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## Thiocyanate-Free Ruthenium(II) Sensitizers with A *bi*-imidazole Ligand in Dye-Sensitized Solar Cells (DSSCs)

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#### ABSTRACT

In this study, tris-heteroleptic Ru(II) sensitizers denoted as SD-15 and SD-16 with 4,4',5,5'tetramethyl-1H,1'H-2,2'-bis-imidazole moiety as ancillary ligand were designed, synthesized and characterized by FTIR- ATR, <sup>1</sup>H-NMR and UV-Vis spectrophotometry. Structural modulations resulted in red shift in low-energy metal-to-ligand charge transfer (MLCT) absorption peak. The novel bis-imidazole based Ru(II) sensitizer was adsorbed on TiO<sub>2</sub> surface via –COOH anchoring groups. Band gap, ground and excited state oxidation potentials were measured. Photovoltaic performance of as-fabricated solar cells was measured and showed that the presence of *bis*imidazole which provided more negative free energy for dye regeneration ( $-\Delta G_{regeneration}$ ) and less driving force for electron injection ( $-\Delta G_{\text{injection}}$ ) into the conduction band edge of TiO<sub>2</sub>. Therefore, SD-15 and SD-16 resulted in lower  $J_{SC}$  of 10.20 and 3.52 mA cm<sup>-2</sup>, respectively, than N719. Open-circuit photovoltage ( $V_{OC}$ ) of SD-15 and SD-16 was 0.58 and 0.52 V less than N719 under same experimental conditions due to decreased eTiO<sub>2</sub> life time of 0.71 ms compared to 8.8 ms of N719 for injected electrons calculated by impedance measurements. Our effort in this research program led to the developments of more stable Ru(II) complexes compared to N719 NCS-based complexes; however, the conversion efficiency was lower. Hence, fine-tuning of biimidazole is needed to identify more efficient NCS-free Ru(II) sensitizers for higher efficiency DSSCs.

#### **1. INTRODUCTION**

In recent years, efforts have been made to explore the efficient ways to harness the sunlight. Solar energy is getting an exceptional attention, which indicates quick advancement, particularly in the field of photovoltaics, opening up new horizon in research and innovation for utilizing renewable energy sources.<sup>1</sup> One of the major advancement in photovoltaics field is dye-sensitized solar cells (DSSCs), introduced by O' Regan and Grätzel in 1991.<sup>2</sup> They have captivated deep consideration because of their low-cost fabrication process and ready to work at more extensive edges and under low light conditions.<sup>3</sup> Sensitizer (dye molecules) is a key component of DSSC, which absorbs light from the visible region and then initiates the movement of electron from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of dyes.<sup>4</sup>

Although the DSSC showed moderate to good efficiency, but still long-term stability of solar devices is not promising.<sup>5</sup> Sensitizers can undergo degradation quickly owing to the presence of thiocyanate (-NCS) moiety, thus lowering the lifetime of solar devices.<sup>6</sup> A number of sensitizers have been tested including N719, N3 and black dye<sup>7,8</sup> but they also are very unstable due to labile nature of thiocyanate moiety present in as-reported sensitizers.<sup>9,10</sup> To enhance the long-term stability of solar devices, a number of attempts have been made to prepare thiocyanate (-NCS) free sensitizers.<sup>11,12</sup> Such sensitizers offer extended and enhanced structural stability to devices for example, pyrid-2-yl pyrazolate or triazolate,<sup>13,14</sup> pyridyl-azolate,<sup>15</sup> pyrid-2-yltetrazolate,<sup>16</sup> 8-oxyquinolate,<sup>17,18</sup> dianionic bipyrazolate<sup>19</sup> based solar devices showed moderate to good efficiency (1.3 to 9.6 %), thus paving the way to explore and design a better and efficient thiocyanate free sensitizers.

