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New heteroleptic benzimidazole functionalized Ru-sensitizer showing the highest efficiency for dye-sensitized solar cells

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ABSTRACT

We designed and synthesized a new ruthenium complex using terpyridine as an anchoring ligand and BOC (*tert*-butyloxycarbonyl) protected bidentate benzimidazole derivative as an ancillary ligand, coded as **GS7**. The complex was characterized using ^{1}H NMR, FTIR, elemental analysis, UV–vis spectrophotometer, and cyclic voltammetry. We also tested photovoltaic performance of this complex for dye-sensitized solar cell (DSSCs). **GS7** when used as a sensitizer for DSSCs with iodine triiodide electrolyte, showed a J_{sc} of 15.25 mA cm^{-2}, a V_{oc} of 0.576 V, a FF of 0.691 and overall power conversion efficiency of (η) 6.07%.

Owing to their versatility and low-cost manufacturing, dye sensitized solar cells (DSSCs) have been intensively investigated over the past decade [1–8]. Extensive research has been focused on the development of new and highly efficient sensitizers, since they play a vital role to the cell's photovoltaic performance. Sensitizers should have absorption over a wide range of solar spectrum and a high molar extinction coefficient for improving the conversion efficiency of DSSC. In order to enhance these efficiencies, various sensitizers such as ruthenium complexes, [8,9] non-ruthenium metal complexes [10–12], and metal free organic sensitizers [13–16] have been synthesized and tested in DSSCs. Among the various sensitizers developed ruthenium based sensitizers were intensively investigated as potential sensitizers with efficient DSSC performance, because their photophysical and electrochemical characteristics can be finely-tuned to achieve optimal material properties. Different strategies have been employed on the anchoring and ancillary ligands in ruthenium sensitizers to improve the photon-to-electricity conversion efficiency [8]. Among the various reported anchoring groups such as phosphate [17,18], boronic acid [19], and carboxylic acid [20,21], carboxylic acid group remained the most common and efficient anchoring group. Many efforts were also made on ancillary ligands by structural modifications such as extending the conjugation [22–28], with electron donating groups [29–34], use of multi-chromophoric dyes [35–37] and recently a new class of cyclometalated ligands [38–42] to enhance the device performance. Key examples of ruthenium complexes for DSSCs include the well studied N3 [42], N719 [43], and N749 [44] dyes. It has been reported that, introduction of 4,4′,4″-tricarboxy-2,2′:6,2″-terpyridine (H_3tctpy) exhibits panchromatic sensitization up to near-IR region [43,45]. Although most of the complexes showed satisfactory sensitization up to 900 nm, they still possess two major drawbacks as follows: i) inferior absorptivity in the visible region, due to the lack of effective auxochrome; and ii) the presence of two or three thiocyanato ligands, which not only decrease the synthetic yield [44,46] but also the stability of the complex decreases owing to dye decomposition by weak Ru–NCS bond. Despite of new Ru complexes for the enhancement, there is still a need for efficient sensitizers to promote the commercialization of DSSCs. Benzimidazole derivatives have been used as layer materials for hole blocking and electron transport in OLED (organic light-emitting diode) devices [47]. Recently E. W. G. Diau et al. reported the Ru complexes having benzimidazole derivatives for DSSC applications [48].

In conjugation with current endeavors, we [49–53] and others have examined terpyridyl Ru complexes in an attempt to optimize near-IR sensitizers. Here we have designed and synthesized new heteroleptic Ru sensitizer **GS7** bearing terpyridine ligand with anchoring carboxylic groups, and newly designed bidentate benzimidazole derivative as ancillary ligand and a thiocyanato ligand to tune the redox properties of Ru center. The photovoltaic performances of fabricated DSSCs using new sensitizer were evaluated and compared with N749 sensitizer.

