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A molybdenum dithiolene complex as a potential photosensitiser for photoelectrochemical cells

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ARTICLE INFO

Article history:

Received 26 May 2012

Received in revised form

20 November 2012

Accepted 3 December 2012

Available online 31 December 2012

Keywords:

Photosensitiser

Molybdenum dithiolene

Band gap

tris(3,5-dimethylpyrazolyl)hydroborate

Photoelectrochemical cell

ABSTRACT

Molybdenum dithiolene complexes with the general formula $[\text{MoTp}^*(\text{NO})(\text{L})]$, where $\text{Tp}^* = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{hydroborate}$ and $\text{L} = \text{toluene-3,4-dithiolate (L1)}$, $1,2\text{-benzenedithiolate (L2)}$, or $3,6\text{-dichloro-1,2-benzenedithiolate (L3)}$, were found to exhibit the chemical and physical properties required for a photosensitiser in a photoelectrochemical cell. These complexes were characterised using micro-elemental, spectroscopic (IR and UV–vis) and electrochemical analyses. Cyclic voltammetry (CV) was used to determine the oxidation/reduction potentials and to calculate the energy band gap. All of the complexes had an energy band gap in the range 1.45–1.48 eV, which extends far into the visible light region. A TiO_2 thin film to be used as a photoanode for photoelectrochemical cells was prepared using the paste technique on a Fluorine-doped Tin Oxide (FTO) plate and characterised using scanning electron microscope (SEM) and X-ray diffractometer (XRD). The $[\text{MoTp}^*(\text{NO})(\text{L})]$ -doped TiO_2 photoanodes were analysed photochemically in a 1.0 M NaOH electrolyte solution using SCE reference and platinum counterelectrodes. The $[\text{MoTp}^*(\text{NO})(\text{L3})]$ -doped TiO_2 photoanode exhibited an increased photoinduced current compared with the undoped TiO_2 photoanode. The Cl atoms on the dithiolene group offered a better interaction between the photosensitiser molecule and the TiO_2 photocatalyst by providing a means for halogen atom-induced chemical bonding. Based on the band edge calculations and the subsequent photocurrent results, these complexes may be potential photosensitisers for use in the preparation of photoelectrodes for photoelectrochemical cells.

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1. Introduction

Photoelectrochemical (PEC) systems containing TiO_2 photoanodes have been extensively studied for use in water splitting since 1972 [1–4]. TiO_2 is a large band gap (3–3.2 eV)

semiconductor that absorbs sunlight in the UV region to achieve photoexcitation and charge separation [5–7]. However, such a cell has a low efficiency because TiO_2 has a limited absorption spectrum for terrestrial solar light [8,9]. Therefore, the effort to convert sunlight to electricity with

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<http://dx.doi.org/10.1016/j.ijhydene.2012.12.015>

a high efficiency by harvesting visible light with photosensitisers has received much attention [10].

In a photosensitiser molecule, the absorption of light in the visible (lower energy) region can be achieved via the introduction of a strong donor ligand such as dithiolene [11]. Dithiolene is capable of tuning (increasing) the energy of the highest occupied molecular orbital (HOMO) of metal complexes, thus resulting in a lower energy requirement for excitations [12]. Additionally, dithiolenes are thermally and photochemically stable [13]. Several dithiolene complexes have been reported that involve molybdenum and tungsten as photosensitiser–catalyst units in homogeneous water splitting systems [14–16]. However, attributed to its instability in homogeneous systems, few of the molybdenum dithiolene complexes that have been investigated were found to be suitable for use as photosensitisers. Therefore, heterogeneous PEC system is expected to provide a more favourable means to study them [17]. It has been noted that the employment of Tp* as a co-ligand was favourable for the formation of molybdenum complexes because the tripodal geometry of the ligand helps stabilise the metal complexes, particularly those containing group six metals such as molybdenum and tungsten [18,19]. In addition, the presence of a nitrosyl group (NO) provides a convenient tool to measure the electronic density variation around the metal centre [20].

The basic requirement for an ideal photosensitiser is that the redox potential of the photoexcited photosensitiser molecule should match the energy of the conduction band edge of the semiconductor oxide, e.g., TiO₂. Meanwhile, the ability of photosensitisers to capture light can be determined from the HOMO and LUMO (lowest unoccupied molecular orbital) energy levels. Upon energy absorption as a result of sunlight irradiation, the electrons in a photosensitiser may be excited from the HOMO to the LUMO, thus leaving an electron hole in the HOMO. The photoexcited electron can then flow from the photosensitiser towards the semiconductor oxide if the energy level of the LUMO of the former is above the energy of the conduction band of the latter [21]. This phenomenon will then lead to an increase in the photocurrent generation in photoelectrochemical cells.