Recently, H. Cheema et al. reported thiocyante-free ruthenium dye (HD-11) with the addition of 3-trifluoromehtyl pyrazole<sup>10</sup> which showed %  $\eta$  upto 5.2%. Similarly, C. P. Berlinguette and co-worker tested phenylpyridine (ppy)<sup>20</sup> as thiocyanate-free sensitizer in DSSC and the molecular structures of both the dyes are shown in Fig. 1. In this work, we report *bi*-midazole based thiocyanate free ruthenium sensitizers and to the best of our knowledge, these has not been investigated in literature for DSSC applications as shown in Fig. 2.



Fig. 1. Molecular structures of thiocyanate-free tris-heteroleptic Ru(II) sensitizers<sup>10,20</sup>

The as-prepared SD-15 and SD-16 compounds were characterized by FTIR and <sup>1</sup>H-NMR. The photophysical and electrochemical characterizations were carried using UV-Visible spectroscopy and cyclic voltammetry. Impedance spectroscopy was used to study interfere charge recombination resistance and electron life time at dye/TiO<sub>2</sub> interface. IPCE and I-V graph for solar cells sensitized with SD-15 and SD-16 were measured under 1 sun illumination with similar conditions.



Fig. 2. Chemical Structure of thiocyanate-free Ru(II) dyes.

#### **2. EXPERIMENTAL**

#### 2.1. MATERIALS AND EQUIPMENTS

All chemicals were purchased from Sigma-Aldrich, Fisher Scientific or TCI-America and were used as received. Silica (230-400 mesh, Grade 60) for purification of dyes was purchased from Fischer Scientific. FT-IR (ATR) spectra were recorded on a Nicolet Nexus 470 FTIR spectrometer (Thermo Scientific, USA) and UV-Visible spectra were measured by using Cary 300 spectrophotometer. The Mass Spectrometry Analysis was carried out on a high-resolution mass spectrometer – the Thermo Fisher Scientific Executive Plus MS, a bench top full-scan Orbitrap<sup>TM</sup> mass spectrometer using Electro-spray Ionization (ESI). Samples were dissolved in methanol, were sonicated for 15 minutes, and then diluted 1:1 with 20 mM ammonium acetate and analyzed via syringe injection into the mass spectrometer at a flow rate of 10  $\mu$ L/min. <sup>1</sup>H-NMR spectra were recorded in a Bruker 500 MHz spectrometer. Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc.) was used to measure fluorescence at room temperature.

#### 2.2. Synthesis of the thiocyanate-free tris-heteroleptic Ru(II) sensitizers

The synthesis of both the ancillary ligands was carried out according to the procedure reported in literature using Knoevenagel condensation type reaction. Detailed synthetic procedures for the proposed thiocyanate-free *tris*-heteroleptic ruthenium(II) complexes SD-15 & SD-16 can be found in the Supporting Information (SI). Typical three step one pot procedure was employed to synthesize the proposed sensitizers according to reported literature.<sup>10</sup> The yield of the crude products was in the range of 65–70%, which were purified through the Silica column for two times to get the highly pure product in 45–50% yield. The pure product was then characterized by FTIR and <sup>1</sup>H-NMR.

**Synthesis of sensitizer SD-15.** Dark red solid (140 mg, yield 69%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.93 (s, 1H), 9.02 (s, 1H), 8.76 (d, *J* = 5.7 Hz, 1H), 8.53 (s, 1H), 8.34 – 8.29 (m, 2H), 8.22 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.66 (m, 4H), 7.62 – 7.57 (m, 2H), 7.51 (s, 1H), 7.16 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 15.7 Hz, 1H), 4.50 (q, *J* = 9.5, 3.7 Hz, 2H), 2.48 (s, 6H), 2.19 (s, 6H), 1.46 (t, *J* = 8.6 Hz, 3H).

Synthesis of sensitizer SD-16. Reddish orange solid (128 mg, yield 66%). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  9.78 (s, 1H), 8.90 (d, J = 5.0 Hz, 1H), 8.85 (s, 1H), 8.63 (m, 2H), 8.42 (d, J = 4.6

Hz, 1H), 7.90 (d, *J* = 5.1 Hz, 1H), 7.27 (d, *J* = 14.3 Hz, 1H), 7.15 – 7.06 (m, 4H), 7.03 – 6.94 (m, 10H), 6.89 (d, *J* = 14.7 Hz, 1H), 2.56 (s, 6H), 2.20 (s, 6H).

