A Novel Ruthenium-tungsten Bimetallic Complex Dye-Sensitizer for Photoelectrochemical Cells Application

(Kompleks Baru Dwilogam Rutenium-tungsten Sebagai Bahan Pewarna Pemeka untuk Aplikasi Sel Fotoelektrokimia)

KHUZAİMÀH ARIFIN, WAN RAMLI WAN DAUD & MOHAMMAD B. KASSIM*

ABSTRACT

A novel bimetallic double thiocyanate-bridged ruthenium and tungsten metal complex containing bipyridyl and dithiolene co-ligands was synthesized and the behavior of the complex as a dye-sensitizer for a photoelectrochemical (PEC) cell for a direct water splitting reaction was investigated. The ligands and metal complexes were characterized on the basis of elemental analysis as well as UV-Vis, Fourier transform infrared (FTIR) and nuclear magnetic resonance (1H and 13C NMR) spectroscopy. Cyclic voltammetry of the bimetallic complex showed multiple redox couples, in which half potentials $E_{1/2}$ at 0.625, 0.05 and 0.61V were assigned as the formal redox processes of Ru(III)/Ru(II) reduction, W(IV)/W(V) and W(V)/W(VI) oxidations, respectively. Photocurrent measurements were performed in homogeneous system and TiO$_2$ was used as the photoanode for photocurrent measurements. Current density generated by the bimetallic complex was higher than that of N3 commercial dye which suggested that the bimetallic complex donated more electrons to the semiconductor.

Keywords: Bimetallic; bipyridyl; dithiolene; dye-sensitizer

ABSTRAK

Kompleks dwilogam baru dengan ligan jejambat tiosianat berasaskan logam rutenium dan tungsten yang mengandungi ko-ligan bipiridil dan ditiolena telah berjaya disintesis. Keupayaannya sebagai bahan pewarna pemeka untuk kegunaan sel fotoelektrokimia (PEC) bagi pembelahan molekul air secara terus juga telah dikaji. Ligan dan kompleks logam telah dicirikan berdasarkan kaedah analisis mikro unsur CHNS; spektroskopi infra-merah, ultralambayang-cahaya nampak, 1H dan 13C NMR. Analisis voltammetri berkitar menunjukkan kompleks dwilogam mempunyai beberapa puncak redoks, antaranya adalah puncak redoks pada potensi separuh $E_{1/2}$-0.625, 0.05 dan 0.61V yang merupakan keupayaan formal redoks bagi proses penurunan Ru(III)/Ru(II) dan pengoksidaan W(IV)/W(V) dan W(V)/W(VI). Pengukuran fotoarus dilakukan dalam sistem homogen dan TiO$_2$ digunakan sebagai fotoanod. Ketumpatan arus yang dihasilkan oleh kompleks dwilogam lebih tinggi berbanding yang dihasilkan oleh bahan pemeka komersil N3 yang bermakna elektron yang didermakan kompleks dwilogam lebih besar berbanding yang didermakan oleh molekul N3.

Kata kunci: Bahan pewarna pemeka; bipiridina; ditiolena; dwilogam

INTRODUCTION

Photosynthesis is a natural process of energy transformation that occurs in plants, algae and bacteria using sunlight. Light energy absorbed by chlorophyll is used to split water molecules into O$_2$ and H$^+$. The H$^+$ binds with CO$_2$ from the atmosphere to form glucose, an energy-rich sugar. Artificial photosynthesis technology mimics the processes of natural photosynthesis to produce hydrogen, which is used in fuel cell technology to generate energy in the form of electricity (Allakhverdiev et al. 2010; Joya & de Groot 2012; Young et al. 2012). Artificial photosynthesis systems use transition metal complexes to harness light, catalyze the reaction and act as the reaction center (Najafpour & Allakhverdiev 2012).

