Dyes and Pigments 88 (2011) 75–83

Contents lists available at ScienceDirect

Dyes and Pigments

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

# The structural modification of thiophene-linked porphyrin sensitizers for dye-sensitized solar cells

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ARTICLE INFO

*Article history:*
Received 17 March 2010
Received in revised form
7 May 2010
Accepted 7 May 2010
Available online 19 May 2010

*Keywords:*
Porphyrin derivative
Thiophene derivatives
π-Spacer unit
Incident photon-to-current conversion efficiency
Dye-sensitized solar cells
Photovoltaic performances

ABSTRACT

Three donor–(π-spacer)–acceptor porphyrin dyes were synthesized for use in dye-sensitized solar cells. The dyes comprised the same donor (porphyrin derivative) and acceptor/anchoring group (2-cyanoacrylic acid) but varying π-spacer consisting of a combination of 4-methylthiophene, 4-hexylthiophene or 3,4-ethylenedioxythiophene groups. The dyes displayed different adsorption behavior and coverage of the $TiO_2$ surface.

## 1. Introduction

In recent years, increasing demands for renewable energy sources have focused attention on the utilisation of solar energy. In this context, dye-sensitized solar cells (DSSCs) have attracted considerable interest owing to their ability to convert solar energy to electricity at low cost. In dye-sensitized solar cells, light is absorbed by a dye and charge separation takes place owing to photoinduced electron injection from the dye into the conduction band of $TiO_2$, the separated charges then move toward respective electrodes, thereby yielding a photocurrent in an external circuit [1]. To develop more efficient dyes for DSSCs, essential design requirements must be satisfied. Firstly, the sensitizing dyes must strongly adhere to the photocatalyst ($TiO_2$) surface to ensure efficient electron injection into the conduction band of $TiO_2$. Secondly, the lowest unoccupied molecular orbital (LUMO) of the dye must be sufficiently higher than the conduction band of $TiO_2$ for efficient charge injection, and the highest occupied molecular orbital (HOMO) of the dye must be lower than the hole-transport material (HTM) for efficient regeneration of the oxidized dye. Finally, the dye must have light-harvesting ability in both the visible and/or near IR regions [2]. To date, the most efficient dye sensitizers employed in DSSCs are polypyridyl ruthenium complexes, with a solar-to-electricity conversion efficiency ($\eta$) of 10–11% [3]. The advantages of such ruthenium complexes are that they exhibit both broad absorption in the near-UV and visible region and appropriate excited-state oxidation potentials for the electron injection into $TiO_2$ [4]. However, these dyes are not readily available because of their high cost and the low availability of noble metals such as ruthenium.

Extensive researches have been devoted to the development of alternative, efficient metal-free dyes, which offer advantages as photosensitizers in that they have high molar absorption coefficients due to intramolecular $\pi-\pi^*$ transitions and their structures can be modified easily and economically. In recent years, whilst various metal-free dyes based on coumarins [5], indolines [6], perylenes [7], merocyanines [8], porphyrins [9], triarylamines [10], and carbazoles [11] have been reported, such compounds display overall conversion efficiencies in the range 5–10%; however, the cell performances of metal-free dyes are either lower than or comparable to that of Ru dye-based DSSCs. Recently, porphyrins

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doi:10.1016/j.dyepig.2010.05.003

have been recognized as the most promising dyes for such application because of their photochemical and electrochemical stability, strong absorbing ability in the visible region due to $\pi-\pi^*$ transitions of the conjugated macrocycle and high molar extinction coefficient [12]. However, the narrow absorption spectra of porphyrins, which poorly matches solar light distribution, limits the performance of porphyrin-sensitized solar cells. In order to solve this problem, many model compounds based on porphyrin have been synthesized for application in DSSCs. For example, Seunghun et al. synthesized $\beta$, $\beta'$-quinoxalino porphyrins containing carboxylic acid binding groups, which showed broadened and red-shifted light absorption band with the aid of $\pi$-extension; DSSCs based on the porphyrin dyes exhibited excellent power conversion efficiency of 5.2% [13]. Campbell et al. also have reported porphyrin dyes with extended $\pi$-systems by modifying a $\beta$-position with an olefinic linkage, which resulted in broad, red-shifted absorption bands; the dyes showed cell efficiency of 7.1% [14].

