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Pyrazole-3-carboxylic acid as a new anchoring group for phthalocyanine-sensitized solar cells

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ABSTRACT

We have designed and synthesized an unsymmetrical zinc phthalocyanine (**PCA-ZnPc-1**) bearing an electron-withdrawing pyrazole-3-carboxylic acid anchoring group and three electron-donating *tert*-butyl groups as a sensitizer for dye-sensitized solar cells (DSSCs). **PCA-ZnPc-1** sensitized solar cell showed a modest power conversion efficiency (1.74%), which may suffer from the flexible and non-conjugated oxygen linker on the sensitizer. However, the obtained efficiency is found to be three to four times higher than that of the unsymmetrical ones bearing only carboxylic acid due to the combination of pyrazole and carboxylic acid moieties within the same anchoring group, which enhances the binding of the dye on the TiO_2 surface and results in an increase of electron injection efficiency. Therefore, the pyrazole-3-carboxylic acid is a promising anchoring group for developing new phthalocyanines to build efficient DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) are an important solar energy conversion technology that have advantages include their ease and low cost of fabrication and tunable aesthetic features such as color and transparency (Mathew et al., 2014; O'Regan and Gratzel, 1991). The main components of DSSCs are semiconducting metal oxide nanoparticles and dye molecules (sensitizer), which collectively act as working electrode of a DSSC, the redox mediator, the transparent conducting and counter conducting electrodes (Gratzel, 2003). In recent years, a number of studies have been conducted to improve the performance of DSSCs by replacing the components with alternative ones (Dürr et al., 2006; Lee et al., 2012; Zhang et al., 2008). The dye molecule, which is a fundamental component of the DSSCs, harvests solar photons and initiates charge separation through photoinduced electron transfer from the dye excited state into the conduction band of the metal oxide. The resulting oxidized dyes are subsequently reduced by the redox mediator (Ooyama and Harima, 2009). Due to its high extinction coefficient in the red/near-infrared (NIR) region and chemical and thermal stability, phthalocyanine has been used as a dye in DSSCs (Giribabu et al., 2007; Ikeuchi et al., 2014; Martín-Gomis et al., 2014). In particular, many research groups have been focused on the field of phthalocyanine-sensitized solar cells after the studies on photovoltaic properties of ABBB-type unsymmetrical carboxylic acid substituted zinc phthalocyanines (**PCH001** and **TT1**) performed by Nazeeruddin et al. (Cid et al., 2007; Martín-Gomis et al., 2014; Reddy et al., 2007). Researchers were able to achieve photovoltaic performances up to 4.1% by using unsymmetrically substituted ABBB-type ZnPcs sensitizers bearing *tert*-butyl donors (referred to as B) and −COOH anchoring group (referred to as A) (Milan et al., 2017; García-Iglesias et al., 2011). Phthalocyanine dyes have a tendency to dissociate gradually from the metal oxide (TiO_2) surface, lose their capability to convert photons to electrons, and reduce the long-term stability of solar cells (He et al., 2012). Therefore, immobilization of the adsorbing dye molecules onto the surface of TiO_2 nanoparticles is very important and usually achieved by addition of an "anchoring group", i.e., a chemical substituent able to adsorb the dye molecule onto the TiO_2 surface, resulting in efficient electron transfer from the dye into the TiO_2 conduction band (Li et al., 2008; Zhang and Cole, 2015). Although the most frequently used anchor in phthalocyanine-sensitized solar cells is a carboxylic acid group, many new anchors have emerged and been tested (Giribabu et al., 2011; López-Duarte et al., 2012; Suanzes Pita et al., 2017). Despite six major types of possible anchoring modes have been identified for carboxylic acid, the structures with bidentate modes (chelating and bridging) usually exhibit superior stability compared to others (Fig. 1a) (Zhang and Cole, 2015).

Pyrazole-3-carboxylic acid possesses two N-donors on the pyrazole ring and two O-donors on the carboxylate and can show flexible

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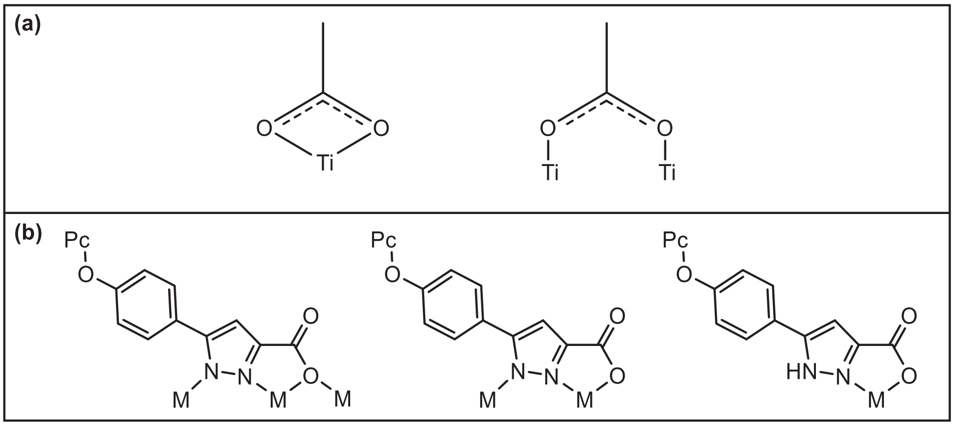

Fig. 1. Possible chelating and bridging modes of (a) Carboxylic acid and (b) **PCA-ZnPc-1**.

