



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis of zinc chlorophyll materials for dye-sensitized solar cell applications

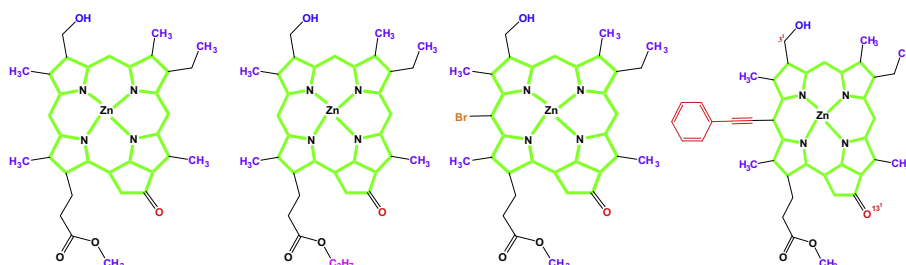
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HIGHLIGHTS

- Zinc chlorophyll materials have been synthesized.
- Zinc chlorophyll materials have been characterized.
- Dye sensitized solar cells were fabricated and characterized.

GRAPHICAL ABSTRACT

Chlorophyll dyes for dye sensitized solar cell.



ARTICLE INFO

Article history:

Received 23 March 2014

Received in revised form 3 July 2014

Accepted 15 July 2014

Available online 1 August 2014

Keywords:

Zinc chlorophyll

Dye sensitized solar cell

Electrolyte

Organometallic synthesis

ABSTRACT

To design sensitizers for dye sensitized solar cells (DSSCs), a series of zinc chlorins with different substituents were synthesized. Novel zinc methyl 3-devinyl-3-hydroxymethyl-20-phenylacetylenylpyropheophorbide-a (ZnChl-1), zinc methyl 20-bromo-3-devinyl-3-hydroxymethylpyropheophorbide-a (ZnChl-2), zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (ZnChl-3), zinc propyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (ZnChl-4) were synthesized and their photovoltaic performances were evaluated in dye-sensitized solar cells. Photoelectrodes with a 7 μm thick nanoporous layer and a 5 μm thick light-scattering layer were used to fabricate dye sensitized solar cells. The best efficiency was obtained with ZnChl-2 sensitizer. ZnChl-2 gave a J_{sc} of 3.5 mA/cm², V_{oc} of 412 mV, FF of 0.56 and an overall conversion efficiency of 0.81 at full sun (1000 W m⁻²).

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Introduction

Over the past two decades dye sensitized solar cells have emerged as an important technology for the development of low-cost, easy processable, clean energy production [1–5]. A typical DSSC is composed of a dye molecule that is anchored to a mesoporous TiO₂ surface. Efficient charge separation in dye sensitized solar cells is achieved by photoinduced electron injection from organic sensitizer into the conduction band of a metal oxide electrode.

The dye cation radical is regenerated by a redox electrolyte. Under simulated AM1.5G illumination (100 mW cm^{-2}), the power conversion efficiency of a cell, η is defined as the product of the generated photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), and the fill factor (FF), as follows: $\eta = J_{sc}V_{oc}FF$ [4,6].

The efficient light harvesting potential of chlorophyll dyes, exemplified by their primary role in photosynthesis, makes them promising candidates for light harvesting antennas in dye sensitized solar cells [7,8]. Porphyrin based dyes have been evaluated as photosensitizers for DSSC due to their strong Soret (400–450 nm) and moderate Q bands (550–600 nm) absorption properties as well as their primary role in photosynthesis mechanism [9–11]. They have demonstrated charge transfer kinetics indistinguishable from those of ruthenium polypyridyl complexes [12], which are the most efficient dyes ever reported. Moreover, optical, photophysical and electrochemical properties can be systematically evaluated. However, they generally show inferior performances to ruthenium polypyridyl complexes as photosensitizers. Main reason for such inferiority would be attributed to the limited light absorption, poor matching to solar light distribution [13,14].

A major challenge in designing molecular based solar cells lies in the choice and organization of the light absorbing pigments. Efficient solar energy conversion requires light absorption over a broad spectral range in the visible and near infrared regions. Chlorophyll photosynthetic pigments are promising light absorbers for solar cells, owing to their high molar absorption coefficients, tuneable photophysical properties and light harvesting properties [15].

In this study, four different chlorophyll derivatives were synthesized according to the slightly modified conditions. Obtained products were characterized by ^1H NMR and mass spectrometry. Their optical properties and cyclic voltammograms were also investigated. Zinc complexes of these tetrapyrrolic species were selected to perform the studies in dye sensitized solar cell. Zinc chlorophyll dyes with different substituents show different performances. Under the optimized conditions, ZnChl-2 sensitizer gave the best results with the overall conversion efficiency of 0.81% (η), short-circuit photocurrent of 3.5 mA/cm^2 (J_{sc}), open circuit photovoltage of 412 mV (V_{oc}), fill factor of 0.56 (FF). It is found that ZnChl-2 gave high efficiency within these classes of dye sensitizers.