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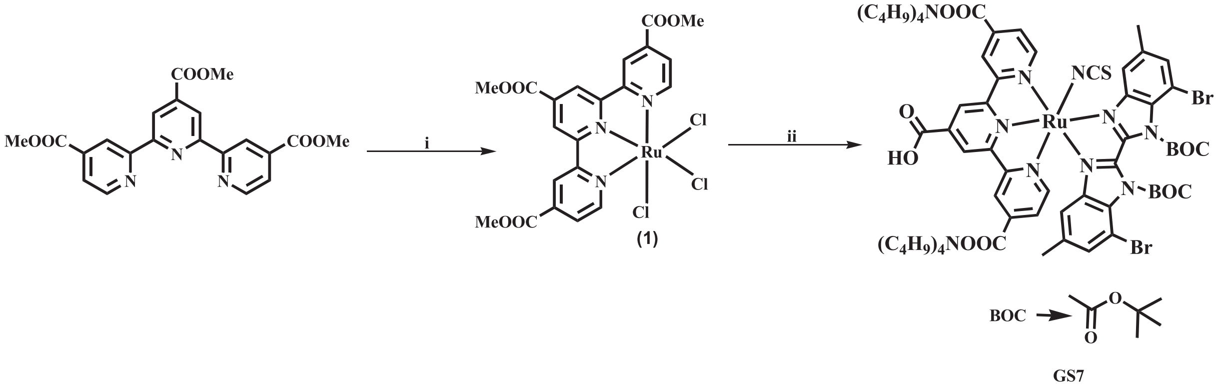
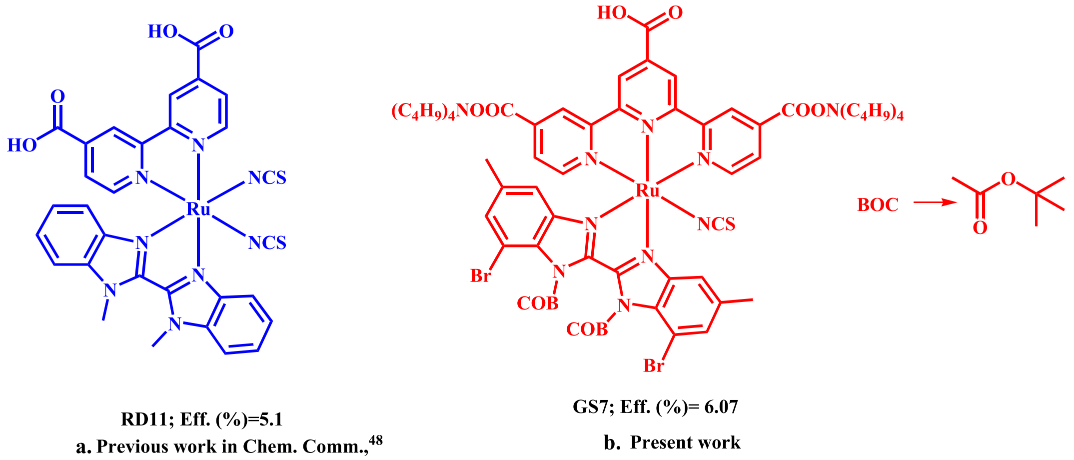


Scheme 1. Synthesis of sensitizer **GS7**. Reagents and conditions: i) $RuCl_3 \cdot 3H_2O$, anhydrous DMF, reflux under dark, 4 h; ii) L1, DMF reflux, 4 h then NH_4NCS, reflux, 2 h then TEA, water, reflux, 48 h.



RD11; Eff. (%)=5.1
a. Previous work in Chem. Comm.,[48]

GS7; Eff. (%)= 6.07
b. Present work

Fig. 1. a. Previous work in Chem. Comm., [48]. b. Present work.

GS7 was synthesized using the stepwise procedures as shown in Scheme 1. The compound (**1**) was prepared by refluxing $RuCl_3 \cdot 3H_2O$ and 4,4′,4″-trimethoxycarbonyl 2,2′-6′,2″'-terpyridine in ethanol:$CHCl_3$ solution. The final step was performed by heating compound (**1**) with ancillary ligand L1 at 120 °C for 4 h using DMF as solvent, followed by hydrolysis to afford the desired Ru-complex **GS7** in good yield. Fig. 1a represents reported benzimidazole derivative by other research group [48], while Fig. 1b represents the **GS7** complex designed by us.

The UV–vis absorption spectrum of new sensitizer **GS7** and N749 in DMF solution is depicted in Fig. 2 and corresponding data is presented in Table 1. Strong π–π* absorption is observed in the UV region corresponding to the coordinating ligand. **GS7** showed broad visible absorption band which is assigned to metal-to-ligand charge transfer (MLCT) band. The UV–vis spectrum of **GS7** exhibited broad and strong absorption in the range from 250 to 850 nm. The high energy absorption band around 300 nm originates from intraligand π–π* transitions of the terpyridine ligand.