The objective of this research is to examine the relationship between a photoanode (TiO₂) and a photosensitiser (molybdenum dithiolene complexes) using an energy band diagram and photoelectrochemical analyses.

2. Experimental details

2.1. Synthesis of molybdenum dithiolene complexes (photosensitiser) and preparation of the TiO₂ photoanode

All experiments were performed under an inert atmosphere of N₂ gas using Schlenk techniques. Toluene, acetonitrile and triethylamine were pre-dried with CaH₂ and distilled. Cyclohexane, dichloromethane and *n*-pentane were used as received and deoxygenated by bubbling with N₂. The potassium tris(3,5-dimethylpyrazolyl)borohydride (KTP*), [MoTp*(NO)(CO)₂], [MoTp*(NO)(I)₂], and [MoTp*(NO)(L)] were prepared using established methods [22–24]. The ligands H₂L1 (toluene-3,4-dithiol), H₂L2 (1,2-benzenedithiol) and H₂L3 (3,6-dichloro-1,2-benzenedithiol) that were employed in the

synthesis of the [MoTp*(NO)(L)]-type molybdenum complexes were used as received (Aldrich). Thin-layer chromatographic (TLC) analyses were performed using silica gel 60 F254, and column chromatography was performed in glass columns packed with silica gel 60 (Merck, grain size 0.063–0.200 mm).

The [MoTp*(NO)(L1)] complex MoL1 was prepared by reacting MoTp*(NO)(I)₂ (0.2 g, 0.29 mmol) and H₂L1 (0.05 g, 0.32 mmol) in 50 ml of toluene in the presence of triethylamine (0.4 ml, 2.2 mmol) at 80 °C. The mixture was refluxed for 16 h, and the reaction progress was monitored using TLC. The solution colour changed from yellow to dark blue.

Upon completion of the reaction, the solvent was evaporated to 1/3 of the original volume prior to the addition of *n*-pentane. A dark-blue precipitate was obtained after filtration and washed with *n*-pentane. The sample was purified via column chromatography (silica gel) using CH₂Cl₂/cyclohexane (1:3) as the eluent. The dark-blue fraction was collected and subjected to a second silica gel column with a CH₂Cl₂/cyclohexane (1:1) system to remove the impurities that were difficult to remove in the first chromatography procedure. The synthesis procedure for [MoTp*(NO)(L2)] (MoL2) and [MoTp*(NO)(L3)] (MoL3) were similar to that of MoL1. The reactions included 0.38 g (0.56 mmol) of MoTp*(NO)(I)₂ and 0.1 g (0.7 mmol) of H₂L2 for MoL2 and 0.35 g (0.52 mmol) of MoTp*(NO)(I)₂ and 0.15 g (0.7 mmol) of H₂L3 for MoL3.

The preparation of the TiO₂ photoanodes and the assembly of these photoanodes with copper wire were based on previous methods that involved loading the photosensitisers (0.004 mM/CH₂Cl₂) onto the photoanodes and allowing them to cure at room temperature for 2–3 h [25–27].

2.2. Characterisation

The IR spectra (4000–400 cm⁻¹, KBr) were collected on a Perkin Elmer Paragon 500 instrument, whereas the UV–vis absorption spectra were collected using a UV-1650 PC SHIMADZU instrument. The Fission EA 1108 was used to determine the C, H, N and S elemental contents of the complexes. The cyclic voltammetry properties of the complexes were recorded on a potentiostat Ametek Versastat 4.

The electrochemical cells consist of a platinum working electrode, a platinum wire as the counter electrode and a Ag/AgCl reference electrode. The complexes (1 mM) were dissolved in CH₂Cl₂ with 0.1 M [(*n*-C₄H₉)₄N]PF₆ and deoxygenated by bubbling with nitrogen gas. A similar electrochemical cell set-up with an optical window was used for the photoelectrochemical (PEC) analyses and included a 450 W xenon full arc lamp light source, a saturated calomel electrode (SCE) as the reference, and photosensitiser-doped and undoped TiO₂ as working electrodes in a 1.0 M NaOH electrolyte solution.

A scanning electron microscope (Zeiss AM10) was used to study the morphology and determine the cross-sectional thickness of the thin-film electrodes. The crystallinity and structure of the TiO₂ photoanodes were examined using X-ray diffraction (Siemen D-5000 X-ray diffractometer) with Cu K α radiation. The percentage of the anatase and rutile crystalline phases was calculated using the following equation [25]:

$$\text{Anatase(\%)} = \frac{100}{1 + 1.265(I_{\text{rutile}}/I_{\text{anatase}})}$$

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