



## Electrochemical and photovoltaic properties of highly efficient solar cells with cobalt/zinc phthalocyanine sensitizers



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### ABSTRACT

The cyclic voltammetry studies indicated that the HOMO and LUMO energy levels of three sensitized metallophthalocyanines could ensure efficient electron injection and thermodynamically favorable dye regeneration. The S-bridged 4-mercaptobenzoic acid substituted cobalt(II) phthalocyanine (4-MKBa-CoPc) sensitized solar cell devices possessed a short-circuit photocurrent density of 9.70 mA/cm<sup>2</sup>, an open-circuit voltage of 0.88 V, and a fill factor of 0.49, corresponding to an overall conversion efficiency of 4.18% under standard AM 1.5 sun light. The present results demonstrated that the cobalt(II) phthalocyanine derivative had dramatically higher solar cell efficiency value as compared to zinc(II) phthalocyanine and as a linker atom, instead of oxygen linker, sulfur atoms slightly improved solar cell efficiency. The above results indicated that a low cost sensitizer made up of symmetrically substituted phthalocyanine with an earth abundant metal at the inner core can reach sufficiently high solar cell efficiency when compared with the alternative sensitizers for DSSCs applications.

### 1. Introduction

Dye sensitized solar cells (DSSCs) have attracted considerable attention due to their low cost and environmental friendly nature for photovoltaic cells (Hagfeldt et al., 2010; Shalini et al., 2015; Vittal and Ho, 2016). DSSCs consist of four components as following; photo anode (wide band gap semiconductor), sensitizers (light harvester), electrolyte (redox couple) and counter electrode (Hagfeldt et al., 2010; Sugathan et al., 2015). The sensitizers are the main component of the DSSCs and researchers are making a lot of effort to reach the higher cell efficiency values. These sensitizers are divided into three main groups as following: metal complex dyes, metal free organic dyes and natural dyes (Çakar et al., 2016; Narayan, 2012; Thomas et al., 2014). The ruthenium bipyridine complexes are the most stable ones and they are reported to have higher efficiencies (up to ~12%) (Gong et al., 2017; Roose et al., 2015). Other metal complex dyes consist of phthalocyanine (Pc) and porphyrin molecules (Abujarad et al., 2017; de la Torre et al., 2016; Singh et al., 2014). An important advantage of this group is that they can act as a sensitizer without any need to use expensive noble metals. Phthalocyanines (Pcs) have been also considered to be promising candidates because of their unique electronic and optical properties. These dyes are well known for their strong absorption

around 300 and 700 nm and also NIR region (de la Torre et al., 2016; Sarker et al., 2012; Shi et al., 2016; Yu et al., 2014). However, ruthenium based solar cells lack of absorption in the red VIS and NIR region. The typical distribution of solar irradiation follows the ratio UV/ VIS/ NIR 7:45:48 respectively (Antonanzas et al., 2016; Kannan and Vakeesan, 2016). Recently, researchers have put a lot of effort into development of light harvesting sensitizers, which is active in the NIR region. Pcs based dyes can harvest wide wavelength photon from the visible to the NIR region due to their complementary light absorption properties (Baranwal et al., 2015; Han et al., 2015; Yu et al., 2014). Therefore, Pcs are excellent alternative sensitizers for the DSSCs.

Herein, similar 4-hydroxybenzoic acid (4-HBa) and 4-mercaptobenzoic(4-MKBa) acid substituted cobalt(II) and zinc(II) phthalocyanine derivatives were selected as dyes for DSSCs. Carboxylated dyestuffs are prone to be adsorbed to the oxide semiconductors, because the surface is filled with hydroxylated oxide groups. So we have selected carboxylic acid side groups in order to anchor the phthalocyanines onto TiO<sub>2</sub> surface, thereby facilitating the electronic transfer from the LUMO orbital of the metal to the 3d orbitals of titanium. Experimental results showed that S-bridged 4-MKBa-CoPc indicated a slightly absorbance increment as compared with O-bridged 4-HBa-ZnPc and 4-HBa-CoPc. In this paper, we aim to study the effect of the linker atom (O/S) and