The spectrum was characterized with strong intermediate energy absorption band at 410 nm, mainly attributed to a combination of benzimidazole based ligand (L1) transitions and ligand-to-ligand charge transfer (LLCT) transitions as well as to some contribution from MLCT transitions. The lower energy absorption band at 540 nm (4629 M^{-1} cm^{-1}) and indistinct shoulder around 720 nm are characteristics of the MLCT transitions. N749 dye, the UV–vis spectrum of which is shown for comparison, presents MLCT transition with absorption maxima at 613 nm.

The UV–vis absorption spectrum of sensitizers **GS7** and N749 on TiO_2 was recorded and shown in Fig. 3. The maximum absorption peak was observed at 519 nm and 591 nm respectively. Compared to solution spectrum, the absorption spectrum on TiO_2 film was blue shifted by ≤25 nm. In addition to MLCT band one shoulder peak was observed at around 700 nm, which is an advantageous spectral characteristic for light harvesting.

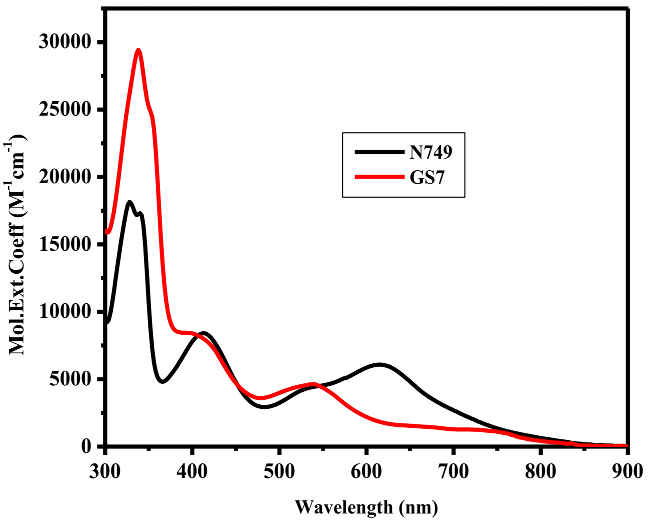


Fig. 2. Absorption spectra of **GS7** and N749 sensitizers in DMF.

Table 1
Optical and DSSC performance parameters of sensitizer **GS7**.

Dye	$\lambda_{max}(\varepsilon)$ $(M^{-1}\ cm^{-1})$ [nm][a]	HOMO [eV][b]	E_{0-0} [eV][c]	LUMO [eV][b]	J_{sc}[d] $[mA\ cm^{-2}]$	V_{oc}[e] [V]	f.f[f]	Eff. (%)
GS7	540 (4629) 727 (1288)	−5.70	1.70	−4.00	15.25	0.576	0.691	6.07
N749	613 (6080)	−5.46	1.53	−3.93	13.74	0.675	0.680	6.31

[a] Absorption spectra were recorded in DMF solutions at 298 K.
[b] HOMO values were measured by photoemission yield spectrometer.
[c] The band gap, E_{0-0}, was calculated from the onset of the absorption spectra.
[d] Current density.
[e] Open-circuit voltage.
[f] Fill factor.

In order to analyze the absorption spectra in detail TDDFT calculations have been carried out. The sensitizer has unit positive charge; hence we used hexafluorophosphate (PF_6^-) counter anion to make it electrically neutral [54] and B3LYP (Table S1), M06 (Table S2) and PBE0 (Table S3) functionals were used. Among the four functionals, B3LYP could correlate well with the experimental results. Major peaks observed in the range of 450 nm–800 nm along with orbital contribution to each excited state are listed in Table S1. The lowest energy excitation (S_0 to S_1) is at 774 nm, involves the transition from HOMO to LUMO, is a low intense ($f = 0.0267$) charge transfer transition which shifts the electron density from ruthenium and NCS to terpyridine, and is a low intense peak ($f = 0.0267$). The most intense peak ($f = 0.1002$) is observed at 498 nm, showing 40 nm blue shift from experimental absorption maxima (540 nm), and this peak corresponds to HOMO to LUMO + 3 transition. From molecular orbital pictures it can be inferred that the charge transfer transition in **GS7** is of MLCT and LLCT types.

The ionization potential of **GS7** bound to a nanocrystalline TiO_2 film was determined using a photoemission yield spectrometer (Riken Keiki, AC-3E, Fig. S1) to ensure that the highest occupied molecular orbital (HOMO) of newly synthesized sensitizer **GS7** matches the redox potential of the redox electrolyte (I^-/I_3^-) for dye regeneration and to verify whether the lowest unoccupied molecular orbital (LUMO) is suited for efficient electron injection into the conduction band of TiO_2 (Fig. S1). An oxidation potential of −5.70 eV, which corresponds to the HOMO level, was obtained for the sensitizer **GS7** adsorbed on a TiO_2 electrode and was low enough for efficient regeneration of the oxidized dye through reaction with iodide.

