

## Synthesis and Application of New Ru(II) Complexes for Dye-Sensitized Nanocrystalline TiO<sub>2</sub> Solar Cells

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To develop photo-sensitizers for dye-sensitized solar cells (DSCs) used in harvesting sunlight and transferring solar energy into electricity, we synthesize novel Ru(II) polypyridyl dyes and describe their characterization. We also investigate the photo-electrochemical properties of DSCs using these sensitizers. New dyes contain chromophore unit of dafo (4,5-diazafluoren-9-one) or phen-dione (1,10-phenanthroline-5,6-dione) instead of the nonchromophoric donor unit of thiocyanato ligand in *cis*-[Ru<sup>II</sup>(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>] (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) coded as N3 dye. For example, the photovoltaic data of DSCs using [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)](CN)<sub>2</sub> as a sensitizer show 6.85 mA/cm<sup>2</sup>, 0.70 V, 0.58 and 2.82% in short-circuit current ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor ( $FF$ ) and power conversion efficiency ( $E_{ff}$ ), which can be compared with those of 7.90 mA/cm<sup>2</sup>, 0.70 V, 0.53 and 3.03% for N3 dye. With the same chelating ligand directly bonded to the Ru metal in the complex, the CN ligand increases the  $J_{sc}$  value by double, compared to the SCN ligand. The extra binding ability in these new dyes makes them more resistant against ligand loss and photo-induced isomerization within octahedral geometry.

**Key Words :** DSCs, New photosensitizers, Chromophore

### Introduction

Dye-sensitized solar cells (DSCs) consist of a cathode coated with Pt, a transparent oxide thin-film anode having a nanoporous structure anchored with monolayers of dye, and an iodine redox electrolyte.<sup>1</sup> The generally accepted mechanism for the photocurrent generation of DSCs results from the initial injection of an electron from the photo-excited dye to the semiconductor oxide conduction band. The electron can flow into an external circuit through a resistor and the energy is utilized, and then connected to the cathode making a closed circuit. The oxidized form of the dye on the semiconductor surface is reduced to its original state by accepting electron from an electron donor I<sup>-</sup> in the electrolyte, which completes the cycle.

After the discovery of *cis*-[Ru<sup>II</sup>(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>] (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) referred to as N3 dye,<sup>2</sup> there has been growing interest among chemists and physicists to develop a new generation of sensitizers for DSCs. It has also been reported that black dye as a photo-sensitizer showed spectacular stability as well as high power conversion efficiency around 10.4%.<sup>3</sup> It is recognized that the higher conversion efficiency of the DSCs is also dependent on the productive light capturing antenna. Absorption by these dyes in the visible and near-IR regions is attributed to metal to ligand charge transfer (MLCT) transition. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are mainly derived from the *d* orbitals of the Ru metal and the  $\pi^*$  orbital of the chelate ligand. The thiocyanato ligand shifts the ground state level negatively, leading to a red shift in the absorption property of the complex, and also contributes to the electron acceptance

from reduced redox species. The Ru complexes are adsorbed on the semiconductor oxide surface *via* either carboxylate bidentate coordination or ester bonding. The presence of functionalized anchoring groups is necessary to ensure monolayer distribution of the dye on the oxide surface, which causes a large electronic interaction between the ligand and the conduction band of TiO<sub>2</sub>, resulting in effective electron injection from LUMO into the conduction band.<sup>4</sup>

The ideal sensitizer should absorb all of the solar light including UV and visible wavelengths including that in the near IR region. For these goals major emphasis has been given on the preparation of bidentate heterocyclic ligands with aromatic ring system such as 4,4'-di(3-methoxystyryl)-2,2'-bipyridine, phenanthroline and biquinoline derivatives instead of dcbpy ligand, which are capable of coordinating with a variety of metal ions including Ru(II).<sup>5</sup> The choice of Ru(II) complexes is of particular interest due to their octahedral geometry with a variety of specific ligands in a controlled manner. Their excited states have long lifetime and long-term chemical stability.<sup>6</sup>

Many attempts have also been made to improve the photoconversion efficiency by introducing donor ligands into the central ruthenium metal instead of the thiocyanato ligand.<sup>7</sup> Although some of the non-thiocyanato complexes improved absorption of visible light, their conversion performance was not satisfactory.<sup>8</sup> There have also been many efforts to modify the properties of the sensitizers and the arrangement of the donor and acceptor ligands of the proposed complexes.<sup>9</sup> All of these works suggest that the development of new photo-sensitizers is still needed at this stage.