#### 2.3. Time correlated single photon counting (TCSPC) measurements

Fluorescence spectra were recorded in a 1 cm path length quartz cell using  $2 \times 10^{-5}$  M solutions on Fluorolog-311. The emitted light was detected in the steady state mode using a Hamamatsu R2658 detector. The emission was measured in the steady state mode by exciting at the MLCT  $\lambda_{max}$  for each dye with exit and entrance slits set at 11 nm with 0.1 s integration time.

## 2.4. Ground state oxidation potential (GSOP) and excited state oxidation potential (ESOP) measurements

The experimental HOMO and  $E_{0-0}$  energy values for SD-15 and SD-16 were measured using a cyclic voltammetry (CV) and the absorption onset, respectively. The CV was carried out in DMF with 0.1M [TBA][PF<sub>6</sub>]<sup>-</sup> as an electrolyte at a scan rate of 50 mV s<sup>-1</sup>. Glassy carbon was used as the working electrode (WE), Pt wire as counter electrode and Ag/Ag<sup>+</sup> in acetonitrile was used as the reference electrode. Fc/Fc<sup>+</sup> was used as an internal reference, voltage measured was converted to NHE by addition of 0.63 V. Figures 3S–4S (SI) show the CV graphs of all the sensitizers.

#### 2.5. TiO<sub>2</sub> electrode preparation and device fabrication

The photo-anodes composed of nanocrystalline TiO<sub>2</sub> and counter electrodes were prepared using literature procedures.<sup>21</sup> Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of 8  $\Omega$ /cm<sup>2</sup>, TEC 8, Pilkington) were washed with detergent, deionized water, dry acetone and absolute ethanol, sequentially. After this FTO glass plates were immersed into a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 min and washed with water and ethanol. Thin layer (8-12 mm thick) of TiO<sub>2</sub> (Solaronix, Ti-Nanoxide T/SP) was deposited (active area, 0.18 cm<sup>2</sup>) on transparent conducting glass by squeegee printing. After drying the electrodes at 500 °C for 30 min, scattering layer (5 mm thick) TiO<sub>2</sub> particles (Solaronix, Ti-Nanoxide R/SP) were printed. The TiO<sub>2</sub> electrodes were heated under an airflow at 350 °C for 10 min, followed by heating at 500 °C for 30 min. After cooling to room temperature, the TiO<sub>2</sub> electrodes were treated with 40 mM aqueous solution of TiCl<sub>4</sub> at 70 °C for 30 min and then washed with water and ethanol. The

electrodes were heated again at 500 °C for 30 min and left to cool to 80 °C before dipping into the dye solution. The dye solutions (0.3 mM) were prepared in 1:1:1 acetonitrile, *tert*-butyl alcohol and DMSO. Deoxycholic acid was added to the dye solution as a coadsorbate at a concentration of 20 mM. The electrodes were immersed in the dye solutions with active area facing up and then kept at 25 °C for 20 h to adsorb the dye onto the TiO<sub>2</sub> surface.

For preparing the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1 M HCl in EtOH, and sonication in acetone bath for 10 min. These washed TCO were then dried at 400 °C for 15 min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 mints. The dye sensitized  $TiO_2$  electrodes were sandwiched with Pt counter electrodes and the electrolyte (Solaronix, Iodolyte AN-50) was then injected into the cell, while the two electrodes were held together with the clips.

#### 2.6. Photo-electrochemical measurements

Photocurrent-voltage characteristics of DSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (100 mW cm<sup>-2</sup>). The measurement was fully controlled by Oriel IV Test Station software. IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV NO Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochromator. Calibration of incident light was performed before measurements using a silicone photodiode (IF035, PV Measurements). All the measurements were carried out without the use of anti-reflecting film.

#### 2.7. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a 450 W-xenon lamp (91160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz - 200 kHz at room temperature. The applied bias voltage was set at the  $V_{OC}$  of the DSCs,

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with AC amplitude set at 10 mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic).

