Electron-rich heteroaromatic conjugated bipyridine based ruthenium sensitizer for efficient dye-sensitized solar cells†

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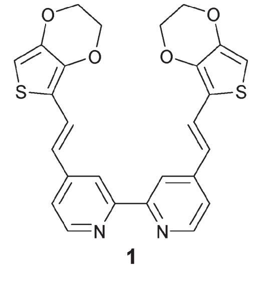
A novel heteroleptic ruthenium complex carrying a heteroaromatic-4,4′-π-conjugated 2,2′-bipyridine [Ru(II)LL′(NCS)$_2$] (L = 4,4′-bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2′-bipyridine, L′ = 4,4′-(dicarboxylic acid)-2,2′-bipyridine) was synthesized and used in dye-sensitized solar cells, yielding photovoltaic efficiencies of 9.1% under standard global AM 1.5 sunlight.

Dye-sensitized solar cells (DSCs) are attracting a growing interest in the conversion of sunlight into electricity by means of low-cost and efficient devices.[1] The sensitizer dye, which interacts with sunlight and promotes the photoinduced electron-transfer to the conduction band of the TiO$_2$ semiconductor and hole-transfer to iodide, plays a key role in the whole photovoltaic process. DSCs are mostly based on Ru(II)-polypyridyl sensitizers such as the *cis*-Ru(SCN)$_2$L$_2$ (L = 2.2′-bipyridyl-4,4′-dicarboxylate) (N3), leading to power conversion efficiencies exceeding 11%.[2] The mismatch between the dye-sensitizer absorption spectrum and the solar emission is one of the major factors for low efficiencies. Therefore it is paramount to design new sensitizers having panchromatic response with improved molar extinction coefficients while keeping the required thermal and photostability.[3] Recently, a number of heteroleptic Ru(II) sensitizers with bipyridine (bpy) ligands π-conjugated with electron-rich benzenoid cores relying on the donor capacities of primary organic functionalities such as OR have been introduced.[3,4] So far, the use of π-excessive heteroaromatic rings as end-groups in substituted bpy ligands has scarcely appeared in the literature[5] despite the fact that electron-rich heteroaromatics, even the unsubstituted rings, may act as efficient donor moieties.[6]

Here we present a novel heteroleptic Ru(II) sensitizer where one of the 2.2′-bipyridyl-4,4′-dicarboxylate groups in the N3 dye has been replaced by a heteroaromatic-4,4′-π-conjugated 2,2′-bpy, bearing conjugated electron-rich heteroaromatic rings as donor end-substituents. DSCs have been fabricated based on the novel sensitizer and their photoelectrochemical properties have been measured under various conditions. DFT/TDDFT calculations have been performed for the sensitizer in solution and for a TiO$_2$ nanoparticle model, highlighting the factors affecting the measured photovoltaic efficiencies.

The heteroaromatic donor end-group of the substituted bipyridine moiety was selected on the basis of the widely known π-electron-rich nature of five-membered monoheteroaromatics (*e.g.* furan, thiophene, pyrrole).[6,7] We chose to increase the weak donor properties of thiophene by replacing it with the 3,4-ethylenedioxythiophene (EDOT) ring. The 4,4′-bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2′-bpy ligand **1** was prepared by double condensation of 4,4′-dimethyl-2,2′-bpy with 3,4-ethylenedioxythiophene-2-carbaldeyde in THF using lithium diisopropylamide as a base. The corresponding diol intermediate was then converted to the π-conjugated ligand **1** by reaction with POCl$_3$ in pyridine (see ESI†). It is worth noting that gram quantities of ligand **1** can be reliably and cheaply prepared. The ligand **1** shows an absorption peak at 366 nm in DMSO with a molar extinction coefficient of 63 000 M^{-1} cm^{-1} and a $\lambda_{\text{cut-off}}$ at 435 nm; no fluorescence emission in DMSO was observed.



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The ruthenium complex [Ru(II)LL′(NCS)$_2$] (L = **1**, L′ = 4,4′-(dicarboxylic acid)-2,2′-bipyridine) (**Ru-EDOT**, see Fig. 1) was obtained in a one-pot synthesis (35% yield) from the sequential reaction of [Ru(*p*-cymene)Cl$_2$]$_2$ dimer with **1**, and reaction of the resulting mononuclear complex with 4,4′-dicarboxyl-2,2′-bipyridine, followed by the addition of an excess of ammonium thiocyanate. The analytical and the spectroscopic data of **Ru-EDOT** are fully consistent with the formulated structure. The absorption spectrum of the sensitizer (Fig. 1) is dominated in the visible region by an absorption

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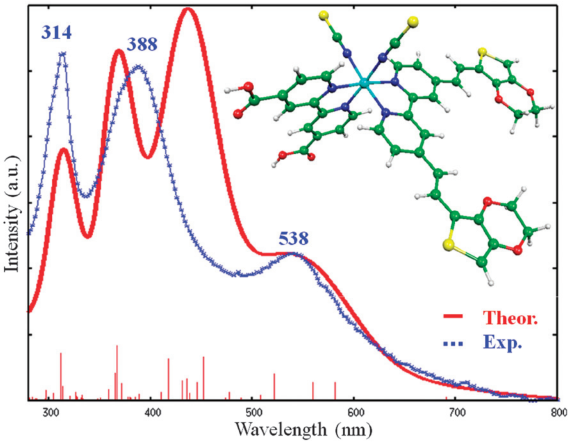