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central metal ion (Co/Zn) differences on solar cell efficiency of DSSCs and the device properties of these sensitizers were compared with ruthenium bipyridine, N719, sensitizers. In this manuscript, spectroscopic, electrochemical and photovoltaic parameters of different linker atom (S/O) or central metal ion (Co/Zn) bearing phthalocyanines were reported. The TiO<sub>2</sub> nanoparticles were used as photo anode material on the prepared DSSCs. The TiO<sub>2</sub> nanoparticles were prepared via microwave hydrothermal process. The FTO/TiO<sub>2</sub> photo anode was prepared by doctor blade technique. The TiO<sub>2</sub> nanoparticles and FTO-TiO<sub>2</sub> photo anode were characterized via XRD and FE-SEM. The energy levels of prepared phthalocyanines were investigated by CV and DPV. The solar cell performance of these sensitizers was investigated via J-V curve and impedance spectroscopy.

## 2. Experimental

### 2.1. Materials and methods

All chemicals and reagents were purchased from Merck and Sigma-Aldrich and used without any further purification. All reactions were carried out under nitrogen atmosphere in dried solvents. The solvents were stored over molecular sieves. UV measurements were performed using a Scinco SD-1000 double-beam UV-vis spectrophotometer (Korea). FT-IR spectra were obtained with a Perkin Elmer Spectrum One FT-IR (with UATR accessory). <sup>1</sup>H NMR spectra were recorded on Agilent VNMR5 500 MHz using TMS as the internal reference. For mass spectra, we have used a Bruker Daltonics MALDI-TOF mass spectrometer.

### 2.2. Synthesis of the phthalocyanine derivatives

The metallophthalocyanines used in this study, namely 2,91,623-tetrakis(4-carboxyphenoxy)phthalocyaninatocobalt (II) (4-HBa-CoPc), 2,91,623-tetrakis(4-carboxyphenoxy)phthalocyaninatozinc(II) (4-HBa-ZnPc) and 2,91,623-tetrakis(4-carboxyphenylsulphonyl) phthalocyaninato cobalt (II) (4-MKBa-CoPc) are shown in Scheme 1 and they were synthesized as reported earlier procedures (Yan et al., 2006; Yildirim et al., 2012).

### 2.3. Assembly of dye sensitized solar cells

The photo anode films were coated on the FTO conductive glass via doctor blade techniques according to our previous paper (Çakar and Özacar, 2017a, 2017b, 2016; Çakar et al., 2016). Firstly, the TiO<sub>2</sub> powder was synthesized via microwave hydrothermal method with microwave radiation, and the power, temperature and time were settled as 380 W, 100 °C and 30 min, respectively. Then, the viscous paste, which includes TiO<sub>2</sub> powder and ethyl cellulose were prepared and coated FTO glass. The optimum TiO<sub>2</sub> film thickness was found to be 20 µm in our previous study (Çakar and Özacar, 2017b), and this value was used for the TiO<sub>2</sub> coating in this study. The TiO<sub>2</sub> thin films with 20 µm thickness were prepared and immersed in appropriate amount of Pc based dyes solution. Then, the photoanodes were used for the measurements of cell efficiency values. The prepared photo anodes were sintered at 450 °C for 30 min in air. The freshly prepared TiO<sub>2</sub> nanoparticles and FTO-TiO<sub>2</sub> photo anode were characterized via XRD and FE-SEM techniques. The XRD and FE-SEM images of TiO<sub>2</sub> and FTO-TiO<sub>2</sub> photoanode are shown in Fig. S1 (Supplementary information). After cooling down, the TiO<sub>2</sub> photo anodes were immersed in a DMSO solution containing 5 mM dye sensitizers for 24 h in dark. The counter electrode was prepared by spreading out a drop of 5 mM H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O solution on FTO glass and sintered at 450 °C for 30 min. The electrolyte solution was a mixture of 0.1 M LiI, 0.05 M I<sub>2</sub> and 0.5 M 4-*tert*-butylpyridine in acetonitrile. The photo anode and counter electrode were assembled in a typical sandwich shape and clipped together as an open cell. The internal space of these cells was filled with electrolyte

solution.

