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## Research Article

# Development of a New Class of Thiocyanate-Free Cyclometalated Ruthenium(II) Complex for Sensitizing Nanocrystalline TiO<sub>2</sub> Solar Cells

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We designed and developed a new class of thiocyanate-free cyclometalated ruthenium sensitizers for sensitizing nanocrystalline TiO<sub>2</sub> solar cells. This complex shows appreciably broad absorption range. Anchoring to nanocrystalline TiO<sub>2</sub> films for light to electrical energy conversion in regenerative photoelectrochemical cells achieves efficient sensitization to TiO<sub>2</sub> electrode. With this new sensitizer, there were a power conversion efficiency of 4.76%, a short-circuit photocurrent density of 11.21 mA/cm<sup>2</sup>, an open-circuit voltage of 0.62 V, and a fill factor of 0.68 obtained under standard AM 1.5 sunlight.

## 1. Introduction

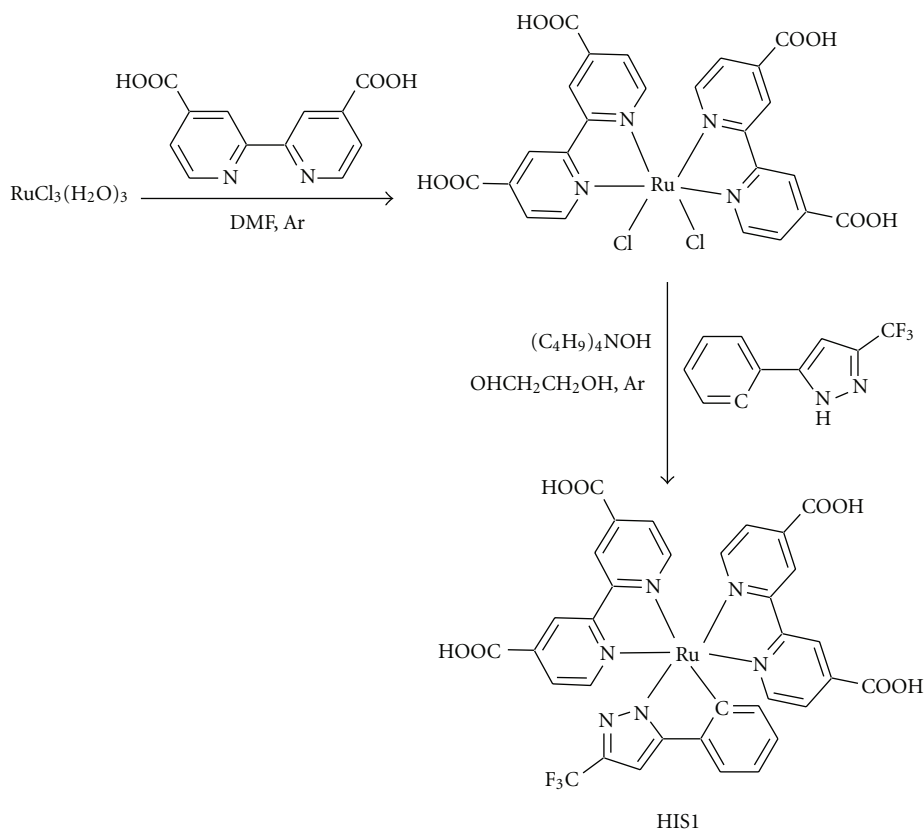
A molecular system that consists of a wideband gap semiconductor photoanode, typically TiO<sub>2</sub>, an anchored molecular photosensitizer, a redox electrolyte, and a platinized photocathode is called dye-sensitized solar cells (DSCs) [1–5]. Among these elements, the sensitizers play a vital role in DSC. A lot of Ru-complex sensitizers [6–16] and organic sensitizers have been developed in DSC [17]. So far, sensitizers such as black dye, N719, and N3 are known as best sensitizers in DSC. Black dye sensitized nanocrystalline TiO<sub>2</sub> solar cells yielding solar to electric power conversion efficiency of over 11% under standard AM 1.5 conditions [12, 13]. Much effort has been made to increase photovoltaic performance (stability) of a device, towards the development of sensitizers, electrode, and photoanode material. A way to improve the stability is the development of a dye without thiocyanate (SCN) donor ligands because monodentate SCN is believed to provide the weakest dative bonding within the metal complexes, making the sensitizer unstable. Few efforts have been made to replace the SCN donor ligands with effective pyridyl pyrazolate chelating chromophores [18] and 2,4-difluorophenyl pyridinato ancillary ligands [19]. More recently, cycloruthenated compounds have been used

