Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 115 (2013) 106–110

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, characterization and light harvesting properties of nickel(II) diimine dithiolate complexes

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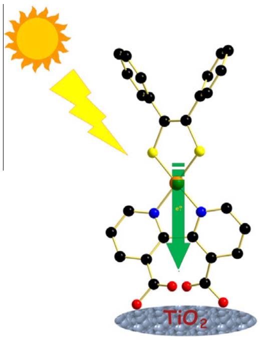
HIGHLIGHTS

- Four Ni(II) diimine dithiolate prepared from Ni(II) dithiolene.
- Their light harvesting properties investigated using these compounds as photosensitizers.
- Quantum chemical calculations have been performed to explain the nature of charge transfer.
- Effect of change in position of anchoring group on light harvesting parameters monitered.

GRAPHICAL ABSTRACT

Four Ni(II) diimine dithiolato complexes have been prepared from [Ni($S_2C_2Ph_2$)$_2$] and effect of position of anchoring group on diimine ligand over electronic, electrochemical and light harvesting properties explored.



ARTICLE INFO

Article history:
Received 4 April 2013
Received in revised form 2 June 2013
Accepted 5 June 2013
Available online 19 June 2013

Dedicated to Prof. Kieran C. Molloy

Keywords:
Diimine
Dithiolate
DFT
Light harvesting
TiO_2

ABSTRACT

Four Ni(II) diimine dithiolato complexes viz. [Ni{($S_2C_2Ph_2$)(1,10-Phenanthroline)}] (**2**), [Ni{($S_2C_2Ph_2$)(3,3′-dicarboxy-2,2′-bipyridyl)}] (**3**), [Ni{($S_2C_2Ph_2$)(4,4′-dicarboxy-2,2′-bipyridyl)}] (**4**) [Ni{($S_2C_2Ph_2$)(2,2′-bipyridyl)}] (**5**) have been prepared from [Ni($S_2C_2Ph_2$)$_2$] (**1**) and characterized by microanalyses, UV–Vis, IR, ^{1}H and ^{13}C NMR. Attempts have been made to explain the nature of charge transfer in these molecules through quantum chemical calculations. The light harvesting properties of all the compounds have been studied using these compounds as photosensitizers in TiO_2-based DSSC. The change in position of anchoring group on diimine derivative leads to different structural, electronic and light harvesting properties about the Ni(II) diimine dithiolate dyes.

Introduction

Last two decades have witnessed a substantial growth in the field of dye-sensitized solar cells (DSSCs) [1–6]. This is due their versatility and cost-effective manufacturing, the organic and

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http://dx.doi.org/10.1016/j.saa.2013.06.022

inorganic DSSC have been considered as a feasible alternative to conventional solid-state *p*–*n* photovoltaic devices [7–10]. Out of these dyes the ruthenium polypyridyl dyes have gained interests of chemists owing to their stupendous performance as sensitizers in DSSCs having efficiencies upto 11% [1,3,11,12]. In addition to ruthenium polypyridyl dyes other metal centered dyes including complexes of Fe [13–19], Cu [20–23], Os [24,25] and Re [26] have been used. Additionally the [Pt(II)(diamine)(dithiolate)] [27–30] and [Ni(dithiolene)$_2$] [31,32] compounds have also been investigated for their light harvesting properties.

Mostly the available solar cell dyes exhibit absorbances at the shorter wavelengths [11,12] and hence longer wavelength dyes are required as they can harness more of the available solar energy and this was established with the help of theoretical calculations [33]. With this viewpoint recently several NIR dye molecules have been reported [31,34,35]. The charge transfer transitions in [Pt{(diamine)(dithiolate)}] compounds can be assigned as a "mixed-metal ligand to ligands" charge transfer (MMLĹCT) involving a HOMO that is a mixture of Pt(d) and dithiolate S(p) and a LUMO that involves a π^* bpy orbitals [27–30]. Similar electronic transitional behavior is also anticipated for the [Ni{(diamine)(dithiolate)}] type complexes [36–41]. Additionally, the substituents on the diimine ligands affects the HOMO and LUMO energy levels and hence the photophysical as well as the electrochemical properties of the molecules. Hence, by tuning the photophysical and electrochemical properties of the dye one can affect the performance of the solar cells.

With these viewpoints and in the quest of the dyes having absorbances in the longer wavelength range we herein wish to report the syntheses, characterization and light harvesting properties of a family of [Ni{(diimine)(dithiolate)}] complexes.

Experimental

Materials and reagents

All chemical reagents were commercially available and used without further purification. The complex bis(1,2-diphenylethylene-1,2-ditholene) nickel(II) (**1**) was synthesized according to the previous report [42]. Dichloromethane (DCM) was used as a medium of cyclic voltammogram, 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 Perkin–Elmer LS45 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.

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. Commercialized 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**–**5** (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$_2$PtCl$_6$ 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. butypyridine 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.

Solar cell efficiency

The photoelectrochemical performance characteristics (short circuit current J_{sc} (mA cm^{-2}), open-circuit voltage V_{oc} (V), fill factor ff and overall conversion efficiency η) were measured under illumination with a 1000 W xenon lamp (Oriel 91193) using a Kiethley Model 2400. The light intensity was confirmed to be a homogenous over an 8 × 8 in^2 area was calibrated with a Si solar cell for 1 sun light intensity (AM 1.5G, 100 mW cm^{-2}). Accidental increase in the temperature inside the cell were prevented by using a cooler with a propeller. Each measurement was repeated for three times to confirm reproducibility.

IPCE measurement

Incident photon-to-current conversion efficiency (IPCE) for the dyes **1**–**5** were measured as a function of wavelength from 400 to 900 nm (PV measurement Inc.) using a standard tungsten-halogen lamp as monochromatic light and a broadband bias light for approximating 1 sun light intensity.

Results and discussion

Synthesis

The Ni(II) diimine dithiolato complexes *viz.* [Ni{(S$_2$C$_2$Ph$_2$)(1,10-Phenanthroline)}] (**2**), [Ni{(S$_2$C$_2$Ph$_2$)(3,3́-dicarboxy-2,2́-bipyridyl)}] (**3**), [Ni{(S$_2$C$_2$Ph$_2$)(4,4′-dicarboxy-2,2′-bipyridyl)}] (**4**) [Ni{(S$_2$C$_2$Ph$_2$)(2,2′-bipyridyl)}] (**5**) were prepared by the reaction between the corresponding bpy and their derivatives with [Ni(S$_2$C$_2$Ph$_2$)$_2$] (**1**) in equimolar ratio in refluxing toluene (see Scheme 1 supplementary informations).

Spectroscopy

The IR spectra for all the five compounds display bands in the region of 1359–1370 cm^{-1} associated with the perturbed C=C stretch. In addition to this, bands occuring in the region of ~1140 cm^{-1} can be assigned to the perturbed C—S bond and the band in the region ~882 cm^{-1} arises due to the stretching of Ph—C(S)=C moiety for all the five complexes. Additionally the bands observed in the range of 1600–1400 cm^{-1} arises because of the stretching of C=C and C=N bonds of the bipyridyl ligands and their derivatives. In the case of **3** and **4** the bands ~3100 cm^{-1} can be assigned to —COOH functional.

The purity and composition of all the five compounds have been checked by NMR spectroscopy. All of the compounds display sharp