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Synthesis, characterisation, electrochemical study and photovoltaic measurements of a new terpyridine and pyridine-quinoline based mixed chelate ruthenium dye

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ABSTRACT

A novel ruthenium-terpyridine based photosensitizer, Ru[(*p*-F-tpy)(pcqH)Cl] PF_6 (**1**); (*p*-F-tpy = 4′-(4-fluorophenyl)-2,2′:6′,2″-terpyridine, pcqH = 2-(2-pyridyl)-4-carboxyquinoline) was synthesized and spectroscopically characterized. The electronic spectrum of the complex shows the lowest energy MLCT band at 536 nm in DMSO. The ground state pK_a values of the acidic ligand (pcqH) and the Ru complex were spectrophotometrically determined. The pK_a of the COOH group in the free ligand is 3.56, and this reduces to 2.89 when bound to the metal. The cyclic voltammetry of the complex shows a reversible $Ru^{II/III}$ oxidation at 0.825 V with respect to Ag/AgCl reference electrodes in DMF. The Cl group is very labile, substitution of the Cl group by H_2O generates aqua species, which has been shown spectrophotometrically. A Pourbaix diagram for the Ru-aqua species has been constructed to show the detailed redox properties of the complex by means of cyclic voltammetry and differential pulse voltammetry at variable pH. Non-linear regression analysis was performed to generate the pK_a values for the Ru-aqua species as 11.89 (Ru^{II}) and 4.00 (Ru^{III}). Photovoltaic measurements with the dye were performed after anchoring onto a TiO_2 surface with the I^-/I_3^- redox electrolyte. Photovoltaic properties, like open-circuit photo-voltage (Voc = −0.35 V), short-circuit photocurrent density (J_{sc} = 1.428 × 10^{-4} amp cm^{-2}), fill factor (ff = 39.4%) and solar-to-electric conversion efficiencies (η = 0.13%), of the DSSCs constructed from the [Ru(*p*-F-tpy)(pcqH)Cl] PF_6 sensitized TiO_2 electrodes were measured. A DFT and TDDFT study has been performed on the complex. The TDDFT calculated absorption spectrum nicely matches the experimental spectrum.

1. Introduction

Photosynthesis has inspired the scientific community to design molecular systems to effectively trap sunlight as a source of alternative energy. Polypyridyl complexes of transition metals with a d^6 electronic configuration have the capability of absorbing light. Therefore these complexes can act as effective photosensitisers, just like chlorophyll-*b* or *b*-carotenoid in PSII [1–3]. With this goal, extensive research has been carried out on Ru-bipyridyl, phenanthroline and other related diimine complexes [4–18]. Ru(bipyridine)$_3^{+2}$ has evolved as the most effective photosensitiser over the years due to its photophysical novelty (an excited state lifetime of 1100 ns) [19], structural robustness and close proximity of the $Ru^{II/III}$ oxidation to that of the Photosystem-II [1,2]. However for the Ru(bpy)$_3^{+2}$ system with substituted bpy ligands, the Ru centered inherent stereogenicity makes it hard to get pure compounds [20]. This synthetic difficulty disappears for Ru-terpyridyl compounds, but the terpyridyl compounds of Ru are photophysically not so appealing due to the very low excited state lifetime (for Ru(terpy)$_2^{+2}$, τ = 0.25 ns) at room temperature [21]. The rigid tridentate moiety of terpyridine results in a distorted octahedral geometry in their Ru(II) complexes. In coordinated terpyridine, the N–Ru–N trans angles reduce to 158.6° from 173.0° in the analogous Ru(II)bpy complexes [22,23]. Hence the ligand field strength weakens, reducing the energy of the d–d metal-centered triplet state (^{3}MC) [24]. Consequently the energy gap between the ^{3}MLCT and ^{3}MC states decreases and thus the ^{3}MC state becomes thermally accessible from the ^{3}MLCT state, causing easy non-radiative decay back to the ground state. For a better excited state property

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of the sensitizer, thermal non-radiative deactivation from the ^{3}MC state should be minimised. This can be achieved either by destabilizing the ^{3}MC state or by stabilizing the ^{3}MLCT state. Proper substitution (electron withdrawing or/and electron donating group) at the para position of the central pyridine ring of the terpyridine can achieve the desired effect [25]. The ^{3}MLCT state can be stabilised by introducing an electron withdrawing group at the para position of the central pyridine of the terpyridine ligand [26,27], whereas an electron donating group cannot destabilise the ^{3}MC state to a great extent [28]. Nevertheless, presence of a phenyl substituent at the para position stabilises the ^{3}MLCT state more than the ^{1}MLCT state [29,30].

Approaches have been made to develop thiocyanate free Ru dyes in order to improve the light absorption capacity as well as to avoid the possibility of getting a mixture of products due to the ambidentate nature of the thiocyanate ligand. One methodology in this respect is to use a cyclometallating ligand [31–33], which fulfills both purposes. Another approach that may be used is to change the ancillary ligand [34]. Substitution of SCN by Cl red shifts the MLCT band by 20–30 nm.