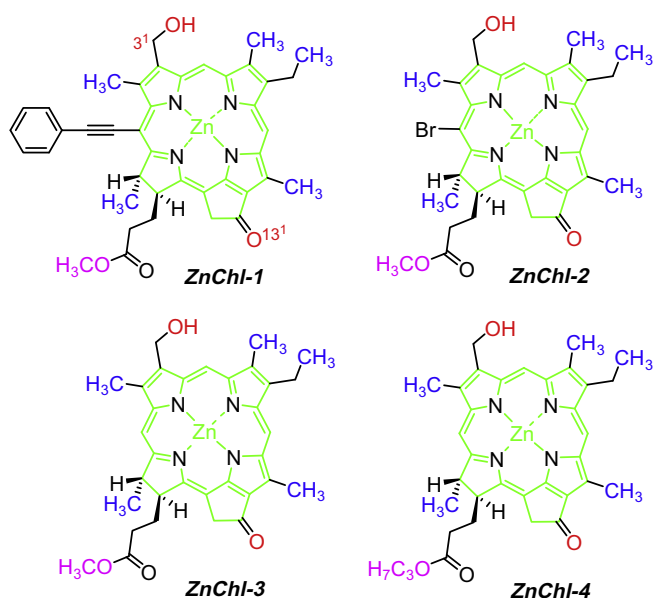


Fig. 1. Molecular structure of the complexes.

Experimental section

All materials were reagent grade and were used as received unless otherwise noted. Molecular structures of Zinc chlorophyll materials were supplied in Fig. 1.

Materials characterization

The UV–Vis absorption spectra of synthesized dyes were recorded in a 1 cm path length quartz cell by using Analytic JENA S 600. The infrared (IR) spectra were obtained by using Perkin-Elmer, FT-IR/MIR-FIR (ATR) spectrophotometer. ^1H NMR spectra were measured on Varian 500 MHz spectrometer. The mass spectra were obtained via electrospray ionization (ESI-MS), and matrix-assisted laser desorption/ionization (MALDI). Cyclic voltammetry measurements of synthesized dye were taken by using CH-Instrument 660 B Model Potentiostat equipment. Dye sensitized solar cells were characterized by current–voltage (J – V) measurement. All current–voltage (J – V) were done under 100 mW/cm^2 light intensity and AM 1.5 conditions. 450 W Xenon light source (Oriel) was used to give an irradiance of various intensities. J – V data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition software.

Synthesis of zinc complexes

Synthetic routes were presented in Fig. 2. And ^1H NMR spectra were shown in Figs. 3 and 4 for all Zinc chlorophyll materials.

3-Devinyl-3-formyl-pyropheophorbide-a (2)

Methyl pyropheophorbide-a (1) was converted to 2 according to the literature procedure [16] with 55% yield. Spectral properties correlate with reported data.

20-Bromo-3-devinyl-3-formylpyropheophorbide-a (3)

3-devinyl-3-formyl-pyropheophorbide-a (2) (850 mg, 1.55 mmol) was dissolved in 500 ml of CH_2Cl_2 , pyridiniumhydrobromide perbromide (595 mg, 1.86 mmol, 1.2 eq.) was added and obtained mixture was stirred for 40 min at RT. Subsequently, reaction mixture was poured into 2% $\text{HCl}_{(aq)}$, extracted with CH_2Cl_2 , dried over anhydrous Na_2SO_4 and concentrated in vacuo. Crude 3 was purified by means of dry column vacuum chromatography (DCVC, silica gel, $\text{THF}:\text{CH}_2\text{Cl}_2 = 2:96$) to afford 753 mg (77.2%) of product 3. ^1H NMR (CDCl_3): 11.49, 10.48, 9.46 (s, each 1H, CHO, 5-H, 10-H), 5.26 (2H, d, $J_1 = 10 \text{ Hz}$, 13^1-CH_2), 5.21 (1H, m, OH), 4.89 (2H, dd, $J_1 = 7.1 \text{ Hz}$, $J_2 = 1 \text{ Hz}$, 17-H), 4.81 (1H, m, 18-H), 4.26 (1H, dd, $J_1 = 9.2 \text{ Hz}$, $J_2 = 3.1 \text{ Hz}$, 3- CH_2), 3.91 (3H, s, $17^2\text{-CO}_2\text{CH}_3$), 3.86 (2H, q, $J = 7.5 \text{ Hz}$, 8- CH_2), 3.63, 3.60, 3.23, (3H each, s, 2- CH_3 , 7- CH_3 , 12- CH_3), 2.71–2.53 (2H, m, 17- CH_2CH_2), 2.50 (3H, bs, 18- CH_3), 2.35–2.19 (2H, m, 17- CH_2CH_2) 1.25 (3H, m, 8^1-CH_3), –1.30 (1H, s, NH), –1.93 (1H, s, NH). MS (ESI) found: m/z 628.1701 [M^+]; calcd. for $\text{C}_{33}\text{H}_{33}\text{N}_4\text{O}_4\text{Br}$ (628.1696). $R_f = 0.61$ (silica gel, $\text{THF}:\text{CH}_2\text{Cl}_2 = 4:96$).

Methyl 20-bromo-3-devinyl-3-hydroxymethylpyropheophorbide-a (Chl-2)

3 (755 mg, 1.2 mmol) was dissolved in the dry CH_2Cl_2 and borane *tert*-butylamine complex (150 mg, 1.68 mmol, 1.4 eq.) was added. After been stirred overnight at 0°C , resulted mixture was washed with 5% HCl , H_2O , and brine. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Crude product was purified by means of dry column vacuum chromatography (DCVC, silica gel, $\text{THF}:\text{CH}_2\text{Cl}_2 = 5:95$) to afford 696.6 mg (92%) of clean Chl-2. ^1H NMR (CDCl_3): 9.600, 9.30 (s, each 1H, 5-H, 10-H), 5.92 (2H, dd, $J_1 = 11 \text{ Hz}$, $J_2 = 4 \text{ Hz}$, 13^1-CH_2), 5.61 (1H, bs, OH), 5.08–4.91 (2H, m,

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