate ligand, and the LUMO is localized on the tctpy anchoring ligand. The presence of the LUMO on the ligand facilitates electron injection from the excited complexes to TiO_2 because **1** is adsorbed on TiO_2 via the carboxy groups of the tctpy anchoring ligand.



Scheme 1. Synthesis of **1**: a) 2,6-pyridinedicarboxylic acid, LiCl, Et_3N, EtOH; b) Et_3N, H_2O, DMF.

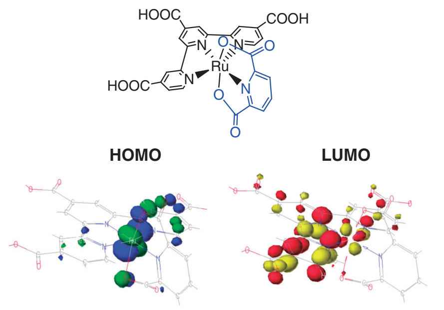


Figure 1. Calculated molecular orbitals of **1**.

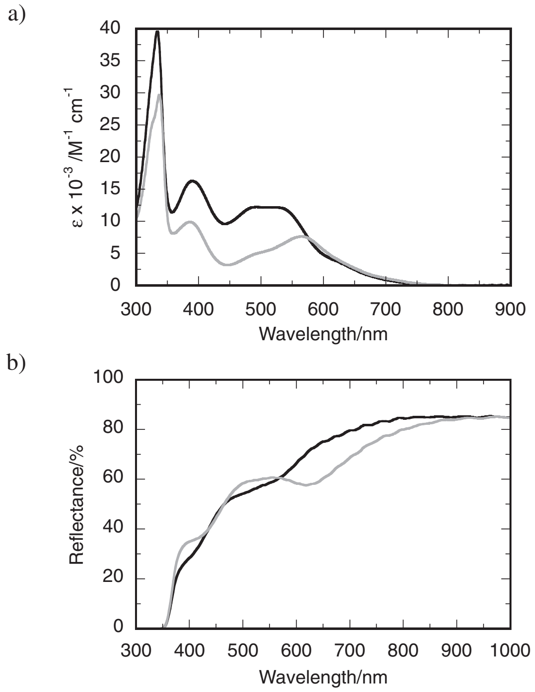


Figure 2. a) Absorption spectra of **1** (black) and N749 (gray). b) Diffuse reflectance spectra of **1** (black) and N749 (gray) adsorbed on TiO_2 film with the thickness of 5 µm.

Figure 2 shows the absorption spectra of **1** and N749 in a 1×10^{-3} M aqueous NaOH solution. Strong π–π^* absorptions are observed for the coordinating ligand in the UV region, and a broad metal-to-ligand charge-transfer (MLCT) absorption is observed in a wavelength region lower than the UV region. The lowest energy band at 522 nm is blue-shifted in comparison with that of N749 since the electron-donating ability of a 2,6-pyridinedicarboxylate ligand might be inferior to that of three NCS ligands.[7c] Notably, the absorption intensity of **1** lower than 570 nm is larger than that observed for N749. The diffuse reflectance spectra of **1** and N749 adsorbed on TiO_2 film are red-shifted and much broadened because of J aggregation and interaction of the anchoring group with the surface titanium ion.[11] A larger red-shift was observed in N749, probably because the aggregation manner is different between **1** and N749.

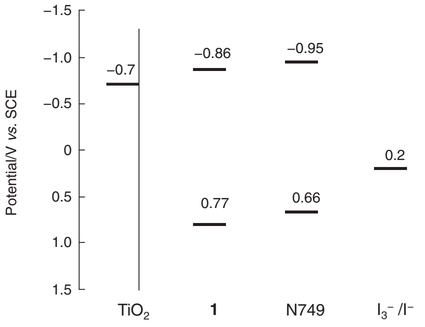


Figure 3. Energy level diagram of TiO_2, **1**, N749, and I_3^-/I^-.

The electrochemical behavior of **1** adsorbed on TiO_2 was investigated by cyclic voltammetry in acetonitrile containing 0.1 M $LiClO_4$. A quasi-reversible wave due to the $Ru^{3+/2+}$ redox reaction is observed between 0.5 and 0.9 V vs. a saturated calomel electrode (SCE). The peak potential of the differential pulse voltammograms for **1** is 0.77 V vs. SCE. This observed potential is sufficiently low for rapid electron transfer from an iodide/triiodide couple to the oxidized complex (Figure 3). The 0–0 transition energy ($E_{0\text{–}0}$) of **1** was estimated from the absorption edge,[6k,11,12] and the calculated excited-state redox potential ($E_{ox}{}^*$) is −0.86 V vs. SCE. Although this $E_{ox}{}^*$ value is relatively similar to the TiO_2-conduction band edge, a thermodynamic driving force for electron injection might be provided by the energy difference between $E_{ox}{}^*$ and the TiO_2-conduction band edge.