Pioneered by Professor Michael Gratzel, these ruthenium polypyridyl complexes are widely used as photosensitizer dyes in wide band gap solar cells. The most efficient photosensitizer to date is N719, with an efficiency of 11.18% [35]. Based on the above approach, we report a new Ru-polypyridyl complex (Fig. 1) which consists of a substituted terpyridine ligand, an anchoring group, 2-(2-pyridyl)-4-carboxyquinoline, and an ancillary Cl ligand. We were successful in our attempt to modulate the energy gap between the d^6-π HOMO and the ligand based LUMO by red shifting the MLCT absorbance maxima up to 536 nm using Cl as an ancillary ligand. The coordinated Cl reduces the $d\pi \rightarrow \pi^*$ energy gap and therefore causes a significant red shift in the MLCT absorbance [36]. For the majority of terpyridine based Ru complexes the low energy MLCT absorbance remains below 500 nm [34,37,38], whereas the complex reported here exhibits the MLCT absorbance at 536 nm. Here, we have used a pyridine ligand and a quinoline based anchoring group, 2-(2-pyridyl)-4-carboxyquinoline, for the dye. The anchoring group in this dye is quite non-conventional as there are no reports, to our knowledge, where such a pyridine-quinoline moiety has been used as the linker group. The extended aromatic heterocycle in this ligand may help in better delocalisation of the electron density involved in the metal to ligand charge transfer (MLCT), thus helping in better electron injection in the conduction band of TiO_2. The presence of only one –COOH linker site may seem counterproductive, but merely increasing the number of linker groups does not always enhance the efficiency of the solar cell. It has been reported that although black dye has three potential COOH linkers, it attaches to the semiconductor surface via only one carboxylic acid group due to steric congestion [39]. Our aim was to get rid of this stereochemical congestion for the attachment of the dye to the semiconductor as well as to study the electrochemical and photovoltaic behaviour of this new heteroleptic Ru complex with a new anchoring moiety. There is a possibility that these new dye molecules will be better attached on the semiconductor surface.

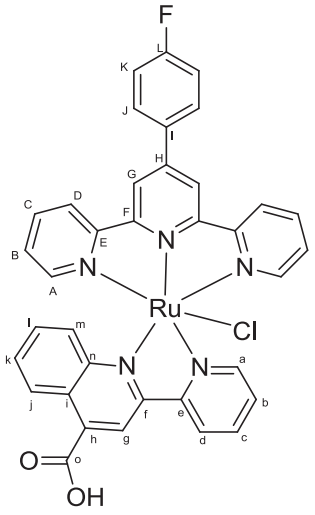

Fig. 1. Labeled structure of [Ru(*p*-F-tpy)(pcqH)Cl]PF_6.

We have also studied the spectroscopic and electrochemical properties of the dye by varying the pH from 0.04–13.17. It has been shown that both the MLCT and redox properties can be significantly tuned by changing the pH. Also an interesting observation is that the Ru–Cl bond is labile in aqueous media [34,40] and gets substituted by H_2O molecules in acidic media (within pH 4). This can provide an idea about the optimal conditions required for dye stability and effective dye regeneration for this class of photosensitisers in Dye Sensitized Solar Cells (DSSCs).

2. Experimental

2.1. Materials and methods

4-F-benzaldehyde, 2,3-indolinedione, tetrabutyl ammonium bromide and silver nitrate were purchased from Spectrochem, 2-acetylpyridine and ammonium hexafluoro phosphate were purchased from Sigma Aldrich and ruthenium chloride was obtained from Arora Mathey India Limited. The ethanol and DMF used were HPLC grade, whereas methanol was dried according to literature procedures [41]. The water used for the spectrophotometric and electrochemical studies was purified by a Milli-Q system. Tetrabutyl ammonium perchlorate was synthesised according to the literature [42].

Infrared spectra were recorded as KBr pellets on a Shimadzu IR-Prestige21 spectrometer. UV–Vis spectra were recorded using a Perkin Elmer Lambda 750 spectrophotometer. The pH values were measured in a Thermos Scientific Orion 4 star pH Benchtop. Thermogravimetric analysis of the dye was executed in a DTG-60 (Shimadzu Corporation, Kyoto, Japan) from 30 to 800 °C in a platinum pan at a heating rate of 10 °C per minute under flowing N_2 (30 ml per min.). Cyclic and differential pulse voltammograms were recorded in a CHI6003E potentiostat, either in DMF or DMF-water solutions, containing 0.1 M TBAP as a supporting electrolyte, with glassy carbon as a working electrode, a Pt wire as a counter electrode and an Ag/AgCl non-aqueous reference electrode. The ferrocene/ferrocenium couple was observed at E^0 (ΔEp) = 0.4 V (100 mV) under these experimental conditions. ^{1}H NMR spectra were recorded on a Bruker AVANCE DPX 400 MHz spectrometer using $Si(CH_3)_4$ as an internal standard. ESI-MS spectra of the samples were recorded on a JEOL JMS 600 instrument. Fluorescence spectra at room temperature were recorded using a Shimadzu RF-5301 PC spectrofluorometer.

2.2. Synthesis

2.2.1. Preparation of the ligands

2.2.1.1. 4′-(p-Fluorophenyl)-2,2′:6′,2″-terpyridine (p-F-tpy). The terpyridyl ligand has been synthesized by following the reported procedure [43]. 4-F-benzaldehyde (0.620 g, 5 mmol) and 2-acetylpyridine (1.21 g, 10 mmol) were dissolved in ethanol. KOH (0.77 g, 10 mmol) was added and the mixture was vigorously stirred. After the potassium hydroxide pellets completely dissolved, ammonia (excess, ca. 20 ml) was added and the mixture was stirred at room