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New terpyridine-based ruthenium complexes for dye sensitized solar cells applications

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ABSTRACT

Three new terpyridine-based ruthenium complexes, named as **MC124**, **MC125** and **MC127**, were synthesized and employed as sensitizers in dye sensitized solar cells. The **MC** dyes were characterized with experimental techniques followed by theoretical calculations. The promising optical properties with higher molar extinction coefficients compared to **N749** prototypical dye, and suitable positioning of energy levels prompted us to employ these dyes in working devices. When used in conjunction with liquid I^-/I_3^- redox electrolyte, the **MC** dyes have shown modest performances, with a maximum PCE of 2.3% reached with **MC124** in combination of CDCA used as co-adsorbent.

1. Introduction

Dye-sensitized solar cells (DSSCs) are considered to be one of the alternative next generation photovoltaic devices due to their ease of fabrication, low materials cost and attractive unique features [1]. Typical DSSCs is based on a photoelectrode with mesoporous anatase TiO_2 layer [2,3], usually composed by a network of nanoparticles (~20/30 nm diameter), sensitized with dye molecules and interpenetrated by a liquid electrolyte (usually I^-/I_3^- redox couple in a volatile organic solvent). The device architecture is completed by a counter-electrode. After the photoexcitation of the chemisorbed dye, charge separation occurs at the dye/TiO_2 interface with electron injection into the semiconductor conduction band (CB). The injected electrons flow across the mesoporous structure of TiO_2 layer and through the external circuit is collected at the counter electrode. The oxidized dye molecules are regenerated by the redox mediator in the telectrolyte solution and finally, the circuit is closed by the electrolyte regeneration at the counter-electrode.

In the past decade, number of modifications have been attempted on sensitizers, TiO_2 photo electrodes, counter electrodes and electrolyte composition in order to improve the overall performance of DSSCs [4–8]. Sensitizers are the key element to the success of this technology as the power conversion efficiency of the device is known to be greatly influenced by light harvesting and electron injection properties of the sensitizer. A large variety of sensitizers have been tested for DSSCs including organic dyes [9–13], zinc porphyrin [14–16] and Ru(II)-based sensitizers [17–19,54].

Although the high power conversion efficiencies (PCE) have been reached with organic dyes (approaching 10%) [20,21] and with porphyrin sensitizers in combination with Cobalt based redox couple (13%) [14–16], the Ru(II)polypyridyl sensitizers are continued to be deeply investigated. Apart from molecular sensitizers, recently perovskite hybrid absorbers ($MAPbI_3$, where MA = methylammonium or other derivatives) have shown 19% efficiency in solid state devices [24–26]. However, health hazards due to lead perovskites are a critical issue that may undermine its future employment and hence scientists are encouraged to continuously stay on the track of traditional DSSCs.

One of the prototypical terpyridyl ruthenium (II) sensitizer $[Bu_4N]_3[Ru(tctpy)(NCS)_3]$, was reported by Nazeeruddin and

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coworkers [27]. This sensitizer, also known as N749 or black dye, has shown an impressive efficiency of 10.4%. When used in combination with an organic cosensitizer, an improved certified record efficiency of 11.4% has been reported [44]. Though ruthenium (II) terpyridyl complexes show better photo response in longer wavelength region than those of bipyridyl complexes, the disadvantage generally lies with its low incident to photon conversion efficiency due to poor molar extinction coefficient and insufficient free energy for electron injection [28]. Extensive research has been pursued on functionalization of the N749 structure, with electron rich units, in order to increase light harvesting capacity and the charge transfer efficiency [29–32]. Other possible strategies employed to improve the efficacy in both the visible and near-IR regions, are the tandem DSSCs [33–35] or the cosensitization [36–41].

Concerning the stability in working devices, the **N749** dyes have shown similar performances compared to other Ru-bipyridyl dyes [42]. The presence of sulphur group in thiocyanate based ruthenium (II) sensitizers makes intimate contact with the iodide redox couple of the electrolyte that helps in the regeneration of dye [43]. Despite of these advantages, thiocyanates are weakly coordinating to the ruthenium (II) center and can be substituted by electrolyte additives, such as tert-butyl pyridine, or solvent molecules, under Stressing thermal and light soaking conditions [44–46].

Being already engaged in synthesis of various ruthenium and metal free sensitizers [47–54], we have designed a new class of ruthenium (II) sensitizers by partially or fully replacing the thiocyanate groups in black dye with bipyridine and terpyridine ligands as shown in Fig. 1, which is presumed to improve the absorption properties in the longer wavelength region. The bipyridines were functionalized with carbazole and fluorene as ancillary groups because of their hole transport capability, electron-richness and elongated conjugation. Furthermore alkyl chains introduced on the fluorene, carbazole and terpyridine moieties are expected to inhibit the dye aggregation and interfacial electron recombination processes. Here taking advantage of the support from theoretical calculations, we demonstrate the synthesis, the characterization and the photovoltaic performance of these three new terpyridine-based ruthenium complexes suitable for applications in DSSCs.

