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Light harvesting properties of ferrocenyl based sensitizer with sulfur rich dithiocarabamates and xanthate as anchoring group

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Dedicated to Professor Ionel Haiduc for his outstanding contribution to chalcogenide chemistry.

Abstract

Three monoanionic dithio compounds *viz.* potassium *N*-benzyl-*N*-methylferrocenyl dithiocarbamate (**1**), potassium ferrocenyl imino ethyl-2-dithiocarbonate (**2**) and potassium *N*-2-hydroxy-ethyl-*N*-methylferrocenyl dithiocarbamate (**3**) have been synthesized and characterized by elemental analyses, IR, UV–Vis, ^{1}H and ^{13}C NMR spectroscopy. For the first time the light harvesting properties of these types of compounds with sulphur as an anchoring group have been investigated. The solar-cell performances of DSSCs based on dye-grafted nanocyrstalline TiO_2 using **1–3** and standard **N3** (bis[(4,4′-carboxy-2,2′-bipyridine)(thiocyanato)ruthenium(III)]) are compared, revealing substantial dependences on the dye structure. The cyclic voltammograms of the dyes have been explained using DFT calculations and the electron injection has been explained using density of states (DOS) plot for $(TiO_2)_{30} + \mathbf{1}$ system. Electrochemical impedance spectroscopy has been performed to measure the charge-transfer resistance for TiO_2/dye/electrolyte interface system and to corroborate the efficiency obtained from the dye-grafted solar cells. The **1**-based device show the best performance: $\eta = 5.39 \pm 0.03\%$, $J_{sc} = 10.70 \pm 0.06$ mA cm^{-2}, $V_{oc} = 0.697 \pm 0.004$ V and $FF = 0.71 \pm 1$. Long term stability of the photocurrent output of the cell using dye **1** as photosensitizer has been monitored during 1000 h.

Keywords: Dye-sensitized solar cells; Ferrocenyl; Sulfur; Density functional theory

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1. Introduction

Dye-sensitized solar cells (DSSCs) are currently under active investigation as alternatives to silicon-based photovoltaic devices for solar energy utilization (Ardo and Meyer, 2009; Calogero et al., 2012; Fan et al., 2011; Grätzel, 2004a,b, 2005, 2009; Hagfeldt et al., 2010; Kumar et al., 2013; Li et al., 2011; Linfoot et al., 2011; Tang et al., 2012; Wang et al., 2011). In the most common type of DSSC, the so called Grätzel cell, the semiconductor is anatase-like TiO_2 and the dye-stuffs are ruthenium-oligopyridine complexes (Martinson et al., 2008; Nazeeruddin et al.,

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2011; O'Regan and Grätzel, 1991). A key process in the operation of dye-sensitized photovoltaic solar cell devices is the charge injection from the dye molecule at the surface of the semiconductor nanoparticle to the conduction band states within the nanoparticle itself (Neale et al., 2005). For Ru(II)-polypyridyl dyes, the generally accepted injection mechanism involves photoexcitation to a dye excited state, from which an electron is subsequently transferred to the semiconductor, typically TiO_2 anatase, conduction band states (Hagefeldt and Grätzel, 2001; Neale et al., 2005; Rehm et al., 1996). Recently, time dependent DFT study of sensitization of TiO_2 nanoparticle by $[Fe(CN)_6]^{4-}$ have been performed which showed direct charge injection process from an occupied dye molecular state to a nanoparticle excited state localized on Ti atoms (Angelis et al., 2004). For the prolific progress in the field of DSSCs, the innovation design of the dye plays a pivotal role in achieving the high efficiency. Hence, plethora of dyes have been utilized which achieved good visible light absorption and efficient charge separation (Angelis, 2010; Bessho et al., 2008; Grätzel, 2009; Hagfeldt et al., 2010; Hamann et al., 2008; Hum et al., 2012; Islam et al., 2011; Kalyansundaram, 2010; Kisserwan and Ghadder, 2011; Kukrek et al., 2006; Singh et al., 2012a,b; Wu et al., 2010, 2012; Yamagichi et al., 2010; Yang et al., 2000, 2002; Yu et al., 2011).

