Heteroleptic ruthenium complex containing substituted triphenylamine hole-transport unit as sensitizer for stable dye-sensitized solar cell

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KEYWORDS
Dye-sensitized solar cell; Mesoscopic solar cell; Heteroleptic ruthenium(II) complex; Stability

Abstract
A new heteroleptic ruthenium(II) complex cis-di(thiocyanato)(4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-bis[(triethylene glycol methyl ether)ditolylamine phenyl]ethenyl)-2,2'-bipyridine) ruthenium(II) (Ru-TPA-EO-NCS) was synthesized and characterized as a sensitizer for dye-sensitized solar cell application. The ligand contributes to enhance the light harvesting yield rendering a high short-circuit current density of 18.3 mA/cm\textsuperscript{2} at full sun condition (1000 W/m\textsuperscript{2}) leading to an efficient dye-sensitized solar cell. The dye is explored for solid-state solar cell based on 2.0 \textmu m thick thin TiO\textsubscript{2} film with organic hole transport material, Spiro-MeOTAD and it turns out to render 3.3% at full sun. The stability of DSCs is an important aspect for their commercialization. In this respect, the dye in conjunction with a solvent-free electrolyte exhibited a good long-term stability without a drop of the current density.

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1. Introduction
The increasing global need for energy coupled with the depletion of easily accessible, hence cheap, fossil fuel reserves, poses a serious threat to the human global economy in the near future [1]. Considering in addition the harmful ecological impact of conventional energy sources, it becomes obvious that development of clean alternative energy sources is a necessity. Since the solar energy is our only external energy source, harnessing its energy, which is clean, non-hazardous and infinite, satisfies the main objectives of all alternative energy strategies. In this respect, the conversion of sunlight to electricity using dye-sensitized solar cells (DSCs) has been researched as one of the most promising methods for future low cost power production from solar light [2,3]. The DSC architecture broadly consists of components: a mechanical support coated with a transparent conductive oxide (TCO),...
a nanocrystalline semiconductor film usually TiO₂, a sensitizer adsorbed on the surface of the semiconductor, an electrolyte containing a redox mediator and a counter electrode [4]. The dye absorbs light to form an exciton, then the charge generation is performed at the semiconductor-dye interface, and the semiconductor and the electrolyte serve as the charge transporting material. Optimization of the device can be done by separately modifying the dye alone to optimize the spectral properties, while carrier transport properties can be improved by optimizing the semiconductor and the electrolyte composition [5]. Among the sensitizer as one of the key components for high power conversion efficiency, the most efficient and successful sensitizers are ruthenium(II) complexes, which have yielded power conversion efficiency of over 11% [6-11] and good stability [9,10,12-16]. The immobilized sensitizer forms a monomolecular film on the TiO₂ surface, thereby facilitating charge transfer by electron injection. Efficient charge transfer occurs after anchoring of the sensitizer through carboxylate group onto the surface of the TiO₂ semiconductor [17]. The sophisticated design of Ru(II) complexes as sensitizers similar to N719 [18] and 2907 [14] have been explored to enhance the light harvesting efficiency by the enhanced optical absorptivity [8,9,19-24].

In a typical liquid electrolyte cell, the open circuit voltage ($V_{oc}$) is between 700 and 800 mV, which is 100-200 mV less than that of solid-state dye-sensitized solar cells (SSDSCs) comprised of organic hole transporting materials (HTM). The higher $V_{oc}$ in SSDSC is due to better matching of the energy difference between the HOMO of the sensitizing dye and the work function of the organic hole conductor. However the thickness less than 3 μm far thinner than that needed to achieve good optical absorption has used to avoid incomplete filling of the pore in the TiO₂ film. In this sense, we and others have introduced sensitizers with a secondary electron donor moiety such as triphenylamine (TPA) to increase molar absorptivity for liquid and solid state DSCs [24-27]. Kuang et al., have reported “ion-coordinating” sensitizer endowed with ethylene oxide (EO) groups, which inhibit Li cation from reaching the TiO₂ surface leading to a respectable efficiency with solid and non-volatile electrolytes [28,29]. Thelekkat et al., have produced a novel bpy-donor antenna dye, (Ru-TPA-EO-NCS, see molecular structure in Fig. 1), which yielded 1.37% with spiro-MeOTAD in a series of donor-antenna type Ru(II) complexes [30]. Here, we have extended our study for the Ru-TPA-EO-NCS to optimize the performance of solid (spiro-MeOTAD) and liquid junction system. Much improved power conversion efficiencies in both systems were obtained and in particular a promising stability, which is an important aspect for DSC commercialization was witnessed with ionic liquid based electrolyte under light soaking and 60 °C for more than 1000 h.