as sensitizers for efficient DSC devices [19–24]. Although the preliminary attempts gave only limited success [20–24], a superior power conversion efficiency is now achieved with a novel thiocyanate-free cyclometalated sensitizer [19]. However, further development of new sensitizer is still a challenging issue for DSC to improve the efficiency. Here, we report on the new class of thiocyanate-free cyclometalated ruthenium(II) complex for sensitizing nanocrystalline TiO<sub>2</sub> solar cells.

## 2. Experimental

**2.1. Materials.** All the solvents and chemicals were of reagent grade and used as received unless otherwise noted. Chromatographic purification was performed by gel permeation on Sephadex LH-20 (from Sigma).

**Synthesis of Complex HIS1.** *cis*-Dichlorobis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium (180 mg, 0.27 mmol) and 5-phenyl-3-(trifluoromethyl)-1H-pyrazole (117 mg, 0.55 mmol) were dissolved in ethylene glycol (30 mL), and the reaction mixture was heated to 170°C under argon for 2 h. Then tetrabutyl ammonium hydroxide (1.1 g, 1.37 mmol) was added to the reaction mixture and further heated to 170°C under argon for 2 h. After evaporating the solvent,



SCHEME 1: Synthetic route for Bis(4,4'-dicarboxy-2,2'-bipyridine) 5-phenyl-3-(trifluoromethyl)-1H-pyrazole Ruthenium (II).

the resulting solid was dissolved in water (15 mL) and was titrated with 0.2 M  $\text{HNO}_3$  to pH 3.8. The reaction mixture was kept in a refrigerator overnight and allowed to warm to 25°C. The resulting precipitation was collected on a sintered glass crucible by suction filtration. The solid was dissolved in a basic water solution (pH 10–11) and purified on a Sephadex LH-20 column by eluting with water. The yield, 167 mg.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$  with a drop of NaOD):  $\delta$  9.04–8.86 (m, 5H), 8.06 (d, 1H), 7.9 (d, 1H), 7.89 (d, 1H), 7.8 (d, 1H), 7.67 (d, 2H), 7.55 (d, 2H), 7.27 (t, 2H), 7.13 (t, 1H), and 6.92 (s, 1H).

**2.2. Fabrication of Dye-Sensitized Solar Cell.** A nanocrystalline  $\text{TiO}_2$  photoelectrode of 20  $\mu\text{m}$  thickness (area: 0.25  $\text{cm}^2$ ) was prepared by screen printing on conducting glass as previously described [25]. The films were further treated with 0.05 M  $\text{TiCl}_4$  and 0.1 M  $\text{HCl}$  aqueous solutions before examination [26]. Coating of the  $\text{TiO}_2$  film was carried out by immersing for 45 h in a sensitizer solution of  $3 \times 10^{-4}$  M acetonitrile/*tert*-butyl alcohol (1/1, *v/v*) solution. Deoxycholic acid (20 mM) was added to the dye solution as a coadsorbent to prevent aggregation of the dye molecules [27, 28]. Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited  $\text{TiO}_2$  film and a platinum-coated conducting glass were used as the working electrode and the counterelectrode, respectively. The two electrodes were separated by a surlyn spacer

(40  $\mu\text{m}$  thick) and sealed by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 M  $\text{I}_2$ , TBP 0.3 M, and 0.1 M LiI in acetonitrile.

### 3. Results and Discussion

Scheme 1 shows the synthetic approach for the synthesis of thiocyanate-free cyclometalated ruthenium (II) complex HIS1.

The absorption spectrum of the complex HIS1 is dominated by metal to ligand charge transfer transitions (MLCTs) and shows MLCT bands in the visible region at 546 nm with a molar extinction coefficient of  $12 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ . There are high-energy bands at 380 nm due to ligand  $\pi$ - $\pi^*$  charge transitions. A comparison of UV-vis spectra of the HIS1 and N719 complexes is displayed in Figure 1.