Despite major advances in porphyrin chemistry, further improvements in photovoltaic performance are needed. This paper concerns the use of a donor–($\pi$-spacer)–acceptor (D–$\pi$–A) system for metal-free dyes intended for use in DSSCs, as means of securing effective photoinduced intramolecular charge transfer [10, 15]. In this work, a series of *meso*-position modified porphyrin sensitzers with porphyrin moieties as donors, thiophene derivatives as $\pi$-conjugated linkers, and cyanoacrylic acids as acceptors and anchoring groups (Fig. 1) were synthesized. The compounds were expected to have broader absorption than the corresponding porphyrin without thiophene cyanoacrylic acid groups, resulting in high short-circuit photocurrent ($J_{sc}$) and high solar-to-electricity conversion efficiency ($\eta$). Herein, three *meso*-4-methylphenyl groups were introduced to reduce the extent of aggregation occurring between neighboring porphyrins adsorbed on $TiO_2$ surface by means of steric hindrance. Different thiophene derivatives employed as $\pi$-linkers for connecting the porphyrin donors (D) and anchor (A) groups, not only extended the light absorption region but also affected the electron injection character of the dyes into the $TiO_2$ surface. The introduction of 3,4-ethylenedioxythiophene (EDOT) into the porphyrin dye was anticipated to enhance photovoltaic performance because EDOT has a small torsional angle with the adjoining phenyl fragment, thereby ensures efficient electronic transfer between D and A. The effects of the different $\pi$-conjugated linkers on the photophysical, electrochemical properties and photovoltaic performances were investigated.

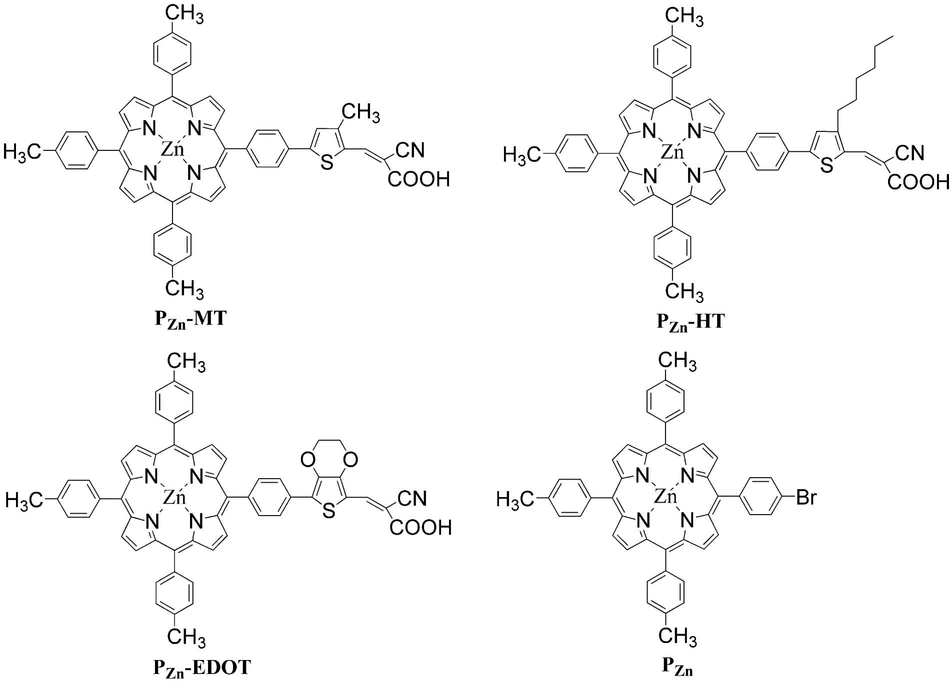
## 2. Experimental

### 2.1. Materials and reagents

All starting materials were purchased from Pacific ChemSource and Alfa Aesar. DMF, $CHCl_3$, $CH_3CN$ and $POCl_3$ were dried and distilled by accustomed methods before use. All other solvents and chemicals used in this work were analytical grade and used without further purification. All chromatographic separations were carried out on silica gel (200–300 mesh).

### 2.2. Analytical measurements

$^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker Avance 400 instrument. UV–vis spectra of the dyes were measured on a Perkin–Elmer Lamada 25 spectrometer. The PL spectra were obtained using Perkin–Elmer LS-50 luminescence spectrometer. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a three-electrode configuration and an electrochemistry workstation (CHI660A, Chenhua Shanghai). The working electrode was a glassy carbon electrode; the auxiliary electrode was a Pt electrode, and saturated calomel electrode (SCE) was used as reference electrode. Tetrabutylammonium perchlorate (TBAP) 0.1 M was used as supporting electrolyte in dry DMF. Ferrocene was added to each sample solution at the end of the experiments, and was used as an internal potential reference [16].



$P_{Zn}$-MT

$P_{Zn}$-HT

$P_{Zn}$-EDOT

$P_{Zn}$

**Fig. 1.** Molecular structures of porphyrin derivatives used in this study.