The excited-state oxidation potential (LUMO) could be calculated from HOMO–E_{0-0} where E_{0-0} is zeroth–zeroth transition value, calculated from the onset of the absorption spectra (Figs. 2 and 4). The excited-state oxidation potential of the **GS7** sensitizer was −4.00 eV, which lies sufficiently above the conduction band edge (−4.2 eV) [55,56] of the nano-crystalline TiO_2. Therefore, an efficient electron injection into the conduction band of TiO_2 is expected to occur with sensitizer **GS7** [57]. A comparison of HOMO and LUMO for **GS7** and N749 is given in Fig. 4 and the results are summarized in Table 1.

The photovoltaic performance of sensitizer **GS7** on a 0.25 cm^2 active area nanocrystalline TiO_2 electrode was studied under standard AM 1.5 irradiation (100 mW cm^{-2}) using an electrolyte with a composition of 0.5 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I_2, and 0.1 M LiI in acetonitrile:n-butanol (1:1). The incident photon-to-current efficiency (IPCE) of the sensitizer **GS7** is shown in Fig. 5 and compared with standard N749 dye; it exhibited efficient sensitization of nanocrystalline TiO_2 solar cell over the entire visible range extending into near-IR region consistent with the UV–vis absorption spectra of **GS7** and N749 adsorbed on TiO_2 film (Fig. 3). The onset of the IPCE spectra is close to ~900 nm, which is an optimal parameter for anticipated best DSSCs. Excellent IPCE performance was observed from 400 to 740 nm. The new sensitizer **GS7** shows an IPCE value of 70% in the region of 445–570 nm. Taking into account the reflection and absorption losses by the conducting glass the IPCE in this range reaches a maximum of 78% at 520 nm. The decrease in the IPCE above 550 nm toward the red is caused by the decrease in the molar extinction coefficient of the sensitizer in that region (Fig. 3). In the 400–640 nm range, the **GS7** exhibits better IPCE performance than N749 due to its higher light harvesting efficiency in this wavelength region (Figs. 2 and 3).

Fig. 6 shows the photocurrent density–voltage curve of the device employing **GS7** and N749 under AM 1.5 G simulated sunlight at a light intensity of 100 mW cm^{-2}, while the short-circuit photocurrent density (J_{sc}), open circuit voltage (V_{oc}), fill factors (FF), and overall cell efficiency (η) data are summarized in Table 1. The solar cell sensitized with **GS7** showed J_{sc} 15.25 mA cm^{-2}, a V_{oc} 0.576 V, and a FF of 0.691, corresponding

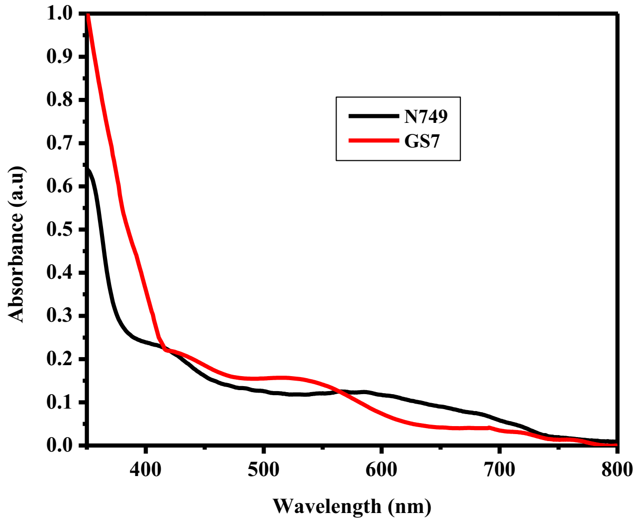


Fig. 3. Absorption spectra of **GS7** and N749 on TiO_2.