### 2.4. Electrochemical and photovoltaic characterizations

The cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) measurements of Pc samples were carried out on CHI 660C electrochemical workstation. The CV analysis were performed in a 0.1 M LiClO<sub>4</sub> solution in acetonitrile with a different scan rates by using traditional three electrode system (glassy carbon working electrode, platinum wire counter electrode and saturated calomel reference electrode). The photocurrent density-voltage curve (J-V) characteristics of the solar cells were measured by CHI 660C electrochemical workstation under 100 mW cm<sup>-2</sup> irradiation from a solar simulator (Xenon lamp, LCS-100, Oriel). The electrochemical impedance spectroscopy measurement (EIS) was carried out by CHI 660C electrochemical workstation in the frequency region from 0.1 Hz to 100 kHz.

## 3. Results and discussion

### 3.1. UV-Vis spectrum of sensitizers

The ultraviolet-visible (UV-Vis) spectra of phthalocyanines feature two main bands, namely B (or Soret) and Q bands, the former being in the UV region of about 300–400 nm, and the latter being in the visible region of about 600–700 nm. The B band results from the transition between deeper π levels and lowest unoccupied molecular orbital (LUMO), whereas the Q band is merely the transition from the highest occupied molecular orbital (HOMO) to the LUMO (Sevim, 2017; Sevim et al., 2013). Fig. 1 shows the UV-Vis spectra of targeted zinc and cobalt phthalocyanines, indicating the aforementioned two typical absorptions of phthalocyanines, which mainly employ π and π\* molecular orbitals of the heteroaromatic π system of the macrocycle. The mentioned UV-Vis spectra of the targeted 4-HBa-ZnPc, 4-HBa-CoPc and 4-MKBa-CoPc in DMF showed B bands typically at 356, 335 and 364 nm, respectively, and Q bands at 677, 663 and 680 nm, respectively.

### 3.2. Electrochemical properties

To determine the oxidation and reduction potential of prepared phthalocyanine complexes, cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques were used. CV and SWV curves of these complexes are shown in Fig. 2. The electrochemical parameters of these dyes are listed in Table 1. The CV curves at different scan rates were taken and the status of the oxidation and reduction peaks were examined, and the obtained redox peaks were found to be common for metallophthalocyanine complexes (Özçelik et al., 2012; Tuncer et al., 2012). The CV records at different scan rates did not change the redox characteristics of the reduction process. The CV curves demonstrated two common ring-based reversible reduction process and one electrochemically irreversible oxidation process.

The SWV measurements were performed for the better understanding of oxidation and reduction potentials of these dyes. The electrochemical parameters of these dyes were calculated from the SWV curves. The highest molecular orbital (HOMO) levels of all prepared phthalocyanine complexes can be calculated from the Leeuw's formula ( $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.71) \text{ eV}$ ) (Shi et al., 2015; Yu et al., 2014) according to the first oxidation potential. The lowest unoccupied molecular orbital (LUMO) levels of all prepared phthalocyanine complexes can be evaluated from the formula ( $E_{\text{LUMO}} = (E_{\text{HOMO}} - E_{0-0}) \text{ eV}$ ). The electrochemical highest occupied molecular orbital (HOMO) energy levels of 4-HBa-ZnPc, 4-HBa-CoPc and 4-MKBa-CoPc were calculated as -5.105, -5.129 and -5.193 eV, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of 4-HBa-CoPc, 4-HBa-CoPc and 4-MKBa-CoPc were calculated as -3.355, -3.479 and -3.573 eV, respectively.

The LUMO energy levels are lower than the conduction band of TiO<sub>2</sub>

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