In this work, we focus on the design of new ruthenium

sensitizers to understand the effects of photochemical and photophysical nature of molecules on photo-conversion efficiency. Here, we synthesize novel Ru(II) dyes containing two chromophore units of dafo (4,5-diazafluoren-9-one) and phen-dione (1,10-phenanthroline-5,6-dione) instead of non-chromophoric donor for N3 dye and describe their characterization using spectroscopic techniques. We also investigate their photo-electrochemical properties for nanocrystalline TiO<sub>2</sub> solar cells.<sup>10</sup> Two ancillary ligands can be regarded as classical chelating reagents, but they exhibit significantly different electronic properties due to the presence of the carbonyl functional group. The more coordinating ability of these ligands makes the complex more resistant against its ligand loss and/or photo-induced isomerization within octahedral geometry than those of the two monodentate ligands.<sup>11</sup> The chemical and stereochemical robustness of the dye can increase the long-term stability in a solar cell, which is one of main requirements for its practical application. The binding ability of nitrogen lone pair of these ligands destabilizes the ground state level of the dye, which leads to lower energy shift of MLCT transitions. The presence of carbonyl functional group in the dafo and phen-dione ligands also enhances the coordinating ability to nanocrystalline the TiO<sub>2</sub> surface. They can also tune the metal *t*<sub>2g</sub> orbital of Ru(II) and possibly stabilize the hole that is being generated on the metal, after having injected an electron into the TiO<sub>2</sub> conduction band.<sup>12</sup>

## Experimental

**Materials.** All the solvents used in the reactions were of the reagent grade. NaOD/D<sub>2</sub>O and phen-dione were purchased from Aldrich and used as received. The following compounds were prepared according to literature methods: dafo and Ru(dcbpy)<sub>2</sub>Cl<sub>2</sub>.<sup>13</sup> Nanocrystalline TiO<sub>2</sub> were obtained from Degussa (P-25). Tin-doped indium oxide (ITO, 10 Ω·cm) electrode was supplied from Samsung Corning Co. in Korea. The ITO substrates were successively washed with acetone, ethanol and deionized water in an ultrasonicator bath for 15 min, and finally rinsed with *iso*-propanol.

**Instrumentations.** Routine UV-vis spectra were recorded on a Hewlett-Packard 8452 A Diode Array spectrophotometer. FT IR spectra were obtained on a Bomen MB 100 spectrophotometer on KBr disc. <sup>1</sup>H spectra were measured on a Varian Gemini 200 MHz FT NMR spectrometer. The chemical shift of spectra was presented in parts per million ( $\delta$ ) and referenced to TMS in NaOD/D<sub>2</sub>O. Elemental analysis data were obtained from the analytical laboratory of the Basic Science Institute of Korea. Redox properties of Ru complexes were monitored by a cyclic voltammetry (BAS 100B, Bioanalytical Systems, Inc.). Electrochemical measurements were performed using a single compartment with a standard three-electrode glass cell of Ag/AgCl and Pt as reference and a standard electrode under nitrogen atmosphere. In order to measure the photocurrent, sandwich-type DSCs were assembled with Ru complex/TiO<sub>2</sub>/ITO and Pt-sputtered ITO electrode in electrolyte composed of 0.1 mol/L

of LiI and 0.05 mol/L of I<sub>2</sub> in CH<sub>3</sub>CN. The Ru complex/TiO<sub>2</sub>/ITO was irradiated by 80 mW/cm<sup>2</sup> white light with air mass 0 and 1.5 filters as a solar simulator in the presence of a water filter (450 W Xenon lamp, Oriel Instruments), and the photocurrent was measured with a Kiethley 2400 source meter. The incident-photon-to-current conversion efficiency (IPCE) measurements were carried out without bias illumination with respect to a calibrated Melles-Friot silicon diode. IPCE was measured by changing the excitation wavelength (Photon counting spectrometer, ISS Inc. and Kiethley 2400 source meter).