Dye-sensitized photoelectrochemical (PEC) cells are a type of artificial photosynthesis system that uses a transition metal complex as the photosensitizer to enhance the sensitivity of the photoelectrode semiconductor to sunlight, which enables a wider range of radiation wavelengths to be absorbed (Abe et al. 2000; Minggu et al. 2010). Ruthenium bipyridyl complexes are the transition metal complexes that are most often used as the sensitizer in solar cells (Grätzel 2003). Currently, research on dye-sensitizers is focused on increasing the efficiency of light absorption (i.e. molar extinction coefficient) and to find alternative dyes with enhanced properties and capabilities (Aiga & Tada 2005; Nazeeruddin et al. 2005; Vougioukalakis et al. 2011). Improvement upon the performance of monometallic complex sensitizers is challenging because the number of possible electron transfers is limited. One way to improve the efficiency of dye-sensitized PEC cells is to use a bimetallic complex as a sensitizer (Argazzi et al. 2001; Kleverlaan et al. 2000; Zhao et al. 2012).
Various bimetallic complexes with combinations of metals, ligands and bridging ligands have been synthesized and used as dye-sensitizers (Arifin et al. 2012a). However, difficulties in the preparation of bimetallic complexes that allow electrons to transfer from one metal center to the other have caused bimetallic complexes to be less efficient than monometallic complexes. One of the major challenges is to facilitate electron transfer, which requires the bridging ligands of bimetallic complexes to be conjugated. Most of the bimetallic complexes that have been reported have large non-rigid bridging ligands, which enable charge recombination to occur because a long duration required for electron and energy transfers to occur from one metal center to the other (Balzani et al. 1996; Chiorboli et al. 1999). In most cases adsorption of the complexes occurs only on the outer surface of the photoelectrodes, which contributes to low efficiencies. Furthermore, most of the simple bridging ligands are non-rigid, which allows steric effects to affect the geometry and causes the determination of the electrochemical properties to be difficult (Hofmeiera & Schubert 2004). An ideal bimetallic complex used as the dye-sensitizer in a PEC solar cell application should have a simple and rigid bridging ligand(s) that satisfies the requirements for efficient intramolecular energy transfer. Bimetallic complexes are still being designed and synthesized to satisfy these conditions to improve the efficiency of solar cells.

In this paper we describe the synthesis of a novel bimetallic complex that was designed to have a rigid but efficient intramolecular energy transfer pathway to satisfy the requirements of dye-sensitizer for PEC applications. The preparation, characterization, electrochemical and PEC analyses of the novel thiocyanate-bridged bimetallic complex, which was based on ruthenium and tungsten metals with bipyridyl and dithiolene co-ligands, are presented. The model complex reported in this paper is a ruthenium-(4,4′-dimethyl-2,2′-bipyridine)-isothiocyanato-tungsten[bis-(phenyl-1,2-ethilenodithiolien)], which is abbreviated as BM. Bipyridyl ligands such as 4,4′-dimethyl-2,2′-bipyridine has been widely used in dye-sensitizers (Balzani & Juris 2001; Chakraborty et al. 1999), while, dithiolene ligands are electron rich and redox non-innocent (i.e. they exhibit a variety of redox states with unique optical properties) (Goddard & Holm 1999; Ward & McCleverty 2002). There are relatively few reports that used bimetallic complexes with thiocyanate as the bridging ligand (Banerjee et al. 2005; Navarro et al. 1997). Thiocyanate, an ambidentate ligand that attaches to a metal center in either an end-on (1,1-μ-SCN, 1,1-μ-NCS) or end-to-end (1,3-μ-SCN) configurations, has been reported to be used as a bridging ligand to link ruthenium and tungsten (Shen & Feng 2002).

**EXPERIMENTAL DETAILS**

Dichloro(p-cymene)ruthenium(II) dimer, 4,4′-dimethyl-2,2′-bipyridine, tungsten hexacarbonyl, ammonium thiocyanate (NH$_4$NCS), benzoin, phosphorus pentasulfide and solvents were purchased from Sigma–Aldrich and used as received. IR spectra were acquired using a Thermo Nicolet 6700 FTIR spectrometer. The $^1$H and $^{13}$C NMR spectra were acquired on an Avance Bruker 400 MHz spectrometer. Electronic absorption spectra were acquired on a Varian Cary 5000 UV−Vis spectrophotometer. Elemental analyses were performed using an Elemental Micro Cube CHNS analyzer. Electrochemical and PEC analyses were performed using a Princeton Applied Research (PAR) Ametek Versastart 4 potentiostat.