**3. Results & Discussion:** The synthesis of proposed *tris*-heteroleptic ruthenium(II) complexes was carried out according to already reported procedure<sup>10</sup> in a typical three step one pot method.

**3.1. Photophysical measurements:** UV-Vis absorption spectra of SD-15, SD-16 and N719, measured in DMF using a concentration of  $2 \times 10^{-5}$  M, are given in Fig. 4 and the results are summarized in Table 1.

Structural modification of N719 by the replacement of NCS with *bi*-imidazole along with carbazole and triphenyl amino ancillary ligand resulted in red shifted absorption spectra of SD-15 and SD-16 respectively. Red shift in absorption spectra was caused by the stabilizing effect of *bi*-imidazole on both HOMO and LUMO. HOMO destabilization was expected with the introduction of strong electron donating carbazole and triphenyl amino groups as ancillary ligand.<sup>22,23</sup> the tuning of ground state oxidation potential is depicted in Fig. 4. The dominant role of *bi*-imidazole in stabilizing ground state can be attributed to the substantial delocalization of HOMO on NCS part as found previously by DFT calculations.

Table 1. Experimental	l Absorption and	emission properties	of <b>SD-15</b> ,	<b>SD-16</b> and <b>N719</b>
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Sensitizers	Absorption $\lambda_{max}(nm)$	$\varepsilon (\mathrm{M}^{-1} \mathrm{cm}^{-1})$	Emission $\lambda_{max}$ (nm)
SD-15	300; 392; 532 (d $\rightarrow \pi^*$ )	62,950; 42,650; 17,000	728
SD-16	302; 413; 523 (d $\rightarrow \pi^*$ )	90,500; 26,250; 21,150	748
N719	310; 381; 529 (d $\rightarrow \pi^*$ )	46,100; 14,400; 12,800	722



Fig. 3. UV–Vis absorption (solid-lines) and emission spectra (dashed-lines) of complexes SD-15 and SD-16, measured in DMF ( $2 \times 10^{-5}$  M)



Fig. 4. Energy level diagram and comparison between GSOP and ESOP of SD-15, SD-16 and N719.

#### **3.2. Electrochemical measurements**

Cyclic voltammetry (CV) was used to measure and compare the ground state oxidation potential (GSOP) of SD-15 and SD-16 in solution. CV graph (SI Fig. S3-S4) was used to calculate the oxidation onset which is equivalent to the GSOP (ground state oxidation potential. Additionally  $E_{0-0}$  was calculated from onset of absorption. The values of  $E_{0-0}$  and GSOP were used to calculate the ESOP (excited state oxidation potential, the values in volts (V) against NHE were converted to electron volt (eV) according to Equation (1).

$$ESOP = [(GSOP(V) + 4.7) - E_{0-0} eV$$
(2)

GSOP and ESOP for SD-15, SD-16 and N719 are compared in Fig. 4, Table 2. GSOP potential of SD-15 (-5.8 eV) was lower in energy compared to I<sub>3</sub>/I<sup>-</sup> redox couple (-5.2 eV or -0.5 V vs. NHE),<sup>24</sup> thus providing ample driving force for efficient dye regeneration. ESOP of SD-15, SD-16 and N719 was 0.31, 0.40 and 0.43 eV higher in energy higher in energy than the conduction band edge of semiconductor nanocrystalline TiO<sub>2</sub> (-4.2 eV)<sup>25</sup> which is expected to result in efficient electron injection for N719. It was found that electron injection free energy for SD-15 and SD-16 was 0.31 and 0.4 eV, since the lowest energy difference between ESOP and TiO<sub>2</sub> conduction band for efficient electron injection is not precisely determined, but usually expected to be more than 0.15 eV.<sup>26</sup> Hence, electron injection free energies of both *tris*-heteroleptic Ru(II) complexes were thermodynamically favorable.