## General Procedure.

[Ru(dcbpy)<sub>2</sub>(L-L)](Cl)<sub>2</sub> (**L-L = dafo or phen-dione**). A solution of 0.033 g of Ru(dcbpy)<sub>2</sub>Cl<sub>2</sub> (0.05 mmol) containing 0.07 g of KOH (1.25 mmol) in 15 mL water/15 mL MeOH was refluxed with continuous stirring for 5 h. It was cooled off and 0.014 g of dafo (0.075 mmol) or 0.016 g of phen-dione (0.075 mmol) was added to the solution. The reaction mixture was again refluxed with continuous stirring for 5 h. It was filtered to remove any unwanted impurities and evaporated to dryness using a rotatory evaporator. It was dissolved in methanol and precipitated by using diethyl ether and centrifuged out. Dissolution in methanol and precipitation was repeated several times until free of any turbidity. It was again dissolved in methanol and yellow orange colored compound precipitated by using 0.5 M nitric acid solution at pH in the range of 3 and 3.5. Finally, it was filtered by using glass frit and successively washed with ~15 mL aqueous HNO<sub>3</sub> solution containing pH 3.5, methanol and diethyl ether.

[Ru(dcbpy)<sub>2</sub>(dafo)](Cl)<sub>2</sub>. Yield: 65%. UV-vis: 480 (14.0 × 10<sup>3</sup>), 454sh (12.4 × 10<sup>3</sup>), 366 (10.0 × 10<sup>3</sup>), 304 (39.1 × 10<sup>3</sup>), 248 (22.8 × 10<sup>3</sup>), 210 (37.9 × 10<sup>3</sup>). Anal Calcd. For C<sub>35</sub>H<sub>22</sub>N<sub>6</sub>O<sub>9</sub>Cl<sub>2</sub>Ru: C, 49.89; H, 2.63; N, 9.98. Found: C, 47.55; H, 2.47; N, 10.28.

[Ru(dcbpy)<sub>2</sub>(phen-dione)](Cl)<sub>2</sub>. Yield: 60%. UV-vis: 482 (14.3 × 10<sup>3</sup>), 454sh (12.3 × 10<sup>3</sup>), 364 (12.0 × 10<sup>3</sup>), 310 (45.0 × 10<sup>3</sup>), 254 (30.0 × 10<sup>3</sup>), 220 (45.0 × 10<sup>3</sup>). Anal Calcd. For C<sub>36</sub>H<sub>22</sub>N<sub>6</sub>O<sub>10</sub>Cl<sub>2</sub>Ru: C, 49.66; H, 2.55; N, 9.66. Found: C, 48.85; H, 2.86; N, 9.14.

[Ru(dcbpy)<sub>2</sub>(L-L)](X)<sub>2</sub> (**L-L = dafo or phen-dione and X = CN, NCS**). To a solution of 0.033 g of Ru(dcbpy)<sub>2</sub>Cl<sub>2</sub> (0.05 mmol) containing 0.07 g of KOH (1.25 mmol) in 15 mL water/15 mL MeOH was added 0.1 mmol of AgX (X = CN, NCS) salt respectively. The reaction mixture was refluxed with continuous stirring for 5 h. It was cooled and filtered to remove AgCl. 0.014 g of dafo (0.075 mmol) or 0.016 g of phen-dione (0.075 mmol) was added to a clear red solution. The reaction mixture was again refluxed with continuous stirring for 5 h. It was filtered to remove any unwanted impurities and evaporated to dryness using a rotatory evaporator. It was dissolved in methanol and precipitated by using diethyl ether and centrifuged out. Dissolution in methanol and precipitation was repeated several times until free of any turbidity. It was again dissolved in methanol and yellow orange colored compound precipitated by using 0.5 M nitric acid solution at pH in the

range of 3 and 3.5. Finally it was filtered by using glass frit and successively washed with ~15 mL aqueous HNO<sub>3</sub> solution containing pH 3.5, methanol and diethyl ether.

[Ru(dcbpy)<sub>2</sub>(dafo)](CN)<sub>2</sub>. Yield: 42%. UV-vis: 504 ( $15.5 \times 10^3$ ), 380 ( $15.3 \times 10^3$ ), 310 ( $38.5 \times 10^3$ ), 250 ( $26.8 \times 10^3$ ), 212 ( $38.8 \times 10^3$ ). FT IR: 2079, 1718, 1562, 1406, 1266, 1232. <sup>1</sup>H NMR: 9.21 (2H, d), 8.69-8.19 (8H, m), 7.89-7.15 (8H, m). Anal Calcd. For C<sub>37</sub>H<sub>22</sub>N<sub>8</sub>O<sub>9</sub>Ru: C, 53.95; H, 2.69; N, 13.61. Found: C, 55.22; H, 2.82; N, 12.95.

