



Asymmetric phthalocyanine derivatives containing 4-carboxyphenyl substituents for dye-sensitized solar cells



Sadik Cogal ^{a,e}, Sule Erten-Ela ^{b,**}, Kasim Ocakoglu ^{c,d}, Aysegul Uygun Oksuz ^{e,*}

^a Mehmet Akif Ersoy University, Faculty of Arts and Science, Department of Chemistry, 15030 Burdur, Turkey

^b Ege University, Solar Energy Institute, Bornova, 35100 Izmir, Turkey

^c Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, 33343 Yenisehir, Mersin, Turkey

^d Mersin University, Tarsus Faculty of Technology, Department of Energy Systems Engineering, 33480 Mersin, Turkey

^e Suleyman Demirel University, Faculty of Arts and Science, Department of Chemistry, 32260 Isparta, Turkey

ARTICLE INFO

Article history:

Received 20 June 2014

Received in revised form

15 August 2014

Accepted 9 September 2014

Available online 19 September 2014

Keywords:

Phthalocyanine

Asymmetric

4-Carboxyphenyl

Dye-sensitized solar cell

Thiophene

Bithiophene

ABSTRACT

The synthesis of two asymmetrical zinc (II) phthalocyanines (ZnPcs) containing 4-carboxyphenyl and 3-thienyl or 5'-hexyl-2,2'-bithiophene substituent was described. These Zinc Phthalocyanines were synthesized by a statistical condensation reaction between two different phthalonitriles. Each of the phthalonitrile precursors was accomplished by the Suzuki-Miyaura cross-coupling reactions with the aryl iodide and corresponding boronic acids. The ZnPc dyes were characterized by MALDI-MS, FT-IR, ¹H NMR, UV–Vis, fluorescence and cyclic voltammetry methods. Compared with 3-thienyl substituted ZnPc-1 dye, the Q-band absorption of 5'-Hexyl-2,2'-bithiophene substituted ZnPc-2 was red-shifted by 13 nm because of the extension of π -system. The ZnPc dyes were used as sensitizers in dye-sensitized solar cells (DSSCs). ZnPc-2 sensitized solar cell devices using a 7 (transparent) + 5 (scattering) μm thin TiO₂ layer yielded a short-circuit photocurrent density of 3.81 mA/cm², an open-circuit voltage of 500 mV, and a fill factor of 0.59, corresponding to an overall conversion efficiency of 1.12% under standard AM 1.5 sun light.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Dye-sensitized solar cells (DSSCs) have received increasing attention due to their high incident to photon efficiency, easy fabrication and low production cost [1]. Tremendous research efforts have been devoted to the development of new and efficient sensitizers suitable for practical use. In TiO₂-based DSSCs, efficiencies of up to 11.4% under simulated sunlight have been obtained with ruthenium–polypyridyl complexes [2–4]. However, the main drawback of ruthenium complexes is the lack of absorption in the red region of the visible light and the high cost. For this reason, dyes with large and stable π -conjugated systems such as porphyrins and phthalocyanines are important classes of potential sensitizers for highly efficient DSSCs. Recently, the porphyrin dyes YD2-oC8 and SM315 showed the highest power conversion efficiencies of 12.3% and 13%, respectively, which broke the ruthenium based DSSCs record [5,6].

Among the various synthetic dyes being investigated for application in DSSCs, phthalocyanines (Pcs) have been considered to be promising candidates because of their unique optical and electrical properties [7]. These dyes are well known chromophores for their strong absorption around 300 and 700 nm, as well as for their excellent electrochemical, photochemical and thermal stability [8,9]. Moreover, the redox properties of Pcs are suitable for the sensitization of wide band gap semiconductors such as TiO₂ [10]. Therefore, Pcs are excellent alternative materials for DSSC applications and considerable research efforts have been made on the synthesis of various Pcs and ZnPcs. Furthermore, to achieve higher efficiency, researchers have focused on extension of the π -system and lowering the symmetry of the macro-cycle, which can result in a broadened Soret band and a red-shifted Q band absorption [11,12]. Recently, several groups have synthesized unsymmetrical phthalocyanines to improve the efficiency of DSSC [13–15]. In order to move the Q-band absorption of phthalocyanine to longer wavelength, the π -electron conjugation system can be extended by using various substituents [16–18]. In this study, we have designed two new unsymmetrical phthalocyanines (Fig. 1) containing 4-carboxyphenyl, 3-thienyl and 5'-hexyl-2,2'-bithiophene substituent and investigated their performance in DSSC. 4-Carboxyphenyl

* Corresponding author. Tel.: +90 2462114082.

