



A novel ruthenium sensitizer with –OMe substituted phenyl-terpyridine ligand for dye sensitized solar cells



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ABSTRACT

A new ruthenium photosensitizer **[Ru(triOMePhtpy)(bpydca)(NCS)]PF₆ (1)** (triOMePhtpy = 4'-(3,4,5-triOMe)Phenyl-2,2':6',2''-terpyridine; bpydca = 4,4'-dicarboxy-2,2'-bipyridine) has been synthesized and characterized by IR, UV–Vis, NMR and Mass spectroscopy. The molecule shows a moderately intense MLCT band at 511 nm. Along with the intraligand transitions in the UV region, the molecule shows several high energy MLCT bands which has been nicely manifested by the TDDFT calculation. DFT optimized structure shows a distorted octahedral geometry around central ruthenium atom, where the phenyl ring attached to the 4' position of terpyridine moiety makes a torsion angle of 34.09° with the central pyridine ring. pK_a of the –COOH functionalities was determined spectrophotometrically by monitoring the variation of MLCT band position with pH and found to be ~3.98. Photovoltaic measurements of the present dye in a typical DSSC configuration was found to exhibit J_{sc} = 5.10 mA cm⁻², FF = 66.02%, Voc = 0.68 V and η = 4.62% at an optimized intensity of 50 mW cm⁻².

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1. Introduction

With the ever increasing energy demands of the world, merely relying upon fossil fuel is not enough. The development of photovoltaic (PV) cells that convert sunlight to electricity is an attractive strategy in the search for renewable source of energy. Among the different PV systems, besides the solid state devices, dye sensitized solar cell (DSSC) is an effective alternate solar cell technology with cost effective and eco-friendly features (Chen et al., 2013; Teh et al., 2013; Clifford et al., 2004; Byrne et al., 2014; Dong et al., 2015). A typically fabricated DSSC consists of TiO₂ based photo anode, dye molecule, I⁻/I₃⁻ electrolyte and a platinum coated FTO counter electrode. Light is absorbed by the sensitizer dye molecule anchored to the surface of a wide band gap semiconductor TiO₂. The carrier electrons are injected from the excited dye molecule (LUMO) to the conduction band (CB) of TiO₂ and are transported to the charge collector. The use of sensitizer dyes with broad absorption band, in conjugation with the TiO₂ films of nanocrystalline morphology, permits to harvest a large fraction of sun-

light (Wang et al., 2009; Mayumi et al., 2014; Park and Han, 2014). The first DSSC was demonstrated by O'regan and Grätzel (1991), using mesoporous nanocrystalline TiO₂ electrodes and [L₂Ru(μ-(CN)Ru(CN)L'₂)₂] dyes (where, L = 2,2'-bipyridine-4,4'-dicarboxy late and L' = 2,2'-bipyridine ligand) (O'regan and Grätzel, 1991; Nazeeruddin et al., 1993; Nazeeruddin et al., 2005, 2001). Thereafter dyes like N3 & N749 and their modifications became the gold standard for developing DSSC photosensitizers. The different approaches used to increase the cell efficiency at the photosensitizer level are (Rees and Baranoff, 2014) (a) introducing NCS ligands to stabilise the dye t_{2g} orbitals, tuning of the redox potential and also to enhance visible light absorption (Wang et al., 2002; Funaki et al., 2009; Vougioukalakis et al., 2010; Onozawa-Komatsuzaki et al., 2009, 2011, 2012; Chen et al., 2009; De Angelis et al., 2010; Finnie et al., 1998; Yang et al., 2011; Lin et al., 2012; Kimura et al., 2013; Numata et al., 2013a,b; Islam et al., 2002, 2006; Gao et al., 2010; Funaki et al., 2009a,b; Moorlag et al., 2002; Funaki et al., 2012; Chen et al., 2009, 2007; Kim et al., 2011; Chandrasekharam et al., 2011; Giribabu et al., 2011), (b) substituted anchoring ligands to minimize the electron recombination at TiO₂-dye interface (Numata et al., 2013a), (c) using of cyclometalated ligands to make -NCS free dyes (Wadman et al., 2007; Caramori et al., 2010; Sepehrifard et al.,

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2013; Park et al., 2010; Singh et al., 2013; Wadman et al., 2010; Kisserwan et al., 2012; Chitumalla et al., 2014; Kisserwan and Ghaddar, 2011; Robson et al., 2011), and (d) use of substituted bulky groups to prevent direct charge recombination from TiO₂ with the redox mediator (Yang et al., 2011; Kimura et al., 2013).