To get an insight into the electron distribution of this new series of complexes for better understanding of the charge injection and dye regeneration process, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of complex HIS1 were calculated using Gaussian-09 program package (Figure 2). The HOMO of cyclometalated complexes of type  $[\text{Ru}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})\text{Ru}(\text{N}^{\wedge}\text{N}^{\wedge}\text{C})]$  and  $[\text{Ru}(\text{N}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{N})^+]$  is typically extended over the metal and, to a lesser extent, the anionic portion of the cyclometalating ligand [29]. The LUMO typically resides

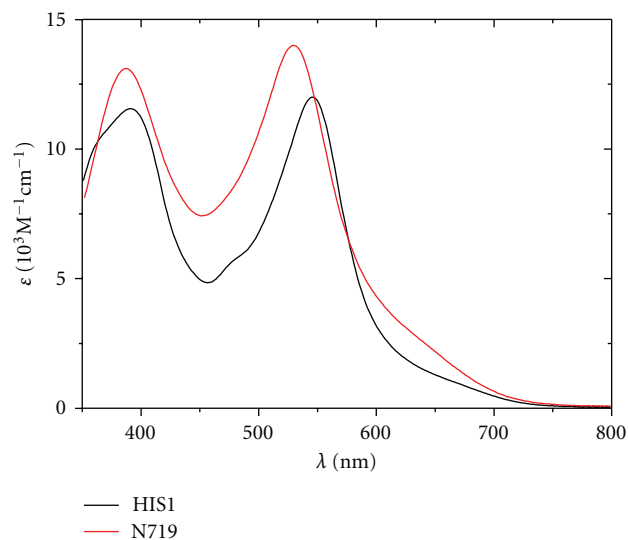
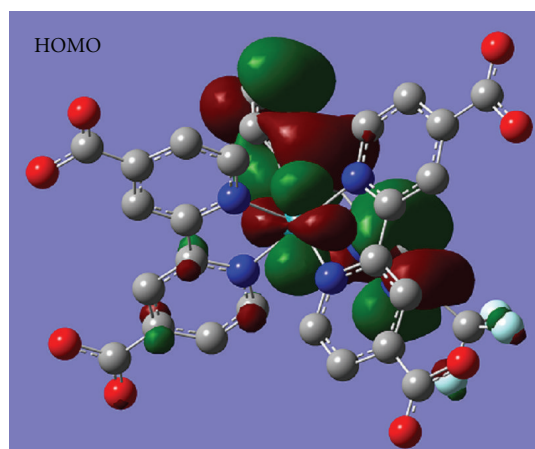
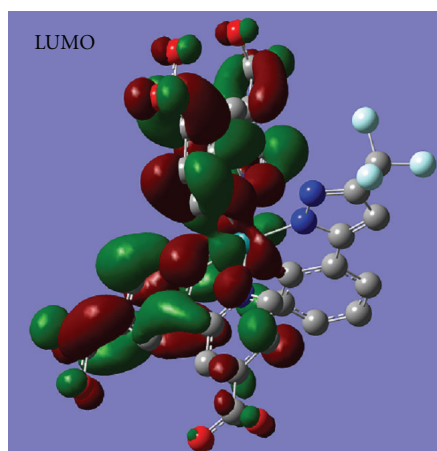


FIGURE 1: UV-vis absorption spectra of complex HIS1 (black line) and N719 (red line), measured in ethanol solution.



(a)



(b)

FIGURE 2: Graphic representation of frontier molecular orbital of complex HIS1.

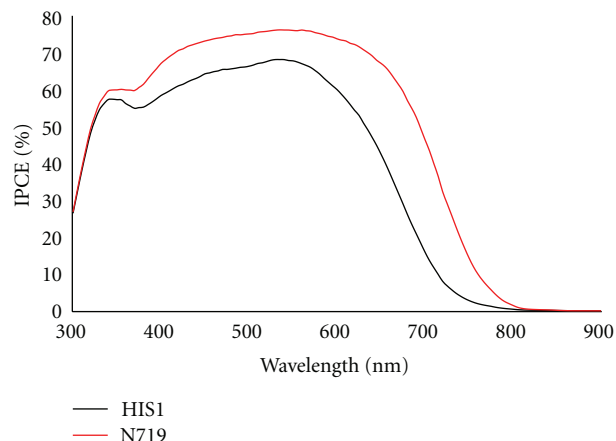


FIGURE 3: Incident photon-to-current conversion efficiency (IPCE) spectra of complex HIS1 (black line) and N719 (red line).

on the neutral polypyridyl ligands along with low-lying excited states delocalized over the polypyridyl portion(s) cyclometalating ligand (Figure 2).