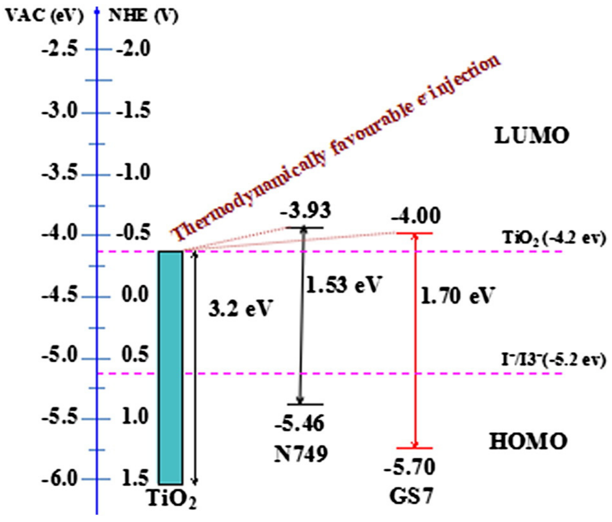


Fig. 4. Energy level diagram and comparison between HOMO and LUMO of **GS7** and N749.

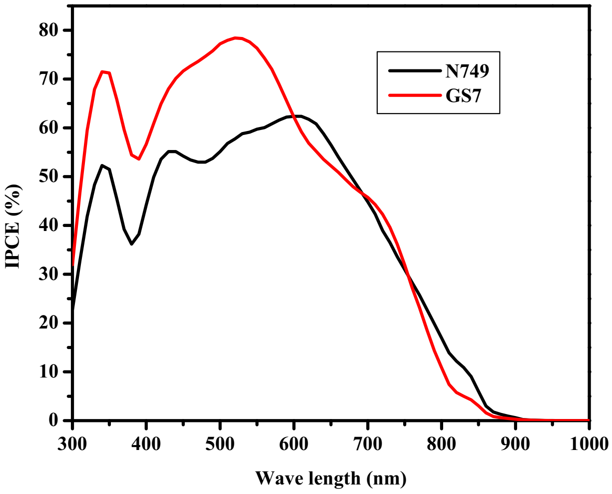


Fig. 5. IPCE spectra of **GS7** and N749 sensitizers.

to an overall conversion efficiency (η) of 6.07%. Under similar fabrication conditions standard N749 dye exhibited an overall power conversion efficiency of 6.31%.

To further understand the lower Voc observed for DSSCs sensitized with **GS7** dye compared to N749, we first measured the relative conduction band position of TiO_2 by means of a charge extraction method. As shown in Fig. 7, DSSCs sensitized with both **GS7** and N749 exhibit a similar linear increase in electron density as a function of Voc, indicating that these cells had the same conduction band edge of TiO_2 regardless of the different molecular structures. Since the conduction band edge was not influenced by **GS7** dye, the decrease in Voc compared to N749 must be ascribed to increase of charge recombination. A theoretical model of intensity-modulated photovoltage spectroscopy (IMVS) for DSSCs considers a charge trapping/detrapping during the charge diffusion and electron transfer from the TiO_2 conduction band. The electron lifetime (τ) in the DSSCs is a central quantity to determine the dynamics of charge recombination which is related to open circuit voltage (V_{oc}) of the cell. Fig. 8 shows the τ as a function of V_{oc}. **GS7** exhibited a shorter τ than the N749 dye at the same electron density, implying that recombination rate between electrons on the TiO_2 surface and an I_3^- ion in the electrolyte was higher for **GS7**. The shorter charge life time in TiO_2 for **GS7**, can be attributed to the electronic effect in the molecular structure and the orientation of anchored dye on TiO_2. It is likely that N749 allows for better geometry orientation and a more compact layer of the anchored dye on the TiO_2 film to take place compared to that of **GS7**. The sensitizer **GS7** shows a shorter life time, which might be due to incomplete dye coverage and/or dye aggregation on the TiO_2 surface, which increases the concentration of I_3^- ions in the vicinity of the TiO_2 surface and thus decrease the electron lifetime (τ).

To summarize, a new type of Ru-sensitizer **GS7** was meticulously designed and synthesized which is having tricarboxyterpyridine ligand as an anchoring ligand and BOC-protected benzimidazol derivative (L1) as ancillary ligand for DSSCs and characterized using electrochemical and spectroscopic methods. The absorption spectra of **GS7** on TiO_2 film reveal that incorporation of ligand (L1) in the ruthenium sensitizer leads to enhanced spectral response and red-shifted absorption maxima in the visible region. A solar-to-electricity conversion efficiency of the DSSC based on **GS7** sensitizer reached 6.07%, which is consistent with the IPCE values. The IMVS data disclosed that the sensitizer **GS7** exhibited a higher charge transport resistance compared to N749 at the