[Ru(dcbpy)<sub>2</sub>(phen-dione)](CN)<sub>2</sub>. Yield: 40%. UV-vis: 508 ( $13.8 \times 10^3$ ), 384 ( $11.7 \times 10^3$ ), 310 ( $45.7 \times 10^3$ ), 250sh (24.1  $\times 10^3$ ), 212 ( $39.7 \times 10^3$ ). FT IR: 2079, 1718, 1560, 1406, 1269, 1232, 773. <sup>1</sup>H NMR: 8.72 (2H, d), 7.99-7.42 (8H, m), 7.29-7.11 (8H, m). Anal Calcd. For C<sub>38</sub>H<sub>22</sub>N<sub>8</sub>O<sub>10</sub>Ru: C, 53.58; H, 2.60; N, 13.16. Found: C, 52.06; H, 2.44; N, 13.52.

[Ru(dcbpy)<sub>2</sub>(dafo)](NCS)<sub>2</sub>. Yield: 57%. UV-vis: 480 (8.10  $\times 10^3$ ), 454sh (7.10  $\times 10^3$ ), 362sh ( $4.80 \times 10^3$ ), 306 (26.7  $\times 10^3$ ), 248sh (14.5  $\times 10^3$ ), 208 (26.8  $\times 10^3$ ). FT IR: 2104, 1718, 1610, 1406, 1232, 770. <sup>1</sup>H NMR: 8.71 (2H, d), 7.99-7.43 (8H, m), 7.29-7.11 (8H, m). Anal Calcd. For C<sub>37</sub>H<sub>22</sub>N<sub>8</sub>O<sub>9</sub>S<sub>2</sub>Ru: C, 49.83; H, 2.42; N, 12.24. Found: C, 47.80; H, 2.66; N, 11.90.

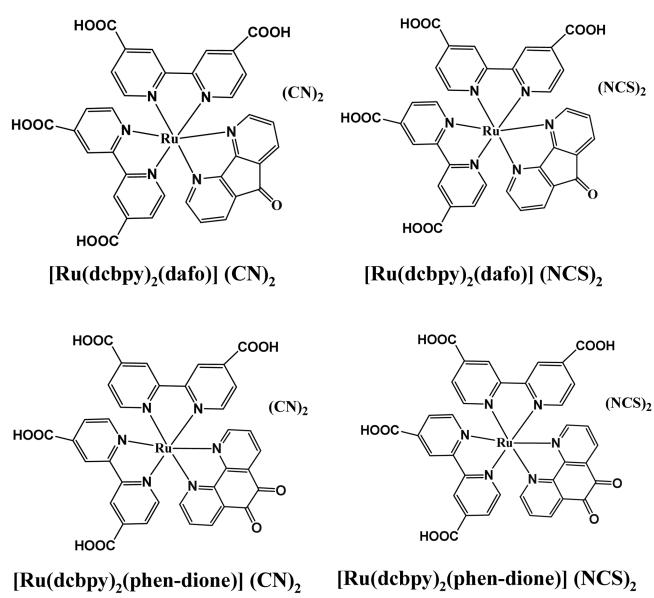
[Ru(dcbpy)<sub>2</sub>(phen-dione)](NCS)<sub>2</sub>. Yield: 52%. UV-vis: 484 ( $23.0 \times 10^3$ ), 456sh ( $18.3 \times 10^3$ ), 364sh ( $18.4 \times 10^3$ ), 308 (80.0  $\times 10^3$ ), 250sh (40.0  $\times 10^3$ ), 222 ( $73.0 \times 10^3$ ). FT IR: 2109, 1719, 1593, 1383, 1230, 771. <sup>1</sup>H NMR: 8.71 (2H, d), 7.99-7.43 (8H, m), 7.29-7.11 (8H, m). Anal Calcd. For C<sub>38</sub>H<sub>22</sub>N<sub>8</sub>O<sub>10</sub>S<sub>2</sub>Ru: C, 49.83; H, 2.42; N, 12.24. Found: C, 47.80; H, 2.66; N, 11.90.

**Preparation of Film Electrode.** Transparent films of electrodes were obtained by spin coating TiO<sub>2</sub> colloidal solution on conducting glass plates (ITO). Then, the films were sintered for 30 min at 450 °C in air. The thickness of the TiO<sub>2</sub> layer was about 7 μm determined using the surface profiler (P-10, TENCOR. Co.). The annealed films were impregnated with 0.5 mM Ru(II) sensitizer in MeOH for 24h at room temperature. Each dye-coated film was soaked in MeOH for 3h to remove unattached dye molecules. The resulting sensitizer-coated TiO<sub>2</sub> film was washed with ethanol and then used to fabricate the DSCs.