Ruthenium-[bis(4,4′-dimethyl-2,2′-bipyridyl)-isothiocyanato] was synthesized by mixture of 4,4′-dimethyl-2,2′-bipyridine (0.1 g, 0.34 mmol) and dichloro(p-cymene)ruthenium(II) dimer (0.05 g, 0.081 mmol) in dry, argon-degassed dimethyl formamide (DMF) (25 mL). The mixture was then heated to 150°C for 4 h. NH$_4$NCS$_{10}$ (0.39 g, 5.1 mmol) was added to the dark green solution and the mixture was heated at 150°C for an additional 4 h. After evaporation of the DMF, a purple residue was suspended in water (150 mL). The mixture was then extracted with diethylether (Et$_2$O) and washed with distilled water producing a purple solution. The Et$_2$O was removed by evaporation resulting in a dark purple solid with a 39% yield. IR spectrum (cm$^{-1}$): 3459 (N-H); 2931 (C-H); 2105 & 1984 (C=O); 1678 (C=C aromatic), 1389 & 1459 (CH$_3$). UV/Vis spectrum $I_{max}$ (nm) ($\times10^4$ M$^{-1}$ cm$^{-1}$) in CH$_2$CN solution: 345 nm (35000) & 400 nm (23000). Elemental CHNS analysis, % (required): C 56.34 (55.57); H 4.13 (4.13); N 15.95 (15.95) & S 8.49 (8.49).

The dithiolene carbonyl complex of tungsten [W(S$_2$C$_2$Ph$_2$)(CO)$_2$] was synthesized via two step reactions, i.e. synthesis of tioester-1,2-dithiol [Ph$_2$C$_2$S$_2$P(O/S)(O)]$_2$ and synthesis of dithiolene carbonyl complex. The tioester was synthesized by dissolve benzoin (30 g) and phosphorus pentasulfide (230 g) in dry, argon-degassed tetrahydrofuran (THF) (40 mL) was irradiated with UV light under an N$_2$ atmosphere. Hydrogen sulfide produced from the reaction was trapped using lead acetate. The mixture was cooled to room temperature and then filtered. The filtrate was concentrated in vacuo, which resulted in a dark red oil with a 37.5% yield. IR spectrum (cm$^{-1}$): 1254 (P=O); 1081; 958 (P-O & P-O-P); 697 (C-S). Elemental CHNS analysis, % (required): C 55.67 (55.07); H 3.73 (3.50); & S 24.60 (25.91).

A solution of tungsten hexacarbonyl (W(CO)$_6$) (1 g) in tetrahydrofuran (THF) (40 mL) was irradiated with UV light under an N$_2$ atmosphere at room temperature for 2 h to generate the W(CO)$_6$THF intermediate. The thioester (0.5 g) was added to the solution and the mixture was stirred for approximately 1 h at room temperature. The solvent was removed under reduced pressure. An orange-red solid was isolated with a 39% yield upon the addition of 30 mL of an Et$_2$O/hexane mixture (1:2 v:v) at approximately -15°C. IR spectrum (cm$^{-1}$): 3026 (C-H); 2071 & 1980 (C=O); 1677 cm$^{-1}$ (C=C); 1155 cm$^{-1}$ & 697 (C-S). Elemental CHNS
Analysis, % (required): C 55.28 (55.07); H 3.00 (2.78) & S 15.56 (17.70).