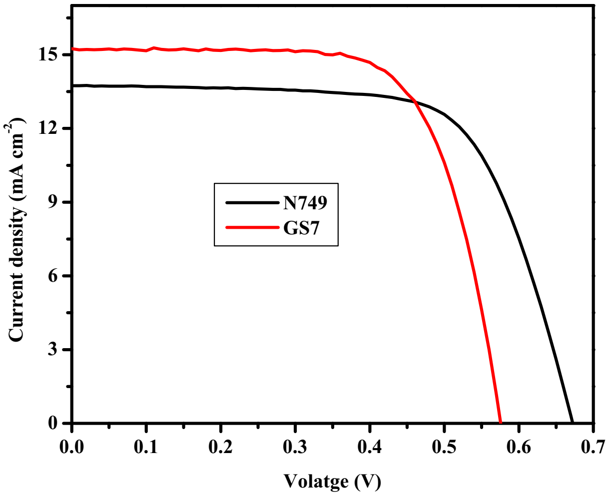


Fig. 6. J–V curves of **GS7** and N749 sensitizers.

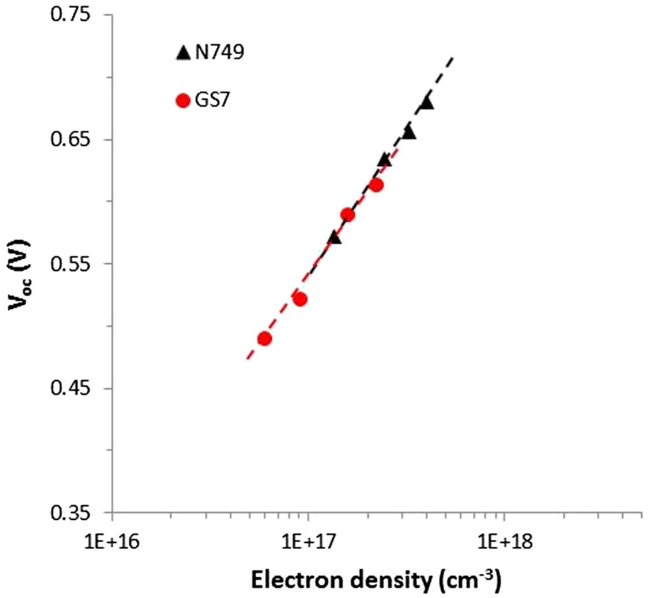


Fig. 7. V_{oc} as a function of electron density for DSSCs sensitized with N749 and **GS7**.

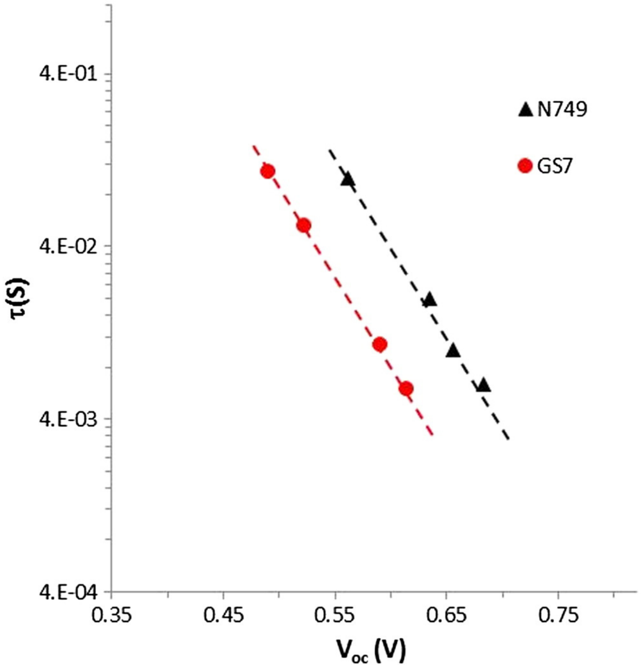


Fig. 8. Electron lifetime (τ) as a function of V_{oc} for DSSCs sensitized with N749 and **GS7**.

TiO_2/sensitizer/electrolyte interface and shorter electron lifetime, which are reflected in the lower open circuit voltage and lower overall conversion efficiency. Our research shed some light on the future design and development of ruthenium sensitizer coordinated with derivatives of benzimidazole as a bidentate ligand, and these types of studies are in progress.

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Appendix A. Supplementary material

Details about the syntheses and characterization of **GS7** sensitizer are provided in a supplementary file, together with the description of the thermogravimetric analysis and AC3 studies. These data include theoretical calculations of **GS7**. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2014.10.033. These data include MOL files and InChiKeys of the most important compounds described in this article.

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