Another approach can be the use of co-ligands that may assist the central metal ion transferring electronic charge density towards the anchoring ligand(s) to ensure higher probability of electron injection into the conduction band of the semiconductor (Le Bahers et al., 2014). With this theoretical insight, we have designed a dye with tri substituted 4'-(3,4,5-triOMe)Phenyl-2,2':6',2''-terpyridine (**triOMePhtpy**) as a co-ligand. The -OMe is a well recognized +R donor group which has shown to increase the absorptivity when attached to terpyridine systems (Han et al., 2008). In phenyl terpyridines although the phenyl ring twists away from the central pyridine ring due to steric hindrance between the hydrogens ortho to the phenyl-pyridine bond, appropriate substituents on the phenyl ring and metal coordination enhances the pi-conjugation between the rings (Presselt et al., 2010). Moreover in the excited state, there is a change in the dihedral angle between the phenyl ring and the central pyridine ring to give a coplanar arrangement (Hecker et al., 1991). Hence this phenyl-terpyridine ligand with electron donating OMe groups attached to the phenyl ring may coordinate to the metal with a higher electron density. Thus designing the Ru dye with the terpyridine motif and NCS as an ancillary ligand and an appropriate linker group such as 4,4'-dicarboxy-2,2'-bipyridine (**bpydca**), we can expect to achieve an increased electron injection on the semiconductor conduction band along with a concomitant reduction in charge recombination with the dye.

In this work we have presented the synthesis of the **[Ru(triOMePhtpy)(bpydca)(NCS)]PF₆** dye (**1**), its spectroscopic characterization and its spectrophotometric, electrochemical and photovoltaic properties. Finally we rationalized the spectrophotometric and photovoltaic observations with a detailed TDFT analysis.

2. Experimental

3,4,5-trimethoxy benzaldehyde, tetrabutyl ammonium bromide and silver nitrate were purchased from Spectrochem. 2-acetylpyridine, 4,4'-dimethyl-2,2'-bipyridine and ammonium hexafluorophosphate were purchased from Sigma Aldrich and Ruthenium chloride was obtained from Arora Mathey India Limited. Ethanol and DMF used were HPLC grade, whereas methanol was dried according to literature procedure (Furniss et al., 1989). Water used for the spectrophotometric and electrochemical studies was purified by a Milli-Q system. Tetrabutyl ammonium perchlorate (TBAP) was synthesised according to literature (Sawyer et al., 1995).

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. Cyclic voltammogram and differential pulse voltammogram were recorded in CHI6003E potentiostat, either in DMF or DMF-water solutions, containing 0.1 M TBAP as supporting electrolyte, glassy carbon as working electrode, Pt wire as a counter electrode and Ag/AgCl non aqueous reference electrode. The ferrocene/ferrocenium couple was observed at E^0 (ΔE_p) = 0.4 V (100 mV) under these experimental conditions. ¹H NMR spectra were recorded on a Bruker AVANCE DPX 400 MHz spectrometer using Si(CH₃)₄ as internal standard. Single pulse decoupled gated NOE ¹³C NMR spectrum was recorded in JNM-ECZ400S/L1 spectrometer. ESI-MS spectra of the samples were recorded on JEOL JMS 600 instrument.

2.1. Synthesis

2.1.1. Preparation of ligands

4'-(3,4,5-trimethoxyphenyl)-2,2':6',2''-terpyridine (triOMePhtpy) (L1): The terpyridyl ligand has been synthesized by following the reported procedure (Wang and Hanan, 2005). 3,4,5-trimethoxybenzaldehyde (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 temperature for 16 h under N₂ atmosphere. The resulting solution was filtered under vacuum and washed with ethanol to give a very light blue colored fluffy solid: yield 0.656 g (40%). The crude product was recrystallised from methanol. Mass (*m/z*): Observed 399.20(M) Calcd. 399.44(M) ¹H NMR (CDCl₃δ): 8.74 (2H,d,H_a), 8.66 (4H,s,H_{g,j}), 7.86 (2H,t,H_d), 7.36 (2H,m,H_c), 7.07 (2H,dd,H_b), 3.99 (6H,s,H_m), 3.93 (3H,s,H_n). ¹³C NMR:156.24 C_f, 155.90 C_e, 153.64 C_a, 150.56 C_h, 149.17 C_k, 139.00 C_c, 136.94 C_i, 134.55 C_i, 123.89 C_b, 121.47 C_d, 118.99 C_g, 104.69 C_j, 61.02 C_n, 56.56 C_m.