Fig. 1 Computed and experimental UV-Vis absorption spectra in EtOH of **Ru-EDOT** along with its optimised structure.

feature at 538 nm, with a molar extinction coefficient of 16 000 M^{-1} cm^{-1}, which is higher than that of the N3 (14 200 $M^{-1}cm^{-1}$) and exhibits a luminescence maximum at 820 nm when excited within the visible absorption band. The cyclic voltammogram of **Ru-EDOT** shows a quasi-reversible oxidation at $E_{1/2}$ = 0.9 V *vs.* NHE which is assigned to the $Ru^{III/II}$ couple, to be compared to 1.12 V *vs.* NHE measured for N3. The 0.22 V cathodic shift of the **Ru-EDOT** oxidation potential compared to N3 is due to the influence of the electron-rich heteroaromatic donor rings that destabilize HOMO orbitals. When scanning towards negative potentials one quasi-reversible wave at $E_{1/2} = -1.59$ V is observed, which is assigned to 4,4′-dicarboxylic acid-2,2′-bipyridine reduction.

A schematic representation of the molecular orbitals for **Ru-EDOT** is shown in Fig. 2. The HOMO is a combination of Ru t_{2g} and SCN π orbitals, as found in similar compounds,[8] appreciably mixed with π EDOT character. This is at variance with the N621 case, featuring an alkyl-substituted bpy ligand, for which we found a pure Ru–SCN HOMO.[2] Such mixing is due to the conjugation with EDOT arms in the bipyridine ligand. Since the HOMOs are the starting orbitals for the low-lying charge transfer transitions of **Ru-EDOT** (see below) the partial EDOT contribution to this orbital suggests that upon dye photo-oxidation, following electron injection into TiO_2, the positive charge is partially localized on the ligand, being stabilized by the electron-donation from the EDOT substituent. The LUMO is a π* orbital localized on the protonated carboxy-bpy ligand, while the LUMO + 1, lying 0.26 eV above the LUMO, is a π* orbital localized on the EDOT-substituted bpy (Fig. 2).

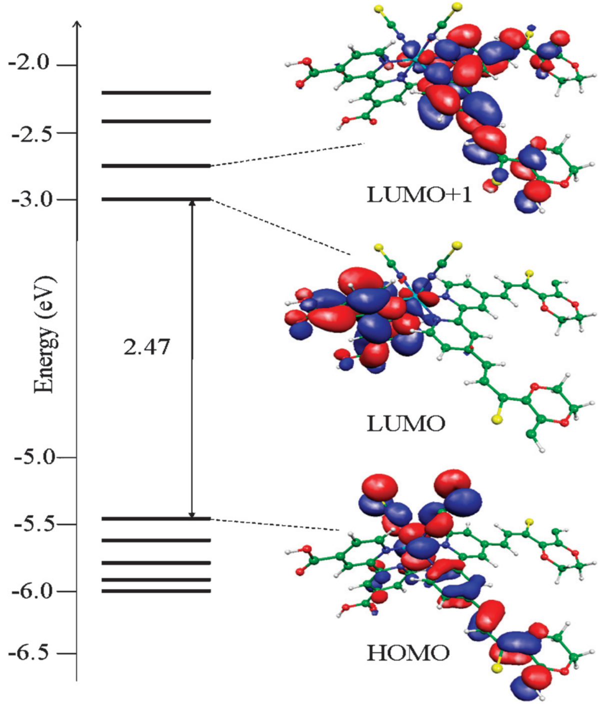

Fig. 2 Molecular orbital energy diagram of **Ru-EDOT**.

The TDDFT calculated absorption spectrum (Fig. 1) is in good agreement with the experimental spectrum for the low-energy region, whereas some discrepancy in the intensity distribution is found at higher energies. The 538 nm absorption band is well reproduced by our theoretical approach (540 nm); this feature is composed by three major contributions all having the LUMO + 1 as the arriving state. The lowest excited state is originated from transition to the LUMO, localized on the carboxylated bipyridine. The starting states are in both cases within the HOMO/HOMO−2 set of mixed Ru-SCN and ligand character. All these transitions are of Ru–SCN to bipyridine π* charge transfer character, with those involving the LUMO + 1, localized on EDOT-substituted bipyridine, showing higher intensities. This is possibly related to the ligand π character of the HOMOs, which introduces some π–π* character in these otherwise charge transfer excitations. The calculated absorption spectrum and the excited states order is perfectly consistent with the high experimental photovoltaic efficiencies. Indeed, excitation at about 540 nm will mainly lead to excited states localized onto the EDOT-substituted bipyridine. Since these heteroleptic sensitizers are adsorbed onto TiO_2 *via* the carboxy-bpy,[9] the presence of lower lying excited states residing on such ligands allows efficient energy transfer to this state, and subsequent efficient electron injection.