There is still a great deal of interest in dithiocarbamate (Beer et al., 2001; Cookson and Beer, 2007; Coucouvanis, 1970, 1979; Fox et al., 2000; Hogarth, 2005; Haiduc, 2004; Kumar et al., 2009; Naeem et al., 2010; Padilla-Tosta et al., 2001; Pratt and Beer, 2004; Singh et al., 2008; Wilton-Ely et al., 2008) and xanthate (Burns et al., 1980; Lin et al., 2009; Loumrhari et al., 1991; Tiekink and Haiduc, 2005; Wilton-Ely et al., 2006) chemistry especially comprising of ferrocene (Singh et al., 2010, 2010; Wong et al., 2005). This interest may be attributed to the redox active behavior of ferrocene moiety (Gibson et al., 2000, 2003; Togni and Haltermann, 1998; Togni and Hayashi, 1995; Long, 1995, 1998). Inspired by these points, recently we had reported the light harvesting properties of transition metal dithiocarbamate complexes having ferrocenyl moiety (Kumar et al., 2010) and phenylmercury(II) methylferrocenyldithiocarbamates (Singh et al., 2010). In the case of transition metal dithiocarbamates, only the square-planar complexes having Ni(II), Pd(II), Pt(II) and Cu(II) metal core have shown better power conversion efficiencies. However, in the case of organomercury(II) complex, was attributed to integrated photophysical properties of both Hg(II) and ferrocenyl entities. Additionally we had reported the light harvesting properties of ferrocenyl moiety with carboxylic and hydroxy as an anchoring group (Chauhan et al., 2011). With these aspects in mind and in the quest of new and lower cost compounds having potential to become efficient dyes in the solar cells, herein, we wish to report the synthesis, characterization and light harvesting properties of three ferrocenyl derivatives having dithiocarbamate and dithiocarbonate/xanthate function as an anchoring group.

2. Experimental

2.1. General considerations

All chemical reagents were commercially available and used without further purification. Dichloromethane (DCM) was used as a medium of cyclic voltammogram and purified by standard method.

Elemental analyses were performed on a Perkin-Elmer 240 C, H, N analyzer. Infrared spectra were recorded as KBr pellets on a Varian 3100 FTIR. ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL300 FTNMR spectrophotometers. Chemical shifts were reported in parts per million using TMS as internal standard for ^{1}H and ^{13}C NMR. The absorption spectra in dichloromethane solution were recorded using a Shimadzu UV-1800 UV–Vis spectrophotometer. Electrochemistry was carried out using a Pt working electrode, Pt rod counter electrode and Ag/AgCl as a working electrode. All electrochemical experiments were carried out in dichloromethane and the supporting electrolyte used was TBAP (0.1 M). After each experiment the reference electrode was calibrated against the ferrocene/ferrocenium couple which was found to be at 0.55 V.

2.2. DSSC fabrication

Transparent conductive glass plates coated with an F-doped SnO_2 (FTO, purchased from Pilkington. Co. Ltd., 8 Ω/γ) were used to prepare both the photo- and counter-electrodes. A Ti(IV) bis(ethyl acetoacetato)-diisopropoxide solution (2% w/w in 1-butanol) was spin-coated onto FTO substrates, which were then heated stepwise to 450 °C and maintained at this temperature for 20 min. The commercially available TiO_2 paste (Ti-Nanoxide T, Solaronix) was casted onto the heat-treated FTO substrates by the doctor-blade technique and then sintered at 450 °C for 30 min. The substrates with thick mesoporous TiO_2 layers (ca. 13–18 μm) were dipped into a dichloromethane solution of **1–3** or **N3** (0.3 mM) and kept overnight. The unadsorbed dye was washed out with anhydrous ethanol. Pt-layered counter-electrodes were prepared by spin-coating H_2PtCl_6 solution (0.05 M in isopropanol) onto FTO glass and then sintered at 400 °C for 30 min. The dye- adsorbed TiO_2 electrodes and Pt counter-electrodes were assembled into a sealed sandwich-type cell by heating at 80 °C using a hot-melt ionomer film (Surlyn) as a spacer between the electrodes. The electrolyte was composed of 0.6 M 3-hexyl-1,2-dimethylimidazolium iodide, 0.05 M iodine, 0.05 M LiI and 0.5 M 4-tert. butylpyridine in acetonitrile. A drop of electrolyte solution was placed in a hole drilled in the counter-electrode and driven into the cell via vacuum backfilling. Finally the hole was sealed using additional Surlyn and a 0.1 mm thick glass cover.

2.3. Solar cell efficiency

The photoelectrochemical performance characteristics (short circuit current J_{sc} (mA cm^{-2}), open-circuit voltage