** Corresponding author. Tel.: +90 2323111231.

E-mail addresses: suleerten@yahoo.com (S. Erten-Ela), ayseguluygun@sdu.edu.tr (A.U. Oksuz).

group was selected as an anchoring moiety to the TiO₂ surface. Substitution of 3-thienyl and 5'-hexyl-2,2'-bithiophene groups at the β -positions of the Pc ring could result in the extension of the π -system. We reported the efficiencies of zinc phthalocyanines using nanoporous TiO₂. ZnPc-2 sensitizer exhibited an efficiency of 1.12% using nanocrystalline 7 (transparent) + 5 (scattering) μm TiO₂ layers.

2. Experimental

2.1. Materials

4-Aminophthalonitrile, 3-thienylboronic acid, 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester, 4-methoxycarbonyl phenylboronic acid, chloroform (CHCl₃), tetrahydrofuran (THF), hexane, tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄], 1,2-dimethoxyethane (DME), 2-dimethylaminoethanol (DMAE), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), zinc (II) acetate [Zn(OAc)₂] and sodium carbonate (Na₂CO₃) were purchased from Aldrich; Silica Gel 60 (0.04–0.063) was purchased from Merck. 4-Iodophthalonitrile (2) was synthesized as described in literature [19].

2.2. Synthesis of 4-(3-thienyl)phthalonitrile (4)

4-Iodophthalonitrile (127 mg, 0.5 mmol), 3-thienylboronic acid (70.05 mg, 0.55 mmol) and Pd(PPh₃)₄ (57.8 mg, 0.05 mmol) were dissolved in 20 mL of DME. To this mixture, aqueous solution of Na₂CO₃ (26.5 mg, 0.25 mmol) was added. The resultant reaction mixture was heated at 80 °C under argon atmosphere for 16 h and then the reaction mixture is allowed to cool to room temperature. The reaction mixture was filtered and solvent was evaporated and the solid obtained was subjected to silica gel column chromatography and eluted with chloroform:hexane (3:1) mixture. Yield: 75%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.26 (m, 1H, Ar-H), 7.40 (m, 1H, Ar-H), 7.50 (m, 1H, Ar-H), 7.67 (m, 1H, Ar-H), 7.84 (m, 1H, Ar-H), 7.91–8.00 (m, 1H, Ar-H). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) = 113.57, 115.39, 115.50, 116.66, 124.26, 125.52, 128.14, 130.36, 131.07, 134.08, 138.18, 140.78. FTIR (KBr) ν (cm⁻¹): 3102, 2230 (CN), 1654, 1594 (Ar C=C), 1523, 1423, 1353, 1264, 1216, 1089, 891, 846, 794, 702, 651, 584, 521.

2.3. Synthesis of 4-(5'-hexyl-2,2'-bithiophene)phthalonitrile (6)

4-Iodophthalonitrile (254 mg, 1 mmol), 5'-hexyl-2,2'-bithiophene-5-boronic acid (414 mg, 1.1 mmol) and Pd(PPh₃)₄ (115.56 mg, 0.1 mmol) were dissolved in 20 mL of DME. To this mixture, aqueous solution of Na₂CO₃ (53 mg, 0.5 mmol) was added. The resultant reaction mixture was heated at 80 °C under argon atmosphere for 24 h and then the reaction mixture is allowed to

cool to room temperature. The reaction mixture was filtered and solvent was evaporated. The obtained solid was subjected to silica gel column chromatography and eluted with chloroform:hexane (3:1) mixture. Yield: 58%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 0.94 (m, 3H, CH₃), 1.36 (m, 2H, CH₂), 1.42 (m, 2H, CH₂), 1.72 (m, 2H, CH₂), 2.84 (m, 2H, CH₂), 6.76 (m, 1H, Ar-H), 7.11 (m, 1H, Ar-H), 7.29 (m, 1H, Ar-H), 7.79 (m, 1H, Ar-H), 7.80 (m, 1H, Ar-H), 7.86 (m, 1H, Ar-H), 7.97 (m, 1H, Ar-H). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) = 14.07, 22.57, 28.74, 30.24, 31.54, 112.74, 115.24, 115.52, 116.73, 124.33, 124.76, 125.22, 127.38, 128.71, 129.48, 132.44, 134.04, 136.88, 139.29, 141.76, 147.38. FTIR (KBr) ν (cm⁻¹): 3106, 3067, 2954, 2920, 2841, 2229 (CN), 1719, 1593 (Ar C=C), 1554, 1495, 1446, 1439, 1411, 1369, 1314, 1280, 1219, 1202, 1175, 1104, 1065, 905, 879, 837, 796, 777, 723, 521, 486, 430.

