

# Novel heteroleptic ruthenium sensitizers containing carbazole linked 4,5-diazafluorene ligand for dye sensitized solar cells



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## ARTICLE INFO

### Article history:

Received 9 July 2014

Accepted 13 November 2014

Available online 20 November 2014

### Keywords:

Dye sensitized solar cells

Ruthenium sensitizer

Carbazole

4,5-Diazafluorene

Photoinduced electron transfer

## ABSTRACT

Two novel heteroleptic ruthenium (II) sensitizers **S1** and **S2** containing an ancillary ligand 9,9-bis(9-ethylcarbazol-3-yl)-4,5-diazafluorene and 9,9-bis(9-phenylcarbazol-3-yl)-4,5-diazafluorene respectively, have been synthesized and characterized by <sup>1</sup>H NMR, UV–Vis absorption spectroscopy, mass spectrometry, elemental analysis and cyclic voltammetry, and used as sensitizers in dye sensitized solar cells. The results show that for the two ruthenium sensitizers, the introduction of carbazole via sp<sup>3</sup> hybridized C9 atom of the 4,5-diazafluorene unit produces significant changes in their optical absorption spectra and subsequently alters the intra-molecular charge transfer processes that influence the photovoltaic performance of the solar cell device. The power conversion efficiency of dye sensitized solar cells fabricated using sensitizers **S1** and **S2** are 0.36% and 0.42% respectively, while **N719** exhibits 3.6% under the same device fabrication and measuring conditions.

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## 1. Introduction

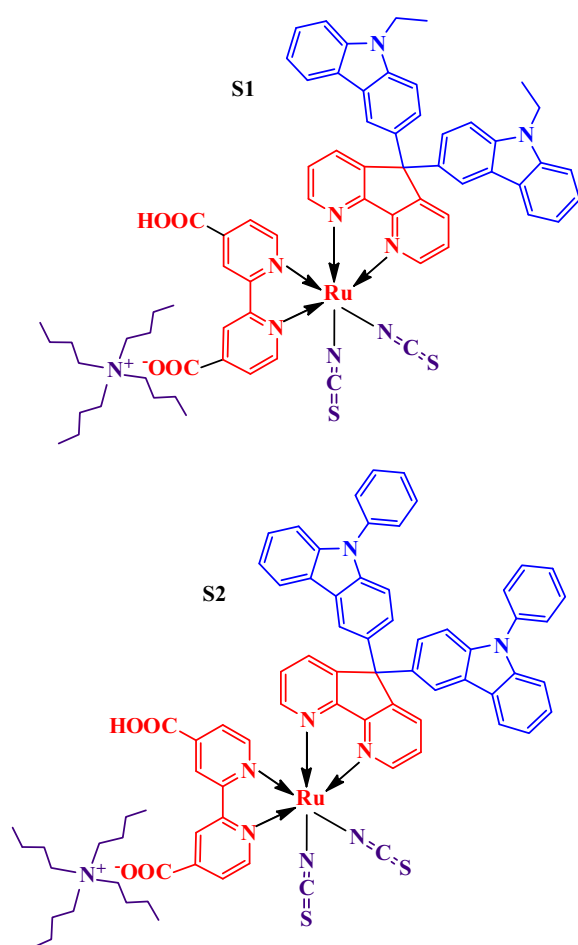
For the past few decades, conversion of sunlight into electricity through dye sensitized solar cells (DSSC's) has been extensively studied as novel system in the field of photovoltaic by virtue of their low cost and easy fabrication techniques. Major components of dye sensitized solar cells include dye sensitized titanium dioxide (TiO<sub>2</sub>) electrode, platinum counter electrode and a redox couple. It is well known that hearts of the art of the DSSC's is sensitizer which initiates the photovoltaic process by absorbing visible light like in photosynthesis. Although **N719** is considered as benchmark dye with its record efficiency of 11% [1], it lacks absorption in the red and near infra-red (NIR) regions and shows low molar absorptivity in both high and low energy metal to ligand charge transfer (MLCT) bands. Hence researchers aimed to prepare novel dyes with high molar extinction coefficient and extended absorption in the red to NIR regions of the solar spectrum. A possible approach in the molecular engineering of new dyes comes from the replacement of one 4,4'-dicarboxylic acid-2,2'-bipyridine (dcbpy) in the

**N719** dye with electron rich segments. In this context, highly extended conjugation units such as thiophene [2], ethylenedioxythiophene (EDOT) [3], triphenylamine [4,5] and alkoxybenzene [6–8] attached to the bipyridyl ligand were designed to prepare novel sensitizers that exhibit an enhanced molar absorptivity in combination with a red-shifted absorption band. Few research groups revealed that ruthenium sensitizers containing carbazole hole transporting units in the bipyridyl ligand enhance the spectral response and energy conversion efficiency of DSSC's [9–13]. Particularly, Shafei et al. [11] reported a novel carbazole containing ruthenium sensitizer exhibiting low energy MLCT peak at 545 nm with high molar absorptivity ( $2.06 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and extended absorption into the near IR region (ca. 870 nm) as well as an excellent power conversion efficiency ( $\eta$ ) of 9.37% (**NCSU-10**) compared to 8.17% of **N719**. Molecular orbital calculations performed on these sensitizers revealed that the highest occupied molecular orbital (HOMO) is delocalized not only on ruthenium and NCS but also on the carbazole moiety with a large coefficient. This clearly indicates that attachment of a carbazole moiety to a bipyridyl through CH=CH without electron donor spacer significantly influences the delocalization of the HOMO into the carbazole moiety and enhances the electron injection yield at the interface of TiO<sub>2</sub>. Also these findings proved that  $\pi$  conjugated