2. Experimental section

2.1. Synthesis

The heteroleptic ruthenium(II) complex cis-di(thiocyanato) (4,4'-dicarboxyl acid-2,2'-bipyridine)(4,4'-bis[(triethylene glycol methyl ether)]dithio[amine phenyl](ethenyl)-2,2'-pyridine) ruthenium(II) (Ru-TPA-EO-NCS) dye was prepared by one pot synthesis by reacting a p-cymene Ru(II) compound with the two ligands bpy-donor antenna dye, (Ru-TPA-EO-NCS) dye was prepared for stable dye-sensitized solar cell, Nano Energy (2011), doi:10.1016/j.nanoen.2011.08.004

2.2. Fabrication of dye-sensitized solar cells based on liquid and ionic liquid electrolyte

Dye-sensitized photovoltaic devices were prepared according to the standard method described in previous work [31]. The FTO glass substrates were immersed in 40 mM TiCl₄ aq. at 70 °C for 30 min and washed with water and ethanol. The mesoporous nano-TiO₂ films composed of 20 nm anatase TiO₂ particles were coated on the FTO glass plates by repetitive screen printing. After drying the nanocrystalline TiO₂ layer at 125 °C, a 5 μm thick second layer of 400 nm sized light scattering anatase particles (CCIC, HPW-400) was deposited by screen printing onto the transparent layer. The TiO₂ electrodes were gradually heated under an air flow and they were treated again by TiCl₄ and sintered at 500 °C for 30 min. The TiO₂ electrodes were immersed into the dye solutions (0.3 mM in 50/50 (v/v) mixture of acetonitrile and tert-butanol and with 10 mM of chenodeoxycholic acid) and kept at room temperature for 20 h. The dye-adsorbed TiO₂ electrode and thermally platinized counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film (Surlon 1702, 25 μm thickness, Du-Pont). A platinized FTO glass was used as counter electrode. A volatile electrolyte, E₁ is composed of 0.6 M M-methyl-N-butyl imidazolium iodide, 0.04 M iodine, 0.05 M Lil, 0.05 M GuNCS and 0.28 M 4-tert-Butyl pyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. The binary ionic liquid electrolyte, E₂ consisted of 0.2 M iodine, 0.5 M N-butyl benzimidazole (NBB), and 0.1 M guanidinium thiocyanate (GuNCS) in a mixture of 1-propyl-3-methylimidazolium iodide (PMII) and 1-ethyl-3-methyl-imidazolium tetracyanoborate (EMIM(CN)₄) (volume ratio 65:35) [15]. The EMIM(CN)₄ was supplied by Merck. In order to reduce scattered light from the

![Figure 1](image-url) Molecular structure of Ru-TPA-EO-NCS.
2.3. Fabrication of solid state dye-sensitized solar cells

Fluorine-doped SnO₂ glass (15 Ω/sq, Pilkington) substrates were cleaned first with the Helmanex solution, rinsed with acetone, and then ethanol. Next, a ~100 nm compact layer of TiO₂ was deposited by spray pyrolysis [32]. A porous layer of 20 nm TiO₂ particles (~2.0μm thick) was coated by the doctor-blading technique, followed by sintering at 500 °C under an oxygen flow. After cooling, the thin TiO₂ films were impregnated in a 0.02 M aqueous TiCl₄ solution for 15 h, and then rinsed with deionized water. The TiCl₄ treated TiO₂ films were annealed at 450 °C for 30 min and then cooled to ~80 °C before immersion into the dye solution for 3 h. Subsequently, the substrates were rinsed in acetonitrile, and then the hole-transporting material 2,2'-spiro-bifluorene (Spiro-MeOTAD) solution (180 mg/mL, in chlorobenzene) with additives of 4-tert-Butyl pyridine (17 μL/mL) and Li[CF₃SO₂]₂ N (19.5 mM) was spin coated at 2000 rpm on top of the TiO₂ film [33–35]. Finally, a 50 nm gold layer was evaporated on the top of the Spiro-MeOTAD. The active area was 0.29 cm².

2.4. Dye-sensitized solar cells characterization

The incident photon-to-current conversion efficiency (IPCE) was measured using a 450 W xenon light source, adapted and mismatch-corrected to produce global standard air mass 1.5 (AM 1.5) sunlight conditions (intensity 1000 W/m²) are shown in Fig. 2 and Table 1. The TiO₂ electrodes were made of ~12 μm transparent layer (20 nm diameter) and ~5 μm scattering layer (400 nm diameter, CCIC, HPW-400). The Ru-TPA-EO-NCS sensitized solar cells with volatile electrolyte, E1 showed 18.30 mA/cm² of short-circuit current density (Jsc), 682 mV of open circuit voltage (Voc) and 72% of fill factor (FF) resulting in high power conversion efficiency of 9.02%. The short circuit photocurrents increased proportionally with light intensity. Fig. 2 (bottom) shows the incident monochromatic photon-to-current conversion efficiency (IPCE), exhibiting a maximum of 87%. Assuming a 10% optical loss in the conducting glass [38], the internal quantum efficiency is over 80% in most of the visible light region. The solid state solar cells showed 6.75 mA/cm² of Voc, 864 mV of Voc and 57% of FF, leading to 3.30% of the power conversion efficiency under 1 sun condition. The Voc showed a linear dependence with the intensity of light; however, the power conversion efficiencies were higher under lower intensities due to higher FF. This result is probably caused by high series resistance in solid state cell [39].

Table 1: Molar extinction coefficients at the respective absorption maxima (λmax) of Ru-TPA-EO-NCS and N719 in methanol with 1 wt% of KOH.

