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Invited paper

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Synthesis of non-peripheral thioanisole-substituted phthalocyanines: Photophysical, electrochemical, photovoltaic, and sensing properties



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ABSTRACT

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Keywords: Phthalocyanine Synthesis Electrochemistry Photovoltaic Sensor Fluorescence H- and J-Aggregation This work reports on the synthesis, characterization, photophysical, electrochemical, photovoltaic and sensing properties of non-peripherally tetra 4-(methylthio)phenoxy substituted metal-free (2), Zn(II) (3) and Co(II) (4) phthalocyanine derivatives. Confirmation of the synthesized phthalocyanine structures which have the good solubility in organic solvents, performed with a combination of elemental analysis, FTIR, ¹H NMR, ¹³C NMR, UV–vis and MALDI-MS spectral data. Electrochemical measurements exhibit that the complex (4) shows the redox reactions taking place on both metal center and the ring while the phthalocyanines (2) and (3) give only ring-based redox reactions. All the complexes were examined for utilization in dye-sensitized solar cells (DSSCs) in the presence of chenodeoxycholic acid and the highest power conversion efficiency was achieved for the complex (3), as 1.09%. The interaction of phthalocyanines (2) and (3) with Ag⁺ and Pd²⁺ ions and their aggregation properties (H- or J-Aggregation) were investigated by UV–vis spectroscopy. Photophysical (fluorescence quantum yield) properties of the complexes (2) and (3) were reported in different solvents, such as tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). The results of spectral measurements in these solvents showed that Φ_F value of the complexes (2) and (3) were found to be lower than the unsubstituted ZnPc.

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1. Introduction

Metallophthalocyanine complexes (MPcs) have attracted great attention in recent years because of their excellent redox properties used in different fields such as non-linear optics, solar cells, molecular electronics, optical storage devices, electrocatalysts, sensing elements in gas and chemical sensors, electrochromic display, organic field effect transistors and photosensitizers in photodynamic cancer therapy [1]. The main target for researchers is to synthesize Pcs having good solubility by attaching various substituents on Pcs ring, such as alkyl, alkoxy, phenoxy, macrocyclic groups and/or inserting the different central metal ions into the inner phthalocyanine core [2,3] because of very low solubility of unsubstituted phthalocyanines in water and organic solvents. On the other hand, tetra-substituted Pcs exhibit more solublity than that of octa-substituted Pcs because of the unsymmetrical arrangement of substituents in the latter one [4]. Moreover, attaching some functional groups at non-peripheral region of Pcs causes to red shifting of the Q-band and diminishes aggregation as regards and the binding of electron donating

http://dx.doi.org/10.1016/j.jphotochem.2017.07.040 1010-6030/© 2017 Elsevier B.V. All rights reserved. sulphur groups at the peripheral region of Pc gives rise to the red shifting of the Q-band to more longer wavelengths, suggesting the varied properties that is important to be used in many fields [5,6].

The performances of MPcs are based mainly on their redox processes which occur on the Pc ring and the metal center. For example, the redox processes occur only at the ring in the Pcs with redox-inactive metal center, such as Zn and Cu, whereas in the presence of redox-active metal centers like Co and Mn, the electrochemical processes occur both at the metal center and at the ring [7–9]. The understanding of the electrochemical properties of the Pc complexes is important for their potential applications in many fields [10]. For example, utilization of Pcs in solar cells is highly fascinating because of their excellent photophysical and electrochemical properties [11]. At present, maximum power conversion efficiencies over 6% have been achieved for dyesensitized solar cells (DSSCs) with both symmetric [12] and asymmetric Pcs [13]. However, the Pcs for solar cells were mainly asymmetric structures were attached with complicated anchoring groups, such as carboxylic acid or pyridine. Although the conversion efficiencies of symmetric Pcs are generally low, symmetric Pcs are low-cost, facile synthesis, high yield, and good solubility compared with asymmetric Pcs [14,15].