Although the general preparation of BM was reported earlier (Ariffin et al. 2011), a detailed synthetic method for producing BM is described here. A solution of ruthenium-[bis(4,4'-dimethyl-2,2'-bipyridyl)-isothiocyanato] (0.06 g) in CH₃CN (5 mL) was added to a solution of tungsten (W(S,C₂Ph₂)(CO)₃) (0.06 g) in CH₃CN (5 mL) and then the mixture was stirred at room temperature for 3 h. A black-brown solid and cloudy-white solution formed after cold water (20 mL) was added. The supernatant liquid was decanted and the solid was filtered, which resulted in a black-brown solid with a 10% yield. ¹H NMR (600 MHz, DMSO) d (ppm): 7.93-9.26 (12H of bipyridyl); 6.92-7.88 (20H of benzene) & 2.49 (CH₃); 113.48 (C=C) & 137.37 (benzene); 151.65; 157.01 & 157.89 (bipyridyl). IR spectrum (cm⁻¹): 3418 (N-H); 2933 (C-H); 2095 & 1980 (NCO); 1734; 1677; 1616 (C=C); 1450 & 1493 (CH₂); 126.76 & 137.37 (benzene); 151.65; 157.01 & 157.89 (bipyridyl). The synthetic method of [Ru(dmtbpy)₂(NCS)₂] was first reported by Schrauzer et al. (1965) and has been further studied by many other researchers. The preparation of (W(S,C₂Ph₂)(CO)₃) was accomplished via the reaction of the photogenerated intermediate, W(CO)₆THF, with a thioester prepared from benzoin and P₂S₅. The (W(S,C₂Ph₂)(CO)₃) complex is a purple-red solid, which was soluble in CH₃CN, THF and dichloromethane, but insoluble in non-polar solvents. The physical characteristics of the (W(S,C₂Ph₂)(CO)₃) prepared in this report were similar to the previous report (Chandrasekaran et al. 2009). Notably, the complex was stable in a solid phase below 4°C (refrigeration) but was unstable in solution form. The nCO signals in the (W(S,C₂Ph₂)(CO)₃) complex was observed at 2071 (w) and 1980 cm⁻¹ (s) which are comparable to the previously reported bis(dithiole) complexes (Asali & Janaydeh 2003). The infrared spectrum also shows other characteristic bands at 2953 cm⁻¹ (C-H aromatic) and 1155 cm⁻¹ (C-S).

The condensation of (Ru(dmtbpy)(NCS)₂) and (W(S,C₂Ph₂)(CO)₃) was performed in DMF at room temperature to give BM molecule as a dark brown solid after 8 h. Decantation of the liquid was an important step in the procedure to avoid loss of the product before filtering. An infrared spectroscopy is very useful to identify the formation of the bimetallic complex quickly through the observation of a band at 2115 cm⁻¹ for NCS group. The NCS frequency shifted to a slightly higher value than that of complex (I), which indicates that the thiocyanate acts as a bridging ligand. The UV/Vis spectrum in DMF showed absorption maxima at 330 nm (ε = 29800 M⁻¹cm⁻¹), 375 nm (ε = 14600 M⁻¹cm⁻¹), 535 nm (ε = 12500 M⁻¹cm⁻¹), which were assign to MLCT bands and the 712 nm (ε = 890 M⁻¹cm⁻¹) band was assigned to the d-d transition of the metal centres.

The ¹H and ¹³C NMR spectra of the bimetallic complexes were observed as groups of multiple signals making an accurate assignment of chemical shifts for the methyl, benzene and bipyridyl moieties to be difficult. In the ¹H NMR spectrum, the methyl protons was observed at approximately 2.49 ppm and the signal has a total integration value of 12. The benzene protons were observed in multiple groups over the range of 6.92-7.88 ppm (2OH), whereas the bipyridyl protons were observed at higher chemical shift as multiple groups over the range...
of 7.93-9.26 ppm (12H). The $^1$H NMR spectra indicates that the BM molecule was asymmetric. The $^{13}$C signals were slightly much easier to interpret, with the chemical shift of the methyl groups appears at 39.91 ppm. The thiocyanate carbon was observed as a singlet at 55.61 ppm. Other peaks included an ethylene carbon at 114.48 ppm; signals for aromatic carbons from the dithiolene group at 126.76 and 137.37 ppm and three signals for the bipyridyl moieties at 151.65, 157.01 and 157.89 ppm. No peaks were observed with chemical shifts above 160 ppm indicating all the carbonyl ligands of the tungsten monometallic complex were removed. The signal for the carbonyl carbon in a similar molecule [W(CO)$_4$(ligand)] was approximately 200 ppm (Pathania et al. 2007).