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<tbody>
<tr>
<td>Ru-TPA-EO-NCS</td>
<td>307</td>
<td>81,322</td>
<td>429</td>
<td>53,446</td>
<td>524</td>
<td>30,861</td>
</tr>
<tr>
<td>N719</td>
<td>310</td>
<td>48,798</td>
<td>398</td>
<td>13,700</td>
<td>535</td>
<td>14,000</td>
</tr>
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</table>

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that of liquid solar cells. Consequently, the TPA donor antenna unit of the Ru(II) dye increases the visible light harvesting capacity due to a larger absorption cross section, resulting in a higher short-circuit current density. Moreover, an impressive $V_{oc}$ of 864 mV is obtained with the solid state hole conductor solar cell, which is 180 mV higher than that obtained with the liquid electrolyte based DSC. This arises from the reduction of the energy offset between the HOMO of the sensitizing dye and the work function of the organic hole conductor decreasing the energy loss associated with the dye regeneration process (Fig. 3, Tables 2 and 3).

Figure 2  Photocurrent–voltage characteristics (top) and incident photon-to-current conversion efficiency plotted as a function of excitation wavelength (bottom) of Ru-TPA-EO-NCS sensitized solar cells with E1 electrolyte (0.6 M M-methyl-N-butyl imidazolium iodide, 0.04 M iodine, 0.05 M LiI, 0.05 M GuaNCs and 0.28 M 4-tert-Butyl pyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile) (mask aperture area is 0.2 cm$^2$).

Table 2  Photovoltaic performances of Ru-TPA-EO-NCS sensitized solar cells with E1 electrolyte.

<table>
<thead>
<tr>
<th>$I_0$ [%sun]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [mV]</th>
<th>$FF$</th>
<th>$\eta$ [%]</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>18.30</td>
<td>682</td>
<td>0.72</td>
<td>9.02</td>
</tr>
<tr>
<td>50</td>
<td>9.33</td>
<td>662</td>
<td>0.75</td>
<td>9.25</td>
</tr>
<tr>
<td>10</td>
<td>1.87</td>
<td>607</td>
<td>0.80</td>
<td>9.12</td>
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Table 3  Photovoltaic performances of Ru-TPA-EO-NCS sensitized solid-state solar cells with Spiro-MeOTAD.

<table>
<thead>
<tr>
<th>$I_0$ [%sun]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [mV]</th>
<th>$FF$</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.75</td>
<td>864</td>
<td>0.57</td>
<td>3.30</td>
</tr>
<tr>
<td>50</td>
<td>3.29</td>
<td>841</td>
<td>0.65</td>
<td>3.62</td>
</tr>
<tr>
<td>10</td>
<td>0.66</td>
<td>784</td>
<td>0.77</td>
<td>3.99</td>
</tr>
</tbody>
</table>

Figure 3  Photocurrent–voltage characteristics of Ru-TPA-EO-NCS sensitized solid-state solar cells with Spiro-MeOTAD (active area is 0.29 cm$^2$).

Figure 4 shows the photocurrent performance during a long time accelerated aging of a Ru-TPA-EO-NCS sensitized solar cell using an ionic liquid electrolyte with high concentration of LiI. In order to undertake the stability evaluation, the TiO$_2$ electrodes consisting of a transparent layer and ~5 μm scattering layer were used. Values for $J_{sc}$, $V_{oc}$, $FF$ and $\eta$ were recorded over a period of 1150 h. The lower $J_{sc}$ with E2 was mainly ascribed to mass transport limitation in the E2 electrolyte [40]. Fig. 5 shows the photocurrent response to a light on–off sequence. The current decay observed in E2 system under high light intensity i.e. 1 sun is indicative of a mass transport limitation whereas the DSC with E1 shows the current remaining constantly. The lower $V_{oc}$ with E2 than that with E1 is plausibly ascribed to a higher iodine concentration being required to avoid adverse mass transport limitation. The overall efficiency remained at 95% of the initial value after 1150 h of light soaking. This 5% decrease stems from the drop, 46 mV in $V_{oc}$ without loss of the $J_{sc}$ nor $FF$. The stable $J_{sc}$ explicates that the Ru-TPA-EO-NCS dye sustains without any noticeable decline in

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Heteroleptic ruthenium complex as sensitizer for dye-sensitized solar cell

4. Conclusion

A novel heteroleptic ruthenium(II) complex substituted with dimethylphenylaniline units incorporating ethylene glycol as donor ligand has been synthesized and demonstrated as a good sensitizer. The ligand contributes to enhanced light harvesting yield leading to a high short-circuit current density of 18.3 mA/cm² and thus a efficient dye-sensitized solar cell. Its application to solid state solar cells using Spiro-OMeTAD as a hole transport material turns out to give respectable PCE of close to 4%. The Ru-TPA-EO-NCS dye exhibits an excellent stability in combination with an ionic liquid electrolyte. During more than 1000 h of light soaking at 60 °C, the device lost only 46 mV of photovoltage with no change in photocurrent. These findings will encourage further optimization of molecular dye structures to increase photovoltaic performance and stability of DSCs.

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