Comparing the lowest **Ru-EDOT** excited state energy to the conduction band edge of a model TiO_2 nanoparticle,[2,10] we found the lowest triplet and singlet excited states to lie 0.42 and 0.64 eV above the TiO_2 conduction band edge, respectively. Such alignment of the excited states ensures a high driving force for electron injection from the dye to the semiconductor, which results in the high experimental photocurrents (see below).

DSCs have been fabricated with the Ru-EDOT sensitizer. The screen-printed double layer film consists of a transparent 7 μm layer and a 5 μm scattering layer. The films were prepared and treated with 0.05 M titanium tetrachloride solution using a previously reported procedure.[2] The dye solutions were prepared in the concentration range of 2–3 × 10^{-4} M in EtOH without and with 10 mM 3a,7a-dihydroxy-5b-cholic acid (cheno) as an additive. The electrodes were dipped into each dye solution for 20 h at room temperature. The fabrication procedure, the testing conditions, and the equipment used were reported before.[2] Two electrolyte solutions were used: M1 (0.6 M *N*-methyl-*N*-butylimidazolium iodide, 0.04 M

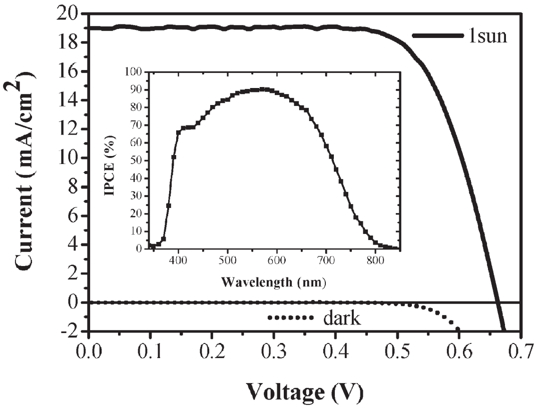

Fig. 3 Current–voltage characteristics of **Ru-EDOT** obtained with a 9 + 5 nanocrystalline TiO_2 film and M1 electrolyte. The inset shows incident monochromatic photon-to-current conversion efficiency (IPCE).

Table 1 Current–voltage characteristics obtained with various TiO_2 thickness layers anchored with **Ru-EDOT** with two different electrolytes

Electrolyte	l/μm	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η (%)
M1	7 + 5	17.7	660	0.73	8.50
M1	9 + 5	19.1	663	0.72	9.10
A6986	9 + 5	19.7	594	0.67	7.90

iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate and 0.28 M *tert*-butylpyridine in a 15 : 85 (v/v) mixture of valeronitrile and acetonitrile) and A6986 (0.6 M *N*-methyl-*N*-butylimidazolium iodide, 0.05 M iodine, 0.1 M LiI and 0.05 M *tert*-butylpyridine in a 15 : 85 (v/v) mixture of valeronitrile and acetonitrile).

Fig. 3 shows the *J*/*V* curve (current density–voltage), and the incident monochromatic photon-to-current conversion efficiency (IPCE) of the solar cell sensitized with **Ru-EDOT**. It is worth noting that the IPCE curve plotted as a function of excitation wavelength exhibits a strikingly high plateau value of 87%. The solar cell sensitized with **Ru-EDOT** shows an excellent efficiency under solar simulated light irradiation (100 mW cm^{-2} 1.5 AM Global) of 9.1% with a J_{sc} of 19.1 ± 0.20 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 663 ± 15 mV, and a fill factor (FF) of 0.72 ± 0.01. Integrating the IPCE curve over the solar spectrum results in a short circuit current of 19.2 mA cm^{-2} in agreement with the measured device photocurrent.

The **Ru-EDOT** sensitized solar cells photovoltaic performance using different TiO_2 thickness and electrolytes is shown in Table 1. When the A6986 electrolyte that contains a high concentration of LiI is used,[11] the photocurrent density increased from 19.1 to 19.7 ± 0.2 mA cm^{-2}; however the photovoltage of the cell decreased due to adsorption of Li cations onto the TiO_2 surface charging it positively, and thereby the Fermi level moves down (positively).[12] We also notice that the open circuit potential of this heteroleptic sensitizer is smaller compared to the prototypical N3 or N719 dyes,[2] as consistently observed for other heteroleptic sensitizers.[9]

In conclusion, a new electron-rich bipyridine ligand has been synthesised and employed in DCSs based on the corresponding Ru(II) sensitizer. The sensitiser excited states have a favourable alignment with the conduction band edges of a model TiO_2 nanoparticle, thus ensuring a high driving force for electron injection from the dye excited states into the semiconductor conduction band. The conjugated π-excessive heteroaromatic rings as donor end-substituents provide directionality in the excited state, and display enhanced oscillator strength leading to a significantly increased short circuit photocurrent of 19.7 mA cm^{-2} on a 9 + 5 μm thick TiO_2 nanocrystalline layer. These results open the way to a series of efficient heteroleptic and homoleptic ruthenium sensitizers with new bipyridine ligands carrying donor heteroaromatic end-groups.

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