As also known, substituted Pcs can create two kinds aggregates, such as H-aggregates (face-to-face) and J-aggregates (head-to-

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tail). They influence their electronic and optical properties. The entity of H-type aggregation can be proved by the decreasing of intensity of the Q-band (monomeric species) and then the appearence of a new broader blue-shifted band (aggregated species). On the other hand, if there is a new broader red-shifted band on the higher wavelengths, this indicates J-type aggregation [16].

In this study, symmetrical and soluble 4-(methylthio)phenol non peripherally substituted metal-free (2), Zn(II) (3) and Co(II) (4) Pcs were designed/synthesized and characterized. The electrochemical results revealed that the redox reactions of all the Pcs are reversible or quasi-reversible processes. The electrochemical, optical and photovoltaic results demonstrated that the only complex 3 can be considered as an alternative sensitizer for DSSCs.

The sensing behavior and aggregation of these Pcs (**2**) and (**3**) in the presence of Ag⁺ and Pd²⁺ soft metal ions have been studied by UV–vis spectroscopy, from these results, we have proved that, the interaction of the complex (**2**) with both Ag⁺ and Pd²⁺ soft metal ions caused the formation of H-type aggregation, but differently there wasn't observed any aggregation/sensitivity towards Ag⁺ metal ions for the complex (**3**) while showing the sensitivity to Pd² ⁺ soft metal ions suggesting the formation of J-type aggregation. In addition, photophysical properties have been discussed such as, the effect of different solvents (THF and DMSO) on fluorescence quantum yields of the complexes (**2**) and (**3**).

2. Experimental

2.1. Metarials and methods

Tetrahydrofuran (THF), chloroform (CHCl₃), 4-(methylthio) phenol, 3-nitrophthalonitrile, Zn(CH₃COO)₂, CoCl₂ and all other reagents were purchased from Alfa Aesar, Merck, Aldrich, Fluka and used with no purification. The purity of the products was controlled in all step by TLC (SiO₂, CHCl₃/MeOH and THF/MeOH). UV-vis spectra was ace:inf>), 4-(methylthio)phenol, 3-nitrophthalonitrile, Zn(CH₃COO)₂, CoCl₂ and all other reagents were purchased from Alfa Aesar, Merck, Aldrich, Fluka and used with no purification. The purity of the products was controlled in all step by TLC (SiO₂, CHCl₃/MeOH and THF/MeOH). UV-vis spectra was acquired in a quartz cuvette on an Agilent Model 8453 diode array spectrophotometer. Perkin-Elmer spectrum two FT-IR spectrophotometer was used to take FT-IR spectra. All the products were purified by chromatography on silica gel (Merck grade 60) from Aldrich. All reactions were achieved under a dry N₂ atmosphere. A Bruker 300 spectrometer instruments was used to take ¹H NMR and ¹³C NMR spectras. Fluorescence meauserement were recorded by Hitachi S-7000 fluorescencespectrophotometer. Mass spectras (MS) were analyzed by MALDI SYNAPT G2-Si Mass Spectrometry.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) and square wave voltammetry (SWV) analyses were performed with a PARSTAT 2273 electrochemical analyzer (Princeton Applied Research) using a three-electrode cell with a glassy carbon working electrode (GCE, 3 mm diameter), a Pt wire counter electrode, and a non-aqueous Ag/AgCl reference electrode. The electrolyte consisted of 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄, Merck) solution in dichloromethane (DCM) containing 0.5 mM of the dye. The solution was purged with high purity argon prior to measurement and blanketed with argon during measurement. In order to calibration of the reference electrode, electrochemical properties of the ferroceen/ferroce-nium (Fc/Fc⁺) redox couple as an external reference was performed under our experimental conditions. The half-wave peak potential ($E_{1/2}$), the peak separation potential (ΔE_p), ratio of anodic to

cathodic peak current (I_{pa}/I_{pc}) of Fc/Fc⁺ were 0.54 V, 109 mV, and \sim 1.00 at scan rate of 0.100 V s⁻¹, respectively. The ΔE_p value is higher than 59 mV which is expected for reversible electrochemical process of Fc/Fc⁺. However, non-ideal electrochemical behavior of Fc/Fc⁺ was reported previously [17].