Ionization potential of complex HIS1 bound to nanocrystalline  $\text{TiO}_2$  film was determined using a photoemission yield spectrometer (Riken Keiki, AC-3E). The ground-state oxidation potentials ( $\text{Ru}^{3+/2+}$ ) value of  $-5.95$  eV obtained for sensitizer HIS1 was low enough for efficient regeneration of the oxidized dye through reaction with iodide. The excited-state oxidation potential,  $E^*$  ( $\text{Ru}^{3+/2+}$ ), of sensitizer HIS1 was estimated to be  $-4.18$  eV.

Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each incident wavelength was calculated from (1), where  $I_{sc}$  is the photocurrent density at short circuit in  $\text{mA cm}^{-2}$  under monochromatic irradiation,  $q$  is the elementary charge,  $\lambda$  is the wavelength of incident radiation in nm, and  $P_0$  is the incident radiative flux in  $\text{Wm}^{-2}$ ,

$$\text{IPCE}(\lambda) = 1240 \left( \frac{I_{sc}}{q\lambda P_0} \right). \quad (1)$$

The photocurrent density-voltage curves and incident photon-to-current efficiency (IPCE) spectra of the cells based on sensitizer HIS1 under the illumination of air mass (AM) 1.5 sunlight ( $100 \text{ mW/cm}^2$ , WXS-155S-10: Wacom Denso Co., Japan). Figure 3 shows the action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for DSC composed of complex HIS1 sensitized nanocrystalline  $\text{TiO}_2$  electrode and an iodine/triiodide redox electrolyte with reference to N719-based DSC constructed under comparable conditions. Although complex HIS1 shows somewhat lower IPCE values, this problem could be solved using structural modification of complex HIS1, a subject for future research. We observed an IPCE of 68% in complex HIS1, while in the case of N719, the IPCE was 76%. The dye-sensitized solar cell based on sensitizer

HIS1 achieves a conversion efficiency ( $\eta$ ) of 4.76%, a short-circuit photocurrent density of 11.21 mA/cm<sup>2</sup>, an open-circuit voltage of 0.62 V, and a fill factor of 0.68 obtained under standard AM 1.5 sunlight. N719-sensitized solar cell under the same cell fabrication and efficiency measuring procedures achieves a conversion efficiency ( $\eta$ ) of 7.56%, a short-circuit photocurrent density of 15.83 mA/cm<sup>2</sup>, an open-circuit voltage of 0.65 V, and a fill factor of 0.73. The photo-induced voltage ( $V_{oc}$ ) is determined by the difference between the quasi-Fermi level of TiO<sub>2</sub> and redox potential of the electrolyte and is able to be enhanced as a slow recombination process of injected electrons in TiO<sub>2</sub> with oxidized species and a negative shift of band edge. *tert*-butylpyridine (TBP) is known to increase  $V_{oc}$  of DSC due to an enhanced electron lifetime and a negative shift of band edge [30, 31]. Hence, the higher  $V_{oc}$  with electrolyte containing 0.3 M TBP is (0.62 V) and without TBP 0.50 V observed.

#### 4. Conclusions

In summary, a new class of thiocyanate-free cyclometalated ruthenium-based dye HIS1 was strategically designed and synthesized. This complex shows appreciably broad absorption range. Anchoring to nanocrystalline TiO<sub>2</sub> films for light to electrical energy conversion in regenerative photoelectrochemical cells achieves efficient sensitization to TiO<sub>2</sub> electrode. With this new sensitizer power, there were a conversion efficiency of 4.76%, a short-circuit photocurrent density of 11.21 mA/cm<sup>2</sup>, an open-circuit voltage of 0.62 V, and a fill factor of 0.68 obtained under standard AM 1.5 sunlight. Further improvement in the solar cell efficiency as well as the dynamic study of electron injection and recombination in complex HIS1 sensitized nanostructured TiO<sub>2</sub> is currently on progress in our lab and will be disclosed in due course.

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