2,2'-Bipyridine-4,4'-dicarboxylic acid (bpydca) (L2): The ligand was synthesized according to a reported procedure (Schwarz et al., 2000) in >93% yield by oxidizing 4,4'-dimethyl-2,2'-bipyridine with stoichiometric amounts of CrO₃ in concentrated sulfuric acid at 40 °C for 3 h, poured onto ice and left overnight. The white crystals were filtered off and recrystallized from water.

[Ru-(triOMePhtpy)]Cl₃ : triOMePhtpy (L1) (0.614 g, 1.5 mmol) and **RuCl₃** (0.40 g, 1.5 mmol) were dissolved in 20 ml dry methanol and heated to reflux under N₂ for 3 h. The resulting deep brown solution was allowed to cool at room temperature, after which the solution was cooled in an ice bath for 0.5 h. The brown solid was collected by vacuum filtration and washed with cold methanol until the filtrate was colorless and then washed with Et₂O and air dried. The product (Yield: 0.662 g, 72%) was used without further purification.

[Ru-(triOMePhtpy)(bpydca)SCN](PF₆)(1): [Ru-(triOMePhtpy)]Cl₃ (0.267 g, 0.5 mmol) and **bpydca** (0.125 g, 0.5 mmol) were taken in an round bottomed flask in 25 ml dimethyl formamide (DMF) and refluxed for 6 h under N₂. The reaction mixture solution was then reduced in rotator evaporator to 5 ml and a saturated aqueous solution of NH₄PF₆ was added to the solution. On addition of more water, precipitation appeared which is collected by filtration in a G4 sintered glass filter. The product is purified by column chromatography using silica as the stationary phase and DCM as mobile phase, eluted with 1:1 DCM/CH₃OH eluent. This Chloro complex (101 mg, 0.104 mmol) is further reacted with ammonium thiocyanate 279 mg (excess) in 20 ml DMF and refluxed for 5 h to give a reddish solution which is reduced in rotavapor to 5 ml and then saturated aq. solution of NH₄PF₆ were added to the solution to give a reddish precipitation. The precipitate is then washed with water, dried and then washed with ether collected by filtration in a G4 sintered glass filter. Crude weight: 95 mg. The product is then purified by column chromatography using silica as the stationary phase and DCM as mobile phase. The deep red colored product (26 mg, 0.031 mmol, yield 29.5%) is eluted with 1:1 DCM/CH₃OH eluent (Scheme 1). Mass (*m/z*): Observed 803.68(M+1) Calcd.802.8(M) ¹H NMR: (d₆-DMSO) δ: 9.46(1H,d,H_A), 9.21(1H,d,H_B), 9.10(2H,s,H_{D,E}), 7.7(2H,d,H_{C,H}), 8.95(2H,d,H_A), 8.63(2H,s,H_J), 8.10(2H,t,H_D), 7.55(2H,s,H_G), 7.45(2H,m,H_C), 7.31(2H,dd,H_B), 4.05(6H,s,H_M), 3.82(3H,s,H_N). ¹³C NMR: 165.4 C_K, 164.718 C_L, 158.192 C_F, 157.2 C_e, 155.7 C_H, 155.1 C_F, 153.6 C_K, 152.2 C_H, 150.9 C_J, 150.6 C_I, 149.1 C_A, 148.5 C_H, 146.7 C_A, 139.2 C_I, 137.6 C_C, 133.4 C_I, 132.1 C_M, 128.0 C_B, 126.7 C_D, 125.6 C_E, 124.5 C_D, 123.4 C_B, 122.8 C_G, 120.8 C_G, 105.6 C_J, 60.3 C_N, 56.5 C_M.

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