## Results and Discussion

Scheme 1 shows the chemical structure of each new Ru(II) dye. Since the dye molecules play a key role in harvesting sunlight and solar energy conversion into electricity, many efforts have been made to develop new sensitizers. Many Ru(II) polypyridyl complexes have been employed to sensitize nanocrystalline titanium oxide semiconductors, since they have intense and highly efficient absorption band of MLCT in the visible region and a long excited lifetime. Although one of them, *cis*-[Ru<sup>II</sup>(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>], is the most frequently used as a sensitizer in DSCs systems, the photoconversion performance still shows that there is room for improvement.<sup>1-8</sup>

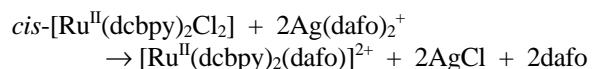
New Ru(II) complexes, [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)]X<sub>2</sub> or [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(phen-dione)]X<sub>2</sub> (X=Cl, CN, NCS), which contain



[Ru(dcbpy)<sub>2</sub>(phen-dione)](CN)<sub>2</sub> [Ru(dcbpy)<sub>2</sub>(phen-dione)](NCS)<sub>2</sub>

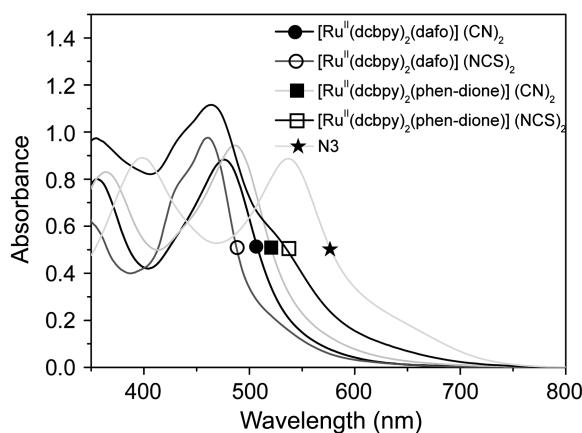
**Scheme 1.** Chemical Structures of New Ru(II) Dyes.

two ancillary ligands of dafo and phen-dione instead of nonchromophoric thiocyanato ligand are synthesized. The ligands exhibit distinct properties such as containing a reactive exocyclic ketone and having a more rigid structure compared to analogue 2,2'-bipyridine. Ru(II) heterocyclic complexes were obtained in the traditional way by reaction of *cis*-[Ru<sup>II</sup>(dcbpy)<sub>2</sub>Cl<sub>2</sub>] with dafo or phen-dione in a basic solution of water and methanol. For example, [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)]<sup>2+</sup> was prepared by metathesis as follows. The procedure required the prior preparation of the Ag<sup>+</sup> complex of the heterocyclic ligand and then its reaction with the appropriate ruthenium precursor. The driving force in the reaction is precipitation of AgCl.<sup>14</sup>



The complexes were initially characterized by electronic spectra. UV-vis absorption spectra of Ru(II) complexes are shown in Figure 1. Each  $5 \times 10^{-5}$  M stock solution for the spectra was prepared in 50 cm<sup>3</sup> of 5:1 H<sub>2</sub>O:EtOH mixture containing 0.1 M NaNO<sub>3</sub>. NaNO<sub>3</sub> was added to avoid precipitation while performing acid-base titration; complexes were insoluble in H<sub>2</sub>O, but sparingly soluble in aqueous basic medium. The pH of the solution was made to 11 by using 0.2 M NaOH solution and then by adding diluted nitric acid gradually decreased its pH. Generally the bands in the UV region at 300 and 250 nm are assigned to intra ligand  $\pi-\pi^*$  charge-transfer transitions of dcbpy as well as dafo or phen-dione ligand, respectively.