2. Experimental

2.1. Materials and instrumentation

The starting materials were purchased from Sigma–Aldrich. The solvents were purified using standard procedures and purged with nitrogen before use. All other chemicals used in this work were analytical grade and were used without further purification, and all reactions were performed under argon atmosphere. Absorption spectra were recorded on a Shimadzu Ultraviolet–Visible light (UV–Vis) spectrometer. Emission spectra were recorded on a J.Y. Horiba model fluorolog3 fluorescence spectrometer. The Differential Pulse Voltametry (DPV) curves were recorded using BAS100 electrochemical analyser where a three electrode cell is used in 0.1 M Bu_4NPF_6, N,N-dimethylformamide as solvent at a scan rate of 100 mVs^{-1}, Pt wire as a counter electrode, Ag/AgCl as reference electrode and calibrated with ferrocene.

2.2. Procedures for synthesis of ligands

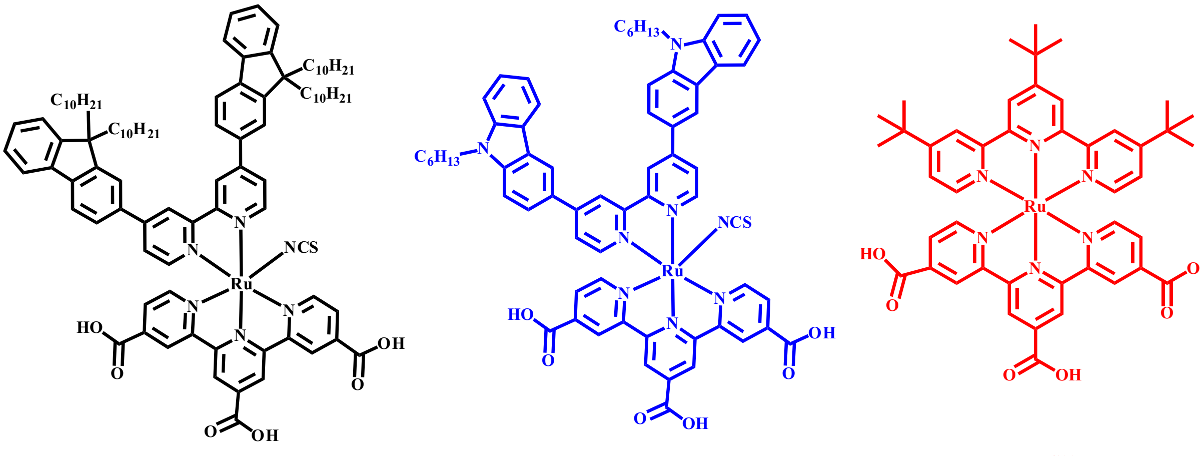
2.2.1. 2-Bromo-9,9-didecyl-9H-fluorene (**1**) (83%)

To an ice-cooled suspension of KOH (0.137 g, 2.459 mmol) in DMSO (10 mL), 2-bromo-9H-fluorene (0.200 g, 0.819 mmol) and 1-bromodecane (0.345 mL, 2.276 mmol) was added. The suspension was stirred at room temperature for 16 h under N_2. The mixture was cooled at room temperature and brine was added. The organic layer was extracted with ethylacetate and the combined organic extractions were dried over Na_2SO_4. After evaporation of solvent, the crude compound was purified over silica gel column and eluted using ethylacetate:hexane (1:9).

^1H NMR (300 MHz, $CDCl_3$, δ): 7.64–7.68 (m, 1H), 7.53–7.56 (m, 1H), 7.42–7.46 (m, 2H), 7.30–7.34 (m, 3H), 1.86–1.94 (m, 4H), 1.22–1.28 (m, 4H), 1.16–1.20 (m, 10H) 1.12–1.15 (m, 4H), 1.00–1.10 (m, 14H), 0.9 (t, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 14.11, 22.65, 23.65, 29.22, 29.52, 29.93, 31.85, 40.24, 55.34, 119.70, 120.92, 120.98, 122.83, 126.08, 128.87, 127.41, 129.82, 130.98, 140.09, 150.26, 152.92. ESI-MS: m/z $[M]^+$: 526.

2.2.2. 2-(9,9-Didecyl-9H-fluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (82%)

A solution of compound (**1**) (0.500 g, 0.952 mmol), bis(pinacolato)diboron (0.265 g, 1.047 mmol), were dissolved in dry dimethoxy ethane (8 mL) and KOAc (0.227 g, 2.856 mmol) was added. The mixture was stirred for 15 min under an argon atmosphere at room temperature. Then $Pd(dppf)_2Cl_2$ (0.041 g, 0.057 mmol) catalyst was added and the reaction mixture was stirred overnight at 80 °C. After being cooled to room temperature, the mixture was poured into water (20 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was pre-adsorbed onto



MC124 MC125 MC127

Fig. 1. Structures of **MC124**, **MC125** and **MC127**.