The elemental analysis result gives 51.25 (52.37), 3.96 (3.92), 6.69 (6.54) and 16.56 (17.70) for C, H, N and S, respectively, with theoretical values in parentheses. BM was soluble in polar aprotic solvents (e.g. DMF and DMSO) but was not soluble in THF, dichloromethane and non-polar solvents which makes drying the complex as a difficult task.

The electrochemical properties of complex BM were investigated by cyclic voltammetry in a 3-electrode cell with a platinum disk working electrode, Ag/AgCl reference electrode and a platinum wire counter electrode in DMF containing 1 × $10^{-4}$ M TBAPF$_6$ as the supporting electrolyte. The voltammograms of BM and the corresponding monometallic complexes are shown in Figure 1. Bimetallic BM complex exhibited multiple redox processes corresponding to one reversible redox couple, three quasi-reversible redox couples and one irreversible redox peak at room temperature.

The reversible redox couple was identified as E3, where the $E_{3/2}$ was observed at 0.61 V (DEP$_1$ = 255 mV, $I_{pc}/I_{pa} = 1$). The $E_{1/2}$ values of the quasi-reversible processes E1, E2 and E4 were observed at -0.625 V (DEP$_1$ = 130 mV), -0.05 V (DEP$_1$ = 500 mV) and 1.17 V (DEP$_1$ = 90 mV), respectively. Furthermore, the potential of the irreversible reduction peak identified as E5 was 1.62 V. Theoretically, a DEP of more than 90 mV indicates that more than one electron was involved for each redox reaction. However, in comparison with the ferrocene internal standard with an $E_{1/2}$ at 0.623 V and DEP$_{Fc/Fc^+} = 450$ mV, the observed reversible and quasi-reversible processes were one-electron redox processes.

The redox couples of E1, E2 and E3 were attributed to the formal reduction of Ru(III)/(II) and oxidation of W(IV)/(V) and W(V)/(VI), whereas E4 and E5 were most likely due to the formal reduction and oxidation of the ligands, respectively. Overall, the redox processes of the metal centres in the BM could be described by the following redox potentials:

$$\text{Ru}(II)\text{W}(IV) \quad \text{[Ru(III)W(IV)]$^0$} \quad \text{[Ru(III)W(V)]$^{2e}$} \quad \text{[Ru(II)W(VI)]$^{2e}$}$$

The electrochemical properties of BM consisted of the constituents monometallic complex properties. The results were similar to the properties of the [(bipy)Ru(m-bpm)PdMe(NCMe)](BF$_4$)$_2$ bimetallic complex reported previously (Argazzi et al. 2001; Inagaki & Akita 2010).

The current density of the electrode under various incident photoenergies was evaluated in a PEC cell (Mark-Lee et al. 2013). Photocurrent values were obtained from the difference in currents measured in the dark and under irradiation. This measurement was performed at various potentials and the current changes during irradiation were monitored and recorded. For the purpose of comparison, the photocurrent of BM and N$_3$ commercial dyes sensitizer were recorded with the same parameters. Current density
A thiocyanate bridged bimetallic complex of ruthenium and tungsten BM, consisted of ruthenium bipyridyl and tungsten dithiolene bridged moieties was successfully synthesized. The photophysical, electrochemical and PEC data showed that BM could be used as a dye sensitizer in an artificial photosynthesis system. The sensitizing performance was slightly better that the commercial N$_3$ dye in homogeneous system with TiO$_2$ photocatalyst. Therefore, further improvement on the BM molecule by introducing an anchoring group (e.g. COOH) to facilitate chemical bonding to photoelectrode can be carried in order to increase the efficiency of the charge transfer process.

**CONCLUSION**

A thiocyanate bridged bimetallic complex of ruthenium and tungsten BM, consisted of ruthenium bipyridyl and tungsten dithiolene bridged moieties was successfully synthesized. The photophysical, electrochemical and PEC data showed that BM could be used as a dye sensitizer in an artificial photosynthesis system. The sensitizing performance was slightly better that the commercial N$_3$ dye in homogeneous system with TiO$_2$ photocatalyst.

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Khuzaimah Arifin & Wan Ramli Wan Daud
Department of Chemical and Process Engineering
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia

Mohammad B. Kassim*
School of Chemical Sciences and Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia

*Corresponding author; email: mbkassim@ukm.my

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