For [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)](X)<sub>2</sub> and [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(phen-dione)](X)<sub>2</sub> (X=Cl, CN, NCS) complexes, most of them show two broad visible bands around 480 and 360 nm, which are assigned to MLCT origin. However, the broad MLCT bands shift to around 500 and 380 nm for the complexes of cyanate anions. The bands in the UV region around 310 and 250 nm for all the Ru complexes are



**Figure 1.** UV-vis Absorption Spectra of Ru(II) Complexes.

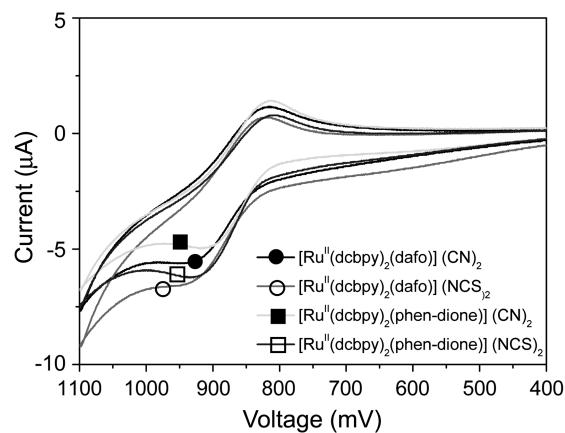
assigned to intra ligand  $\pi-\pi^*$  charge transfer transitions of dcbpy as well as dafo or phen-dione ligands.

Deprotonation of the COOH groups in the  $[\text{Ru}^{II}(\text{dcbpy})_2(\text{dafo})](\text{NCS})_2$  complex blue shifts the lower energy MLCT  $d_{\pi-\pi^*}$  charge-transfer bands from 480 to 466 nm and from 360 to 348 nm as shoulder peak with a higher molar absorption coefficient. The blue shift is due to an increase in the energy of LUMO of ligand, causing the  $\pi-\pi^*$  and  $d_{\pi-\pi^*}$  transitions to occur at higher energies. However, the band at 250 nm due to  $\pi-\pi^*$  charge-transfer transitions of the dcbpy ligand, is unaffected in the pH range of 2 to 11.<sup>15</sup> The molar extinction coefficient of the prepared complexes is generally higher than that of *cis*- $[\text{Ru}^{II}(\text{dcbpy})_2(\text{NCS})_2]$ . There are also two shoulder peaks around 346 and 440 nm, which are tentatively attributed to MLCT transitions.

FT IR spectra of all the prepared complexes show a strong broad band in the region of around  $1720 \text{ cm}^{-1}$  due to the C=O stretching on the carboxylate group.<sup>16</sup> The weak peak around  $1230 \text{ cm}^{-1}$  is due to  $\nu(\text{C}-\text{O})$  stretching. The spectra of the complexes also shows the presence of carboxylate asymmetric ( $\nu(-\text{COOas})$ ) between  $1560$  and  $1610 \text{ cm}^{-1}$  and symmetric ( $\nu(-\text{COOs})$ ) around  $1400 \text{ cm}^{-1}$  together with a strong  $\nu(\text{NC})$  of the cyanate anions at  $2079 \text{ cm}^{-1}$  and of the thiocyanate anions at  $2104 \text{ cm}^{-1}$ .<sup>16a</sup> The C-H stretching vibrations of the heteroaromatic pyridines expected about  $3100 \text{ cm}^{-1}$  are weak because of a very strong moisture background.

The  $^1\text{H}$  NMR spectra of the complexes  $[\text{Ru}^{II}(\text{dcbpy})_2(\text{dafo})]\text{X}_2$  where X is CN or NCS show a strong doublet at 9.21 and 8.71 ppm for 6,6-positioned two protons of bis-dcbpy and a singlet at 8.69 and 7.99 ppm for 3,3-positioned four protons of bis-dcbpy ligands.<sup>3b,3c,17</sup> The doublet at 8.48 and 7.78 ppm is assigned to 1,8-protons of the dafo ligand chelated to the ruthenium metal center. The multiplet around 8.30 and 7.50 ppm is assigned to two 2,7-protons of the dafo ligand. There are multiple peaks between 7.89–7.15 ppm and 7.29–7.11 ppm, which are assigned to the mixing of the coupling of four protons 6,6-positioned protons of the bis-dcbpy ligands as well as the 3,6-protons of the dafo ligand.

The  $^1\text{H}$  NMR spectra of the complexes  $[\text{Ru}^{II}(\text{dcbpy})_2(\text{phen-dione})]\text{X}_2$  (X = CN, NCS) also show a strong



**Figure 2.** Cyclic Voltammogram of Ru(II) Complexes in 0.1 M  $[\text{N}(\text{Bu})_4]\text{[BF}_4]$  as Supporting Electrolyte with a Scan Rate of 50 mV/s.

