Journal of Electroanalytical Chemistry 624 (2008) 84–90

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Electrochemical properties and electronic structures of two neutral nickel bis(1,2-dithiolene) complexes

Alix Sournia-Saquet, Bénédicte Garreau-de Bonneval *, Kathleen I. Chane-Ching, Lydie Valade

LCC – UPR 8241, 205, Route de Narbonne, 31077 Toulouse, Cedex 04, France

ARTICLE INFO

Article history:
Received 19 March 2008
Received in revised form 3 July 2008
Accepted 1 August 2008
Available online 7 August 2008

Keywords:
Neutral nickel bisdithiolene complex
Cavity microelectrode
Electrochemical bandgap
Spectroelectrochemistry
Optical bandgap

ABSTRACT

The synthesis, spectroscopic and electrochemical characterizations of two neutral bisdithiolene nickel complexes are described. Electrochemical reversibility and bandgap have been measured by different techniques. The influence of the nature and length of the alkyl chain, the type of electrode (Pt microdisk for solutions, ITO-coated glass, Pt wire, and CME (cavity microelectrode) for condensed state) and the solvent have been investigated. Optical transmission measurements in the visible–near-IR (VIS–NIR) region allowed the determination of the optical bandgap.

1. Introduction

Molecular engineering plays a fundamental role in improving the characteristics of organic-based electronic devices such as solar cells, OFETs, and OLEDs, with either small molecules or polymeric semiconductors. Until now, one of the major challenges facing molecular electronics investigators was the assembly of individual molecules. Extensive research in that field has been done to study the effect of side chain type on molecular organization, thus transport properties [1,2]. Nickel bisdithiolenes were first synthesized in the 1960s and the results of the subsequent extensive research were reviewed [3–6]. High electron mobilities have been recently found for these complexes [7,8]. That makes them interesting candidates for material science in the context of conductivity and photovoltaics. Many studies on the non-innocent role of the ligand in bonding and electron transfer concerning nickel bisdithiolene complexes show that the redox processes are of ligand-based and not metal-based character, and that these complexes are best described as ligands bound to d^8 central metal ion [9–13]. Moreover, the extensive delocalization of the frontier molecular orbitals over the entire complex contributes to a low reorganization energy during electron transfer and thus to encourage high values of electronic transfer constants. These attractive features make them particularly suitable for photovoltaic applications. Within this aim, we develop organic-based materials for solar cells involving the use of nickel bisdithiolene complexes as the acceptor layer in donor–acceptor (D–A) type cells. These complexes show high absorption coefficients within the 800–1300 nm range, that is covering the near-IR region of the solar spectrum. Moreover, these planar molecules show tendency to π-stacking. Our aim is to take advantage of these properties for building solar cells based on nano-structured bulk heterojunction (BHJ) using D and A molecular materials with complementary optical and transport properties. The charge separation and collection by external electrodes in D–A based solar cells is governed by the energy gap of each component of the system. The objective of the electrochemical and spectroelectrochemical studies reported in this paper is to sort out a general straightforward method of evaluation, in the condensed state, of the electrochemical gap of new photovoltaic organic materials.

The study was performed on two nickel bisdithiolene complexes taken as model compounds: one bears a linear alkyl chain and is a solid, $[Ni(S_2C_2(SC_7H_{15})_2)_2]$ (**C1**), while the other bears a branched alkyl chain and is obtained as an oily material $[Ni(S_2C_2(SC_8H_{17})_2)_2]$ (**C2**). We have first studied in a classical way the electrochemical properties of **C1** and **C2** in solution. The obtained results are considered as indicative but not realistic as in the real conditions of use, the materials are in condensed state. For this reason, we have pursued the study by using deposits on ITO for electrochemical study of non-dissolved materials corresponding much better to the real conditions of use in photovoltaic cells. These results were further compared with those obtained on Pt electrodes or in a cavity microelectrode (CME). These complete analyses proved that CME is particularly adapted to such a study: it is easy to use, provides quick results and does not need preparation of any solution. Optical properties and spectroelectrochemical

---

* Corresponding author. Tel.: +33 5 61 33 31 52; fax: +33 5 61 55 30 03.
E-mail address: benedicte.debonneval@lcc-toulouse.fr (B. Garreau-de Bonneval).

0022-0728/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2008.08.001

studies of **C1** and **C2** are reported. These interesting properties prompted us to improve the method of their synthesis and to investigate their electrochemical behaviour.

2. Experimental

Air-sensitive reagents were used in an argon atmosphere. Solvents were dried and purified by standard procedures.

2.1. Syntheses

The preparation of the bis(alkylthio)-substituted 1,3-dithiole-2-thione precursors **P1** and **P2** was carried out according to a published procedure. Subsequent complex **C1** was obtained as in [14] and the procedure was adapted to produce the branched alkyl containing new complex **C2**. **C1** is obtained as dark green crystals while **C2** is isolated as viscous oil. The final step of the synthesis is outlined in Scheme 1.

