



Synthesis and photovoltaic performance of the porphyrin based sensitizers with 2*H*-[1,2,3]triazolo[4,5-*c*]pyridine and benzotriazole as auxiliary acceptors



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ABSTRACT

Two novel zinc porphyrin dyes containing either benzotriazole or 2*H*-[1,2,3]triazolo[4,5-*c*]pyridine as auxiliary acceptors, respectively, were synthesized for dye-sensitized solar cells. These two auxiliary acceptors were firstly applied into porphyrin based dyes. The photophysical and electrochemical properties of the dyes were investigated. These two dyes show the whole visible light absorption when they are adsorbed on the TiO₂ film, which means that they are promising sensitizers for dye-sensitized solar cells. The absorption intensity of the triazolopyridine containing dye is higher than that of the benzotriazole containing dye, resulting in a better light harvesting. Thus, the dye-sensitized solar cell based on the former dye achieved higher conversion efficiency of 6.65% than the cell based on the latter dye (6.17%) with chenodeoxycholic acid as the coadsorbant.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted wide attention because of their high light-to-electricity conversion efficiencies, ease of fabrication, and low production costs. In recent years, significant efforts have been devoted to improving cell efficiencies [1,2]. Several ruthenium, organic and porphyrin dyes have been synthesized and investigated in terms of their performance in DSSCs. Ruthenium dyes offer high efficiency of 11%, but their application might be limited due to the scarcity of ruthenium metal and environmental concerns. Organic sensitizers have lots of advantages but their efficiencies should be improved [3–14].

Porphyrin based dyes are particularly promising DSSC sensitizers due to their structural similarity to chlorophylls, and their tunable strong absorption [15–21]. Thus, numerous porphyrins have been reported for developing efficient DSSCs [19,22–28]. In spite of the successful examples, typical porphyrins exhibit poor light harvesting capability beyond 700 nm. In order to broaden the absorption spectrum, much effort has been expended. For example,

incorporating benzothiadiazole (BTD) unit as an auxiliary acceptor has achieved good results [29–31].

As we know, benzotriazole and 2*H*-[1,2,3]triazolo [4,5-*c*]pyridine as auxiliary acceptors have been applied in organic sensitizers [32–37]. Recently, Lin et al. applied the concept of **D–A–π–A** using pyrido[1,2,3]thiadiazole (PyT), a more electron-deficient entity than BTD, as the auxiliary acceptor. Disappointingly, the PyT dyes exhibited lower cell performance than the BTD dyes in spite of the more red-shift ICT band. In comparison, replacement of BTD by a less electron-deficient benzotriazole (BTA) entity was found to improve the cell performance although the BTA dye exhibited a blue shift of the ICT band. With this encouragement, the study was extended to the 2*H*-[1,2,3]triazolo[4,5-*c*]pyridine (PT) entity. They reported two isomeric PT-based dyes, PTN1 with the N atom facing toward the acceptor and NPT1 with the N atom facing away from the acceptor, and found that the latter had a better performance [38–40].

In this work, we designed two novel porphyrin based sensitizers **DHC-1** and **DHC-2** containing either benzotriazole or 2*H*-[1,2,3]triazolo[4,5-*c*]pyridine as auxiliary acceptors, respectively (Fig. 1). To the best of our knowledge, the benzotriazole and 2*H*-[1,2,3]triazolo[4,5-*c*]pyridine units were incorporated into porphyrin based sensitizers as the auxiliary acceptors for the first time. The insertion