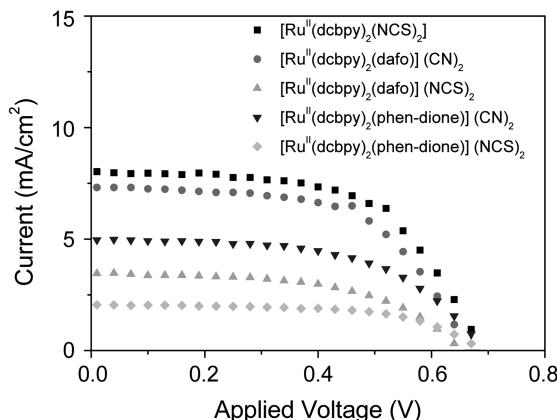
doublet at 8.72 ppm for 6,6-positioned two protons of bis-dcbpy and a strong singlet at 7.90 ppm for four protons of bis-dcbpy ligands. The doublet around 7.80 ppm and the sextet around 7.50 ppm are assigned to 4,7-protons and 3,8-protons of the phen-dione ligand chelated to the ruthenium. Multiplet peaks between 7.29–7.11 ppm result from the mixing of coupling of four protons 6,6-positioned protons of the bis-dcbpy ligands as well as the 3,6-protons of the phen-dione ligand. The  $^1\text{H}$  NMR spectra of both complexes are complicated in nature and show a similar pattern of splitting except 4,7-positioned protons of the phen-dione ligand to more or less upfield chemical shift in comparison to the 1,8-protons of dafo ligand.

The redox properties of the prepared Ru complexes are monitored by cyclic voltammetry of Pt standard electrode in MeOH containing 0.1 M of  $[\text{N}(\text{Bu})_4]\text{[BF}_4]$  as supporting electrolyte with a scan rate of 50 mV/s. As shown in Figure 2, each ruthenium complex indicates Ru(II)/Ru(III).<sup>18</sup> The  $E_{\text{ox}}$  of four different complexes with CN, NCS, dafo, phen-dione showed small changes on the HOMO level. The  $[\text{Ru}(\text{dcbpy})_2(\text{dafo})](\text{CN})_2$  gives oxidation potential of 833 mV, which is the lowest value among them.  $[\text{Ru}(\text{dcbpy})_2(\text{phen-dione})](\text{CN})_2$  shows 816 mV, and the difference between them is only 20 mV. The phen-dione ligand generally increases the oxidation potential by lowering HOMO level. Upon irradiation, the oxidation peak of ruthenium complex shifts to Ru(III)/Ru(IV), which is independently monitored by the chemical oxidation with Ce(IV) sulfate.<sup>18,19</sup> However, LUMO level of newly prepared dyes are different depending on the combination of ligands as shown in Table 1. The maximum absorptions of the dyes are blue shifted from the one of N3 dye, 536 nm.  $[\text{Ru}(\text{dcbpy})_2(\text{phen-dione})](\text{NCS})_2$  shows the maximum absorption at 463 nm with a band gap of 1.70 eV.  $[\text{Ru}(\text{dcbpy})_2(\text{dafo})](\text{CN})_2$  has the biggest band gap of 1.89 eV with an absorption maximum at 460 nm.

The photovoltaic performance of the DSCs with new Ru dyes on  $\text{TiO}_2$  films is investigated by measuring the  $J-V$  characteristics. A sandwich-type cell is prepared in the presence of  $\text{LiI}/\text{I}_2/\text{acetonitrile}$ . The cell is illuminated by 80

**Table 1.** Photo-electrical Parameters of New Dyes

Dye	$E_{ox}^a$ (mV)	Band gap (eV)	LUMO <sup>b</sup>	HOMO <sup>b</sup>
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (dafo)](CN) <sub>2</sub>	833	1.89	-3.56	-5.45
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (dafo)](NCS) <sub>2</sub>	836	1.92	-3.52	-5.45
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (phen-dione)](CN) <sub>2</sub>	816	1.81	-3.63	-5.44
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (phen-dione)](NCS) <sub>2</sub>	819	1.70	-3.75	-5.45

<sup>a</sup> vs. Ag/AgCl. <sup>b</sup> vs. vacuum**Figure 3.** *J-V* curve of DSCs with Ru(II) Complexes.