Nanocrystalline TiO_2 photoelectrodes (area: 0.25 cm^2; thickness: 31 µm) were fabricated using a screen-printing method. The TiO_2 pastes were obtained from the Sumitomo Osaka Cement Co., Ltd. TiO_2 films were immersed in an ethanol solution of the sensitizer for 22 h at 25 °C. The concentrations of **1** and N749 were 4×10^{-4} and 2×10^{-4} M, respectively.[13] Each solution contained a deoxycholic acid as a coadsorbate to suppress dye aggregation on TiO_2 surfaces.[14] The concentrations of deoxycholic acid in the solutions were 4×10^{-2} M for **1** and 2×10^{-2} M for N749. Photoelectrochemical measurements were performed using a two-electrode solar cell consisting of the dye-coated TiO_2 electrode, a platinum film counter electrode, a polypropylene film spacer (thickness: 60 µm), and an electrolyte solution consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.05 M iodine, 0.1 M lithium iodide, and 0.05 or 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile. The highest performance of DSSCs sensitized with **1** was obtained when the TBP concentration in the electrolyte was 0.05 M. In contrast, DSSCs sensitized with N749 showed the highest conversion efficiency when 0.5 M TBP was used.

The photocurrent action spectra of DSSCs sensitized with **1** and N749 are shown in Figure 4. The incident photon-to-current conversion efficiency (IPCE) for each DSSC is plotted as a function of wavelength. A maximum IPCE value of 71% was observed at 500 nm. Although the HOMO is mainly localized on the metal center, an electron transfer from iodine redox should occur efficiently. This result suggests that the proximal contact between the soft sulfur atom of the NCS ligand and an electron donor in the electrolyte is not essential for the efficient regeneration process. Although IPCE values in the longer wavelength region are lower than those of N749, IPCE values of **1** are higher than those of N749 in the 440–600 nm region under similar cell fabrication. This is consistent with the results obtained from diffuse reflectance spectroscopy experiments.

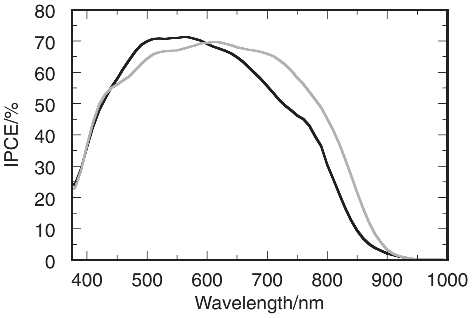


Figure 4. Photocurrent action spectra of DSSCs sensitized with **1** (black) and N749 (gray).

Note that the broad IPCE curve for **1** covers the whole visible range extending into the near-IR region, and the onset of the action spectrum is near 920 nm. Preliminary photovoltaic experiments were performed under AM 1.5 irradiation (100 mW cm^{-2}). The results for DSSCs sensitized with **1** and N749 are as follows: short-circuit photocurrent = 17.4 and 19.6 mA cm^{-2}; open-circuit voltage = 0.58 and 0.68 V; fill factor (ff) = 0.64 and 0.71; and overall solar-light-to-electrical-conversion efficiency = 6.5 and 9.5%, respectively. Although **1** shows lower efficiencies than N749, the efficiencies of DSSCs sensitized with **1** could be further improved not only by the optimization of cell fabrication but also by structural modifications of the 2,6-pyridinedicarboxylate ligand. We believe our current study is particularly important because the possibility of the molecular design of robust near-IR sensitizers has been expanded.

In summary, a new class of thiocyanate-free ruthenium(II) complexes containing a 2,6-pyridinedicarboxylate ligand was synthesized as a near-IR sensitizer for DSSCs. The solar cells sensitized with **1** exhibited efficient panchromatic sensitization over the entire visible wavelength extending into the near-IR region. A maximum IPCE value of 71% was observed at 500 nm, and the onset of the action spectrum was near 920 nm. This result suggests that the proximal contact between the soft sulfur atom of the NCS ligand and an electron donor in the electrolyte is not essential for the efficient regeneration process. We are currently investigating the optimization of ligand structure and cell fabrication as well as long-term stability of the complex.

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