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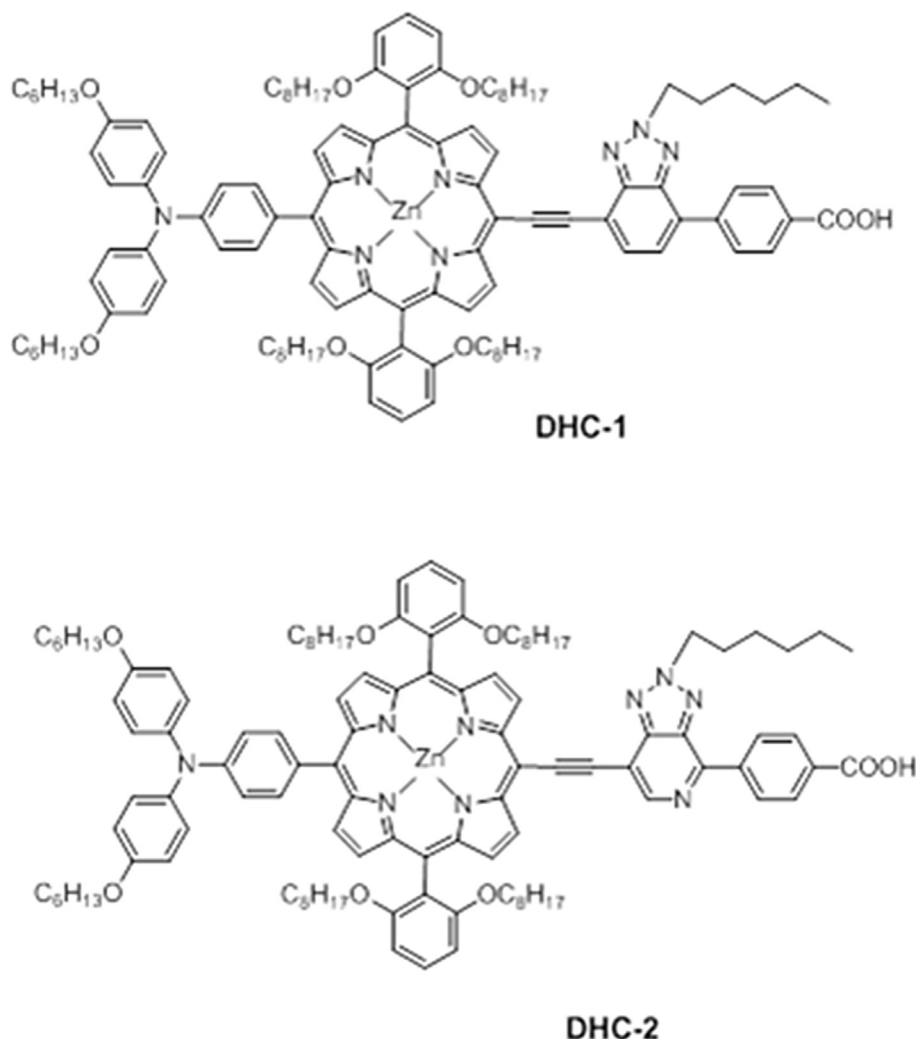


Fig. 1. Molecular structure of DHC-1 and DHC-2.

of the auxiliary acceptors was expected to broaden the absorption range. We studied the effect on the absorption spectra and the photovoltaic performance by the replacement of one atom C to N in the benzotriazole ring. The photophysical and electrochemical properties of the sensitizers as well as their application for DSSCs were also discussed.

2. Experimental

2.1. Materials and instruments

All reagents were purchased from J&K, Adamas and Aladdin. THF, toluene and 1,4-dioxane were distilled over sodium under argon atmosphere. Other solvents were applied without further purification. The column chromatography separations were performed on silica gel (300–400 mesh). All reactions were performed under argon atmosphere and monitored by thin layer chromatography (TLC).

^1H and ^{13}C NMR spectra were measured on Bruker 400 MHz instruments in CDCl_3 . The melting point was conducted on a SGW-X-4B microscopic melting point apparatus. HRMS spectra were recorded on an Agilent Technologies 1290 Infinity mass spectrophotometer. UV–vis absorption spectra of dye solutions and dye-adsorbed TiO_2 films were measured on Shimadzu UV-2450

spectrophotometer and UV-3010 spectrophotometer, respectively. The emission spectra of the dyes in THF solution were performed on a Fluorolog III photoluminescence. The FT-IR data were performed on a VERTEX 33 Bruker. Cyclic voltammetry (CV) measurements were recorded on a CHI660E electrochemical workstation using a typical three electrode electrochemical cell in a solution of tetrabutylammonium-hexafluorophosphate (TBAPF_6) in dry MeCN with a scan rate of 50 mV s^{-1} . Dye loaded TiO_2 film was used as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. The ferrocene/ferrocenium (Fc/Fc^+) redox couple acted as an internal potential reference. The electrochemical redox potentials of dyes versus NHE were calibrated by addition of 0.63 V to the potential versus (Fc/Fc^+). The current density–voltage (J - V) characteristics of the DSSCs were measured by recording J - V curves using a Keithley 2400 source meter under simulated AM1.5G (100 mW cm^{-2}) illumination with a solar light simulator (Oriel, Model: 91192). The incident monochromatic photo-to-current conversion efficiency (IPCE) was performed on a Spectral Products DK240 monochromator from 300 to 800 nm region. The electrochemical impedance spectra (EIS) were measured on Zahner Zennium electrochemical workstation under dark station under a forward bias of -0.7 V with a frequency range of 0.1 Hz–100 kHz.

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