$\boldsymbol{E}_{0-0}$	GSOP (HOMO)	ESOP (LUMO)
1.95	-5.84	-3.89
1.93	-5.73	-3.80
1.99	-5.76	-3.77
	1.95 1.93 1.99	1.95 -5.84   1.93 -5.73   1.99 -5.76

**Table 2.** Excited state oxidation potential ( $E^*$ ), ground state oxidation potential and the lowest singlet–singlet electronic transitions ( $E_{0-0}$ ) for SD-15, SD-16 and N719 experimental.

#### 3.3. Photovoltaic device characterizations

Photovoltaic characterizations were carried out in order to establish the structure–property relationship with the replacement of NCS and influence of change in energy levels of SD-15 and SD-16 on solar cells, Photocurrent action spectra for SD-15 and SD-16 are shown in Fig. 5 and details about solar cell preparations and assembly are given in SI. Higher IPCE response was recorded for SD-15 than SD-16 due to the presence of strong electron donating carbazole moiety. Incident photon to current conversion efficiency (IPCE) response of higher than 40% from 400 nm to 600 nm was exhibited by SD-15. SD-15 showed higher molar absorptivity in solution, however absorbed photons were not translated to photocurrent which can be attributed to lower thermodynamic free energy of electron injection. However, this can can concluded based on IPCE results that electron injection free energy should be higher than 0.15 eV in order to get efficient electron injection.<sup>26</sup>



Fig. 5. IPCE obtained with dyes SD-15 and SD-16 anchored on nanocrystalline TiO<sub>2</sub> film.

I-V characteristics of the solar devices prepared from SD-15 and SD-16 are in Fig. 6. Better IPCE response of SD-15 translated in term of higher  $J_{SC}$  of 10.20 mA cm<sup>-2</sup> compared to 3.52 mA cm<sup>-2</sup> of SD-16. Lower  $J_{SC}$  for both SD-15 and SD-16 than N719 is attributed to low free energy for electron injection into the conduction band of TiO<sub>2</sub>.

Solar cells with SD-15 and SD-16 gave overall power conversion efficiency (%  $\eta$ ) of 3.3 with  $V_{\text{OC}}$  of 0.58 V and *ff* of 0.56 and 1.0 with  $V_{\text{OC}}$  of 0.52 V and *ff* of 0.58 compared to (%  $\eta$ ) of 7.7

for N719 ( $V_{OC} = 0.77$  and ff = 0.71). The fundamental energy loss or loss of potential in a solar cell can be calculated by following the relation as discussed previously.<sup>27</sup>

Potential loss in a solar cell = Energy of charge generating photon  $- V_{OC}$  obtained from solar cell.

Energy of charge generating photon can be calculated from the onset of IPCE spectra which was 1.57 eV for N719 and 1.70 and 1.97 eV for SD-15 and SD-16 respectively. The potential loss for SD-15 and SD-16 based solar cell was 1.12 and 1.45 V compared to 0.80 V of N719. Hence, though both ruthenium(II) complexes have much better UV/Vis absorption properties (Fig. 3), its ground and excited state energy levels are not favorably positioned to result in efficient electron injection and dye regeneration as it is evident from Figures 4 and 5 and potential loss calculations in solar cell.



Fig. 6. Photocurrent-voltage characteristics of DSSCs sensitized with the Ru-complexes SD-15 and SD-16.

The photovoltaic parameters including the short-circuit photo- current density ( $J_{SC}$ ), open-circuit voltage ( $V_{OC}$ ), fill factors (*ff*) and overall cell efficiencies (% $\eta$ ) are summarized in Table 3.

#### Table 3

Photovoltaic characteristics of SD-15 and SD-16

Sensitizers <sup>a</sup>	$J_{\rm SC}$ (mA cm <sup>-2</sup> )	<i>V</i> oc ( <i>V</i> )	ſſ	η (%)
<b>SD-15</b>	10.20	0.58	0.56	3.32
<b>SD-16</b>	3.52	0.52	0.58	1.06

<sup>a</sup> Conditions: co-adsorbate, DCA 20 mM; irradiated light, AM 1.5 solar light (100 mW cm<sup>-2</sup>).  $J_{SC}$ , short-circuit photocurrent density;  $V_{OC}$ , open-circuit photo-voltage; *ff*, fill factor;  $\eta$ , total power conversion efficiency.