2.3. Solar cell fabrication and characterization

Fluorine-doped tin oxide (FTO) glass plates (Solaronix, TCO22–15, $15 \Omega \text{ cm}^{-2}$, >80% transmittance in the wavelengths between 400 and 700 nm) were washed with water and ethanol. Then, the plates were dipped in 40 mM TiCl₄ aqueous solution at 50 °C for 30 min and washed with water. A transparent layer of TiO₂ nanoparticles (Solaronix, Ti-Nanoxide T/SP) was prepared by the doctor blade method on FTO plates, which was then gradually heated to 500 °C and baked at this temperature for 30 min under ambient condition. A home-made scattering layer of TiO₂ nanoparticles was synthesized according to the published procedure [18] and deposited by using the same method for the former layer on the treated FTO plates after that these plates cooled up to room temperature. Then, it was gradually heated to 500 °C for 30 min again. Finally, the double layer of TiO₂ coated plates were again treated with the TiCl₄ at 50 $^{\circ}$ C for 30 min and sintered at 500 $^{\circ}$ C for 30 min. The active areas of the photanodes were controlled at ${\sim}0.16\,\text{cm}^2$ with adhesive tape. After cooling down to room temperature, the dye-sensitized photoanodes were obtained by dipping the coated plates into the each Pc solution (0.3 mM) of ethanol/tetrahydrofuran (2/1, v/v) solution containing various chenodeoxycholic acid (CDCA) concentrations at ambient temperature for 72 h. The Pt counter electrodes obtained by a thermal deposition of Pt paste (Solaronix, Platisol T) on the surface of FTO plates at 500 °C for 30 min. The dye-sensitized photoanodes and the Pt counter electrodes were assembled in sandwiched type cell using a spacer (Solaronix, Meltonix 1170-25). The electrolyte solution (Solaronix, Iodolyte AN-50) was injected into the interface between the photoanode and counter electrode.

The DSSCs were irradiated under light irradiance of 100 mW cm⁻² (AM1.5) from a 150 W solar simulator (Newport, 96000). The above-mentioned potentiostat/galvanostat was used to obtain the current-voltage (*J*-*V*) curves. The intensity of the incident light was calibrated using a standard Si detector (Newport, 918D-SL-OD3) and an optical power meter (Newport, 1917-R). In order to confirm the reproducibility of the cells, three *J*-*V* measurements were performed for each synthesized Pc and it was found that the dispersion is lower than 8% for each DSSC.

2.4. Synthesis

2.4.1. 3-(4-(methylthio)phenoxy)phthalonitrile (1)

4-(methylthio)phenol (0.809 g, 5.78 mmol) was dissolved in 10 cm^3 dry DMF and then finely dried K₂CO₃ (~2.00 g, excess) was added to this mixture. Then 3-nitrophthalonitrile (1.00 g, 5.78 mmol) was added to this mixture dropwise by stirring effectively at 40 °C under the N₂ atmosphere. The reaction mixture was kept for 3 day at this temperature under N₂ atmosphere. After the reaction mixture was cooled to room temperature, it was poured into ca. 200 cm³ ice-water media. The occured precipitate was filtered and then washed with ca. 100 cm³ water up to the washings became neutral. The occured precipitate was filtered and dissolved in CHCl₃ and washed with%5 NaHCO₃ to eliminate the beginning residual compounds. The creamy solution was then treated with anhydrous Na₂SO₄ until become dry and filtered. It was purified by chromatography over a silica gel column by using a eluent that is a mix of CHCl₃: MeOH (100/5), giving white powder, (1). Finally, the pure powder was dried in a vacuo.

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