2.4. Synthesis of 4-(4-methoxycarbonylphenyl)phthalonitrile (8)

4-Methoxycarbonylphenylboronic acid (300 mg, 1.67 mmol), 4-iodophthalonitrile (381 mg, 1.50 mmol) and Pd(PPh₃)₄ (173.34 mg, 0.15 mmol) were dissolved in 20 mL of DME and stirred under argon for 10 min. Then, aqueous Na₂CO₃ (318 mg, 3 mmol) was added slowly in a few portions, and the mixture was heated at 80 °C for 12 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was dissolved in 100 mL CHCl₃, washed three times with distilled water and dried over Na₂SO₄. The drying agent was removed by filtration and CHCl₃ evaporated in vacuum. The resulting solid was purified by column chromatography on silica gel by using CH₂Cl₂ as an eluent. Compound **8** was obtained as a white solid (250 mg, 65.4%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.23–8.21 (1H, Ar-H), 8.08 (1H, Ar-H), 8.01 (1H, Ar-H), 7.99 (1H, Ar-H), 7.96–7.94 (1H, Ar-H), 7.71 (1H, Ar-H), 7.69 (1H, Ar-H), 4.00 (m, 3H, CH₃). FTIR (KBr): ν (cm⁻¹) = 3422, 3104, 3071 (H-Ar), 2956, 2849, 2389, 2291, 2230 (CN), 1714 (C=O), 1600 (Ar C=C), 1484 (Ar C=C), 1426, 1384, 1295 (C-O), 1186, 1109, 1015, 956, 918, 841, 765, 695, 519.

2.5. Synthesis of 2-(4-carboxyphenyl)-9(10), 16(17), 23(24)-tris(3-thienyl)phthalocyaninato zinc(II) (ZnPc-1)

4-(3-Thienyl)phthalonitrile (1.05 mmol, 220.76 mg), 4-(4-methoxycarbonylphenyl)phthalonitrile (0.35 mmol, 91.79 mg) and Zn(OAc)₂ (10 mmol, 183 mg) were dissolved in 10 mL DMAE. The mixture was added by three drops of DBU and heated at 130 °C under argon atmosphere for 12 h. The reaction mixture was then allowed to cool to room temperature and the solvent was removed under vacuum. The residue was washed with a MeOH:H₂O (5:1) mixture. The solid obtained was purified by column chromatography on silica gel. A THF eluent removed most of the symmetric tetrakis(3-thienyl)phthalocyanine and a THF:DMF (10:1) eluent to separate the **ZnPc-1 methyl ester**. This fraction was dissolved in 20 mL of THF:MeOH (3:1) mixture and was hydrolyzed at 60–70 °C for 1 h. The reaction mixture was then allowed to cool to room temperature and the organic solvent was removed under vacuum. The pH of the reaction mixture was set to pH 3–4 by adding 1 M HCl solution, and the precipitate was formed. The precipitate was collected and washed several times with MeOH:H₂O mixture and dried to give **ZnPc-1** as a green solid (11% overall yield for two steps). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 9.42–9.11 (broad, m, 12H, Ar-H), 8.41–7.97 (4H Ar-H), 6.89–6.53 (12H, thienyl, Ar-H). FTIR (KBr): ν (cm⁻¹) = 3630, 3059 (Ar-H), 2953, 2912, 2866 (aliphatic C-H), 1691 (C=O), 1653, 1607, 1526, 1486, 1435, 1411, 1390, 1363, 1320, 1276, 1229, 1168, 1081, 1059, 888, 859, 832, 778, 759, 742, 688, 667, 623, 520, 461, 430. UV–Vis (THF): λ_{max} , nm (log ϵ , M⁻¹.cm⁻¹) = 358 (4.92), 618 (4.62) and 684 (5.30). MALDI TOF MS: calcd for C₅₁H₂₆N₈O₂S₃Zn ([M+H]⁺) 944.41; found 944.07.

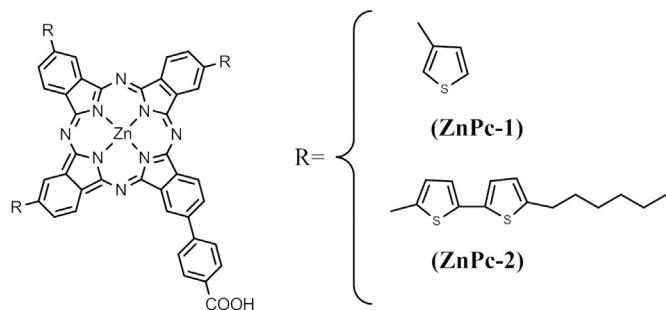


Fig. 1. Molecular structures of ZnPc-1 and ZnPc-2.

Download English Version:

<https://daneshyari.com/en/article/6600337>

Download Persian Version:

<https://daneshyari.com/article/6600337>

[Daneshyari.com](https://daneshyari.com)