2.2. Electrochemical experiments

Voltammetric measurements were carried out with an Autolab PGSTAT100 potentiostat controlled by GPES 4.09 software. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. A saturated calomel electrode (SCE) separated from the solution by a bridge compartment was used as reference electrode. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface. Working electrodes were: a Pt microdisk (0.5 mm diameter) for studies in solution, and a Pt wire, an ITO-coated glass electrode [15] or a cavity microelectrode (CME) for studies in the condensed state.

The CME [16,17], provided by the “French Cavity Microelectrode Network”, consists in a platinum microelectrode (50 μm in diameter) sealed in a large glass tube (8 mm in diameter). A small cylindrical cavity (35 μm in diameter and 30 μm in depth) is performed by LASER ablation of the platinum wire. Due to the LASER beam conic shape, the bottom of the cavity is only 16 μm in diameter. This cavity displays a volume of 1.6×10^{-8} cm^3. Two protocols were applied to fill the cavity with the material to be studied. In protocol 1, the CME was used as a pestle in an agate mortar containing a small amount of powder of the material and a pre-treatment of the electrode at −2 V/SCE is applied for a few seconds. In protocol 2, the material is introduced in the cavity as a high concentrated solution in a good solvent and obtained under condensed form by evaporation of the solvent; no pre-treatment of the electrode is needed.

The supporting electrolyte, (n-Bu_4N)[PF_6] (Fluka, 99% puriss electrochemical grade) was used as received. For studies in solution, electrochemical media were containing 0.1 mol L^{-1} of supporting electrolyte, and 10^{-3} mol L^{-1} of **C1** or **C2**. Before each measurement, the solutions were desaerated by bubbling Argon and the working electrode was polished with a polishing machine (Presi P230).

2.3. Optical spectroscopy

Visible–near-IR (VIS–NIR) absorbance spectra were recorded using a Varian Cary 5000 spectrometer. A 1 cm quartz cell was used. For studies in solution, the concentration was adjusted in order to obtain an absorbance ranging between 0.5 and 1 at λ_{max}.

VIS–NIR spectroelectrochemistry spectra in the condensed state were recorded between 800 and 1500 nm using a homemade cell: the working electrode was an ITO-coated glass electrode [15]. Thin films of **C2** were obtained by depositing 20 μL of a toluene solution (18.6×10^{-3} mol L^{-1}) onto the ITO surface and allowing slow evaporation of the solvent under normal pressure at room temperature. The active area position was adapted to the optical beam pathway (approximately 1 cm^2). **C1** could not be studied on ITO, because the deposition procedure always led to small crystallites on the surface and never to good optical quality films. Platinum and silver wires were used as counter and reference electrodes, respectively, and located on the cell sides in order not to disturb the beam. The AgCl/Ag reference electrode was calibrated vs. SCE E(V vs. AgCl/Ag) = E(V vs. SCE) + 0.053 in acetonitrile with 0.1 mol L^{-1} (n-Bu_4N)[PF_6]. Solutions were desaerated by argon bubbling prior to each experiment.

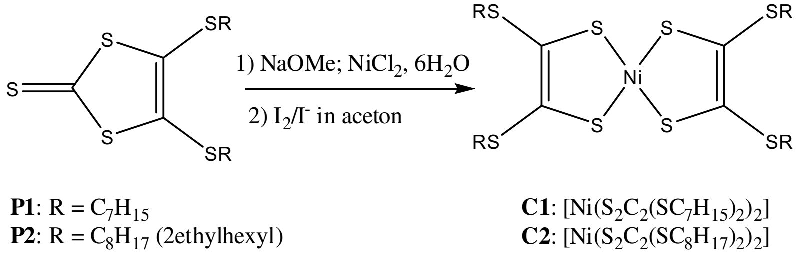
3. Results and discussions

3.1. Electrochemical studies of *C1* and *C2* nickel complexes in solution – reversibility study and electrochemical bandgap determination

Reversibility of the redox systems involved in solar cells is required for photovoltaic application. In order to perform a mechanistic study of electrons exchange in **C1** and **C2**, square wave voltammetry (SWV) and cyclic voltammetry (CV) were applied.

We first checked the molar conductivity of their solution (10^{-3} mol L^{-1}) in dichloromethane. The obtained values (Λ_{C1} and $\Lambda_{\text{C2}} \sim 1$ S cm^2 mol^{-1}) are similar to those obtained for neutral compounds [18]. For a mono-anionic nickel complex (1:1 compound) [19] this value would be around 45 S cm^2 mol^{-1}. The “Equilibrium potential” of solutions of complexes **C1** and **C2** in dichloromethane is ca. 0.2 V/SCE, as found for other neutral complexes [20]. Complexes **C1** and **C2** are stable in the neutral state in diluted solution.

The cyclic voltammogram of **C1** in a dichloromethane solution (Fig. 1) exhibits five electrochemical processes: among them, three attributions are gathered in Table 1. The three processes at −0.78, −0.13 and +0.73 V/SCE labelled (1), (2) and (3) are attributed to electron exchanges on the core of **C1**. Based on combined experimental studies (Sulfur K-edge XAS) and theoretical calculations, insight into the non-innocent nature of the dithiolate ligand has been obtained [11,21,22]. It is well established, on the basis of the dom-



Scheme 1.