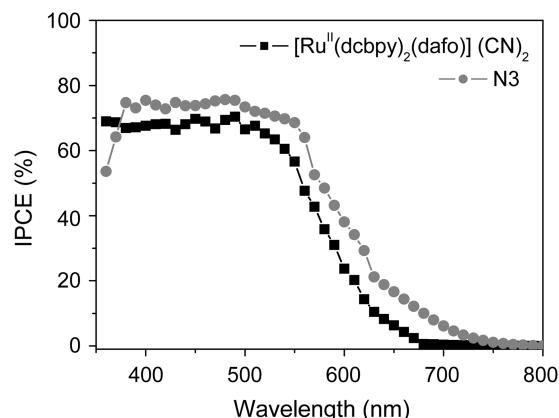
mW/cm<sup>2</sup> white light with air mass 0 and 1.5 filters as a solar simulator in the presence of a water filter. Figure 3 shows the typical *J-V* curves of the DSCs. The solar cell with the [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)](CN)<sub>2</sub> shows the highest conversion efficiency of 2.98% with  $J_{sc}$  of 7.33 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.66 V, and  $FF$  of 0.61 shown in Table 2. As a reference, a solar cell with N3 dye is prepared under the identical conditions. Compared to the cell with N3 dye, new dyes show good  $FF$  in the range of 0.56–0.61. However,  $J_{sc}$  is relatively decreased from 7.33 mA to 2.07 mA. With the same chelating ligand, the  $J_{sc}$  of Ru complex with CN ligand almost doubled in value compared to SCN ligand.  $V_{oc}$  of cells with NCS was also smaller than that of CN ligand. Though the number of compounds prepared is not enough to draw any definitive conclusion, the CN ligand seems to be a good choice to design an efficient photosensitizer.

The photocurrent is determined by the amount of absorbed light and the internal conversion efficiency. An experimentally accessible value is the incident photon to current

**Table 2.** Performance Parameters of DSCs Containing Ru(II) Dyes

Dye	$I_{sc}^a$ (mA/cm <sup>2</sup> )	$V_{oc}^b$ (V)	$FF^c$	$E_{ff}^d$ (%)
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (NCS) <sub>2</sub> ]	8.01	0.70	0.60	3.31
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (dafo)](CN) <sub>2</sub>	7.33	0.66	0.61	2.98
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (dafo)](NCS) <sub>2</sub>	3.46	0.65	0.54	1.22
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (phen-dione)](CN) <sub>2</sub>	4.97	0.69	0.56	1.92
[Ru <sup>II</sup> (dcbpy) <sub>2</sub> (phen-dione)](NCS) <sub>2</sub>	2.07	0.69	0.60	0.86

<sup>a</sup>short-circuit current. <sup>b</sup>open-circuit voltage. <sup>c</sup>fill factor. <sup>d</sup>power conversion efficiency

**Figure 4.** Incident photon-to-current conversion efficiency (IPCE) of [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)](CN)<sub>2</sub> and N3 dye on TiO<sub>2</sub>/ITO.

efficiency, IPCE (%), which is defined and calculated using equation

$$\text{IPCE} = (1240 * I_{sc}) / (\lambda * P_{in})$$

where  $\lambda$  [nm] is the incident photon wavelength,  $I_{sc}$  [uA/cm<sup>2</sup>] is the photocurrent of the device and  $P_{in}$  [W/m<sup>-2</sup>] is the incident power. Figure 4 shows the IPCE spectra of the [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)](CN)<sub>2</sub> and N3 dye on TiO<sub>2</sub>/ITO. The IPCE spectrum of [Ru<sup>II</sup>(dcbpy)<sub>2</sub>(dafo)](CN)<sub>2</sub> reaches up to 70% by the monochromatic illumination at 490 nm. As a reference, IPCE of N3 dye on TiO<sub>2</sub>/ITO is 76%, which is smaller than previously reported value.<sup>1a</sup>

## Conclusion

New types of ligand were used to prepare photosensitizers for the nanocrystalline DSCs. Chelating ligands of dafo and phen-dione were coordinated with the octahedral Ru complex containing either CN or SCN anion. The Ru complexes showed similar HOMO and LUMO level compared to those of N3 dye. Compared to cells with N3 dye, new dyes showed good fill factor in the range of 0.54–0.61. With the same chelating ligand on Ru complex, the CN ligand increased the  $J_{sc}$  up to double the value compared with the SCN ligand.

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