coordination modes when coordinates with metal ions (Gong et al., 2011; Jian et al., 2009; Liu et al., 2015). The N and O atoms of pyrazole-3-carboxylic acid can chelate to metal ions and form very stable complexes (Saçmaci and Kartal, 2008). It is expected that such chelation can enforce the binding of phthalocyanine dyes onto the TiO_2 surface and decrease their dissociation from the surface, which results in the enhancement of electron injection efficiency and stability of the cell (García-Iglesias et al., 2011; Shi et al., 2015). Based on considerations above, we report for the first time that pyrazole-3-carboxylic acid is an alternative anchoring group to carboxylic acid in phthalocyanine dyes. To demonstrate its potential, unsymmetrical zinc phthalocyanine containing pyrazole-3-carboxylic acid (**PCA-ZnPc-1**) was synthesized and its optical, electrochemical and photovoltaic properties were investigated. Possible chelating and bridging modes of pyrazole-3-carboxylic acid substituted zinc phthalocyanine **PCA-ZnPc-1** are shown in Fig. 1b (Suanzes Pita et al., 2017). It was found that DSSC with **PCA-ZnPc-1** showed a promising power conversion efficiency of 1.74%, possibly due to its good adsorption affinity to the TiO_2 surface.

2. Experimental

2.1. Materials and methods

IR spectra were recorded on a Thermo Scientific iS10 FT-IR (ATR sampling accessory) spectrophotometer, and electronic spectra on a Shimadzu UV-2450 and 2600 UV–Vis spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer using TMS as an internal reference. Mass spectra were measured on an Agilent 6530 LC-MS/QTOF, Shimadzu Axima Performance and Bruker Microflex LT MALDI TOF-MS. Elemental analyses were performed on a Thermo FlashEA 1112. Melting points were determined on an Electrothermal Gallenkamp apparatus. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Special reagents 4-nitrophthalonitrile, 4-*tert*-butyl phthalonitrile and 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid were purchased from Sigma-Aldrich. 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid ethyl ester has been reported previously (Zagorevskii and Zykov, 1963). Here, this compound was synthesized using a Fischer esterification reaction as a different method than the literature.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed using a potentiostat/galvanostat (PARSTAT 2273, USA). The voltammograms were recorded in degassed 0.1 M tetrabutylammonium tetrafluoroborate/dimethyl sulfoxide (TBATFB/DMSO) solution containing 0.3 mM **PCA-ZnPc-1** in a three-electrode conic cell (working volume 10 mL). The cell equipped with glassy carbon working electrode (GCE, 3 mm diameter), Pt wire counter electrode and Pt disk as a pseudo-reference electrode. The working electrode potentials were calibrated using ferrocene/ferrocenium (Fc/Fc^+) redox couple solution as an external reference. Electrochemical impedance (EIS) measurements were recorded under dark at a forward bias of −0.55 V with an AC amplitude of 10 mV at room temperature.

A double layer TiO_2 photoanode was prepared by previously reported procedures, (Hu et al., 2017; Karaca et al., 2018) as described below. An adhesive tape (Scotch™, 3 M) with a window of 0.196 cm^2 area and 50 μm depth was applied to the conductive surface of the fluorine-doped tin oxide-coated glass electrode (FTO) (Solaronix, TCO22-15, 15 $\Omega\,cm^{-2}$). A thin TiO_2 blocking layer was deposited onto FTO by dipping the tape-coated FTO in 40 mM aqueous solution of $TiCl_4$ for 30 min at 70 °C followed by rinsing with deionized water. Then, an anatase TiO_2 paste with an average particle size of ~20 nm (Solaronix Ti-Nanoxide T/SP) was coated on this electrode by the doctor blade method. The tape was removed and the TiO_2 electrode was gradually heated at 500 °C, followed by heating at the same temperature for 30 min in air. After cooling, the coating and heating processes were repeated over the previously coated electrode to obtain double layer TiO_2. The TiO_2 electrode was cooled to room temperature and again treated with the $TiCl_4$ solution, which was then heated at 500 °C for 30 min. After cooling to 80 °C, the resultant TiO_2 photoanode was sensitized with 0.1 mM **PCA-ZnPc-1** in a methanol solution for 2 h. 5 mM chenodeoxycholic acid (CDCA) as a co-adsorbent was also added into the dye solution to suppress the aggregation of dye. As a reference DSSC, the TiO_2 photoanode was also dipped in an ethanol solution containing 0.5 mM N719 (Solaronix, Ruthenizer 535-bisTBA) and 5 mM CDCA for 6 h. Pt-coated FTO was used as counter electrode. The sensitized TiO_2 photoanode and the counter electrode were assembled using a 25 μm–thick sealing spacer (Solaronix, Meltonix 1170-25) and an I^-/I_3^- electrolyte solution (Solaronix, Iodolyte HI–30).

The DSSC's photocurrent–voltage (*J*–*V*) characteristics were carried out using the above-mentioned potentiostat/galvanostat under a solar simulator (96000, Newport, USA) with AM 1.5G illumination (100 mW cm^{-2} = 1 sun). The measurement of incident photon to current conversion efficiency (IPCE) was recorded by using a monochromator (74004, Oriel, USA). The cells were covered with a black mask (0.196 cm^2) during the photovoltaic measurements.

2.2. Synthesis of 3-(4-hydroxyphenyl)-1H-pyrazole-5-carboxylic acid ethyl ester

To a solution of 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid (204 mg, 1 mmol) in 12 mL ethanol was added a catalytic amount of conc. H_2SO_4 (2 drops) and refluxed under heating overnight. The reaction mixture was evaporated to remove the solvent and then the yellow-white precipitate was stirred in diethyl ether. The resultant white solid was filtered and dried under reduced pressure. Yield 229 mg (98.7%) M.p: 142–143 °C. FT-IR (ATR): ν_{max}, cm^{-1} 3387 (OH), 3284 (NH), 3053 (CH, aromatic), 2988–2943 (CH, aliphatic), 1745 (C=O).