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linkage between carbazole and bipyridyl extends the absorption spectra of the sensitizer into the NIR region with subsequent enhancement in molar extinction coefficient. Although efficient charge transfer occurs in the highly conjugated chromophores, there exists difficulty in tailoring the properties of the resulting donor–acceptor systems through independent modification of the structures of the donor and acceptor. On the other hand, spiro-conjugated donor–acceptor systems exhibit ultrafast electron transfer and open new possibilities for the development of novel charge transfer chromophores [14,15]. In this context, donor–acceptor systems possessing diazafluorene as electron acceptor and carbazole or triphenylamine as electron donor have been investigated for sensor [16] and OLED applications [17,18] and dye sensitized solar cells [19,20]. Significantly, one of the most widely-used hole transporting material in solid state DSSC is spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene), but it achieves only 5% efficiency due to the incomplete filling of the mesoporous TiO<sub>2</sub> films (>2 μm) with spiro-OMeTAD [21]. In a systematic approach, Ono et al. [22] studied the photovoltaic properties of red ruthenium sensitizer containing 9,9-bis(4-methoxyphenyl)-4,5-diazafluorene as one of the polypyridyl ligands. Toward this end, we decided to synthesize novel ruthenium sensitizers **S1** and **S2** (Scheme 1) consisting of ambipolar host materials 9,9-bis(9-ethylcarbazol-3-yl)-4,5-diazafluorene and 9,9-bis(9-phenylcarbazol-3-yl)-4,5-diazafluorene, comprising two electron-donating carbazole units and an electron-accepting 4,5-diazafluorene and made an endeavor to investigate their optical, electrochemical and photovoltaic properties.



**Scheme 1.** Structure of the ruthenium sensitizers **S1** and **S2**.

## 2. Experimental

### 2.1. Materials

Transparent titania electrode (10–12 μm, Cat. No. 74111), platinum electrode (drilled, Cat. No. 74201), 1-methyl-3-propylimidazolium iodide and Surllyn polymer frame (Meltonix 1170-25) were purchased from Solaronix. Dichloro(p-cymene)ruthenium(II)dimer, di-tetrabutyl ammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (**N719**, 95%), 4,4'-dicarboxylic acid-2,2'-bipyridine (98%), 3-methoxy propionitrile, lithium iodide crystalline powder (99.9%), iodine (≥99.99%), 4-tert-butyl pyridine (96%), 1,10-phenanthroline, 9-ethylcarbazole (97%), 9-phenylcarbazole (97%), methane sulphonic acid, glacial acetic acid, Triton X-100, tetrabutylammonium hydroxide (TBAOH) and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) were purchased from Sigma Aldrich. Column chromatography was performed using silica gel (Merck, 70–240 mesh) and Sephadex LH-20 (GE Healthcare). All other chemicals used were of analytical grade purchased from Merck and used without further purification.

### 2.2. Analytical measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 500 MHz and 100 MHz spectrometer, respectively. The reported chemical shifts were in ppm against tetramethylsilane (TMS). Elemental analyses were performed using Fison EA 1108 analyzer. UV–Vis absorption spectra were recorded in a 1 cm path length quartz cell using JASCO V-650 spectrometer (Tokyo, Japan). Mass spectra (MS) analyses were performed using a 3200 QTRAP Mass spectrometer (AB SCIEX, USA, MA) with an infusing flow of 10 μL/min. Instrument control and data collection system were carried out using Analyst 1.5.2 software (AB SCIEX, USA, MA). MS detection was carried out in a positive and negative electrospray ionization mode, testing ionization voltages from 1000 to 5000 V and from –1000 V to –4500 V, capillary temperatures from 250 °C to 600 °C. Several nitrogen flows were used as nebulizing gas and drying gas ranging from 15 to 50 psi of pressure. Electrochemical measurements were performed using a CHI-604C electrochemical analyser. A conventional three-electrode cell assembly consisting of a glassy carbon (GC) working electrode, a platinum wire auxiliary electrode and a silver wire as reference electrode was employed. The cyclic voltammogram were recorded at scan rate of 0.1 V s<sup>–1</sup> using the sample solutions containing 3 × 10<sup>–4</sup> M of the sensitizer and 0.1 M TBAPF<sub>6</sub> in anhydrous N,N'-dimethylformamide (DMF) as supporting electrolyte under argon atmosphere.

### 2.3. Dye-sensitized solar cell fabrication

The transparent titania electrodes were impregnated with a 0.05 M titanium tetrachloride solution and sintered at 500 °C and cooled to 50 °C before being dipped into the dye solution. Dye solution was prepared in the concentration range 3 × 10<sup>–4</sup> M in ethanol and the electrodes were dipped into the dye solution for 24 h. After the dye adsorption was complete, the electrode was withdrawn from the solution and dried under a stream of argon. The platinum counter electrode and the dye-coated TiO<sub>2</sub> films were then put together with a thin transparent film of Surllyn polymer frame (25 μm). The sandwiched electrodes were tightly held, and then heat (130 °C) was applied around the Surllyn frame to seal the two electrodes. A thin layer of electrolyte, consisting of 0.6 M propyl methylimidazolium iodide (PMII), 0.05 M I<sub>2</sub>, 0.1 M LiI, and 0.5 M tert-butylpyridine in 3-methoxypropionitrile, was introduced into the inter-electrode space from the counter electrode side through predrilled holes. The drilled holes were sealed with a microscope cover slide and Surllyn to avoid leakage of the electrolyte solution.

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