#### 3.4. Electrochemical impedance spectroscopy characterization

Electrochemical impedance spectroscopy (EIS) successfully models the charge transfer and chemical capacitance at the interface of  $TiO_2/dye/electrolyte$  and pt/eletrolyte in DSSC under operational conditions.<sup>10,28–31</sup> Typical EIS measurements result in Nyquist and Bode plots.

In Nyquist plot, high frequency semicircle can be correlated with charge transfer at the counter electrode and intermediate frequency is related to electron transport through mesoporous TiO<sub>2</sub> and back electron transfer from TiO<sub>2</sub> to electrolyte.<sup>28–32</sup> Gräetzel et al. discussed the sizes of these semicircles as bigger the radius of middle semicircle, higher the charge recombination resistance (R<sub>ct</sub>) from TiO<sub>2</sub> to electrolyte corresponding to Nernst impedance, whereas radius of same semicircle corresponds to resistance of charge diffusion ( $R_d$ ) under Gerischer impedance.<sup>28,33</sup> In EIS Nyquist plots (Fig. 7), two semicircles were observed. Small semi- circle at lower frequency models the cathode charge transfer resistance which is directly related with *ff*. In efficient solar cell, Nernst impedance or  $R_{ct}$  is greater than  $R_d$  as observed for N719,<sup>28</sup> whereas R<sub>d</sub> is greater than R<sub>ct</sub> for SD-15 based solar cell whereas SD-16 has only one semicircle. Intermediate impedance semicircle for SD-15, can be assigned to Gerischer impedance due to the fact,  $V_{OC}$  obtained by employing SD-15 was less than N719, whereas higher R<sub>ct</sub> results in higher  $V_{OC}$  as observed previously.<sup>31</sup>



Fig. 7. EIS Nyquist plots for DSCs sensitized with SD-15 and SD-16.

In Bode frequency plot (Fig. 8), lifetime for injected electrons into TiO<sub>2</sub> conduction band can be determined by using the formula ( $\tau_{CB} = \frac{1}{2\pi f}$ ), where  $\tau$  is the lifetime of electrons in TiO<sub>2</sub> and f is mid frequency peak in Bode plots. The frequency peak of the DSSCs based on SD-15 and SD-16 was 224 Hz whereas only 18 Hz for N719, corresponding to eTiO<sub>2</sub> of 0.71 ms and 8.8 ms, respectively thus resulting in lower  $V_{OC}$  for both SD-15 and SD-16 (shorter eTiO<sub>2</sub>) compared to N719, which correlates well with the actual  $V_{OC}$  reported for the solar cells respectively. Higher  $R_d$  and shorter eTiO<sub>2</sub> for SD-15 and SD-16 can be attributed to lower free energy of electron injection resulting in shorter diffusion compared to N719 and strong electron withdrawing nature of HOMO due to the presence of *bi*-imidazole moiety.



Fig. 8. EIS Bode plots for DSCs sensitized with SD-15 and SD-16.

#### Conclusion

Two novel *tris*-heteroleptic thiocyanate-free Ru(II) complexes based on *bi*-imidazole moiety along with carbazole in SD-15 and triphenyl amino group in SD-16 were successfully synthesized and characterized for DSSCs. The presence of strong electron-donating carbazole and triphenyl with *bi*-imidazole in ruthenium(II) sensitizers resulted in red shift of the low energy MLCT and higher molar absorptivity compared to N719. The different ligands in complexes changed the overall characteristics of the ruthenium complexes. SD-15 gave the highest solar-to-power conversion efficiency of 3.32% under AM 1.5 irradiation and the efficiency performance is in good agreement with molar absorptivity data. This study suggests that *bi*-imidazole chromophore opens up an alternative route to afford a good class of NCS-free Ru(II) complexes for DSSC research based on ruthenium metal. More research needs to be done to fine-tune the molecular structure bi-imidazole for the developments of higher efficiency sensitizers.

#### **Supporting Information Available**

The supporting information includes the detailed synthetic procedures, spectroscopic data and fabrication techniques.

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