

Unsymmetrical alkoxy zinc phthalocyanine for sensitization of nanocrystalline TiO₂ films

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Abstract

A new photosensitizer, unsymmetrical alkoxy zinc phthalocyanine based on ‘push–pull’ concept, has been synthesized and fully characterized by CHN, MALDI-TOF, UV–Vis, fluorescence spectroscopies and cyclic voltammetry. The new phthalocyanine photosensitizer has eight alkoxy and two carboxyl groups that act as electron releasing (*push*) and withdrawing (*pull*), respectively. Moreover, the alkoxy groups increase the solubility of the new photosensitizer in common organic solvents, and the two carboxyl groups serve to graft on to nanocrystalline TiO₂. The new photosensitizer was tested in dye-sensitized solar cells and its performance was compared with PCH001.

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1. Introduction

Nanocrystalline dye-sensitized solar cells (DSSCs) are currently attracting widespread interest for the conversion of sunlight into electricity because of their low cost and high conversion efficiency [1,2]. In these cells, dye sensitizer is one of the key components for high power conversion efficiencies. The most successful charge-transfer sensitizers employed so far in such cells are bis(tetrabutylammonium)-*cis*-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (the N719 dye) and trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye), produced solar-energy-to-electricity conversion efficiencies (η) of up to 11% under AM 1.5 irradiation and stable operation for millions of turnovers [3,4]. In spite of this, the main drawbacks of these sensitizers are the lack of absorption in the red region of the visible spectrum and also relatively low molar extinction coefficient above

600 nm. In contrast, phthalocyanines possess intense absorption bands in the near-IR region and are known for their excellent chemical, light and thermal stability; and have appropriate redox properties for sensitization of wide-bandgap semiconductors, e.g., TiO₂, rendering them attractive for DSSC applications [5]. Several groups have tested phthalocyanines as sensitizers for wide-bandgap oxide semiconductors, although they all have reported power conversion efficiencies around 1% until recently [6–10]. The low efficiency of cells incorporating phthalocyanines appears to be due to aggregation, solubility and lack of directionality in the excited state. One of the essential requirements for the light-harvesting systems of a molecular/semiconductor junction is that the sensitizer possesses directionality of its electronic orbitals in the excited state. This directionality should be arranged to provide an efficient electron transfer from excited sensitizer to the TiO₂ conduction band by good electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the sensitizer and Ti 3d orbital.

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Taking into account of the above requirements, recently, we have synthesized an unsymmetrical zinc phthalocyanine sensitizer (PCH001) based on 'push–pull' concept [11]. This phthalocyanine has three bulky *tert*-butyl groups, which enhances the solubility, minimizes the aggregation as well as electron releasing ability (*push*). It also contains two carboxyl groups, not only provides anchoring to the nanocrystalline titanium dioxide semiconductor and also acts as electron withdrawing (*pull*) groups. Using PCH001 sensitizer, we have obtained an overall conversion efficiency (η) of 3.05% with A1376 redox electrolyte. This is the first phthalocyanine showing such a high η in DSSC. Here in this manuscript, we have extended the 'push–pull' concept and synthesized a new unsymmetrical phthalocyanine, PCH003, which has eight butyloxy groups that act as electron releasing as well as to further enhance the solubility of phthalocyanine in common organic solvents when compared to PCH001 and the two carboxyl groups act as electron withdrawing and also serve as an anchoring group on to TiO₂. The PCH003 was characterized by CHN, MALDI-TOF, UV–Vis, ¹H NMR, fluorescence spectroscopies and cyclic voltammetry. We have tested new unsymmetrical zinc phthalocyanine in DSSC and compared its performance with PCH001 and other phthalocyanines reported in the literature.

2. Experimental

The 3,4-dihydroxy phthalonitrile, 4-nitro phthalonitrile, 1,8-diazabicyclo [5.4.0]–undec–ene (DBU), 1-pentanol and tetrabutylammonium perchlorate (TBAP) are procured from Aldrich. K₂CO₃, acetone, chloroform, dichloromethane and hexane are obtained from BDH (India) and were purified prior to use [12]. Column chromatography was performed on Aceme silica gel (60–120).

2.1. Synthesis

Synthesis of 3,6-dibutoxy phthalonitrile (1): 3,6-dihydroxy-1,2-dicyanobenzene (1.60 g, 10 mmol) and K₂CO₃ were dissolved in 60 ml of dry acetone and stirred at room temperature for 30 min. To this 1-bromobutane (2.70 g, 20 mmol) was added. The resultant reaction mixture was refluxed under nitrogen atmosphere for 60 h. The solvent was evaporated under reduced pressure. The obtained solid material was extracted with dichloromethane solvent and washed with water. The solvent was removed with rotary evaporator. The obtained solid material was subjected to silica gel column chromatography and eluted with dichloromethane to get the desired product in 80% yield. Elemental analysis of C₁₆H₂₀N₂O₂ (calculated mass % in parentheses): C, 70.50 (70.56); H, 7.45 (7.45); N, 10.25 (10.29). EI-MS: *m/z* 273 [M]⁺. ¹H NMR (CDCl₃): 7.15 (s, 2H); 4.05 (t, 4H); 1.80 (m, 4H); 1.51 (m, 4H); 1.05 (t, 6H).

Synthesis of 4-(1,1,2-tricarboethoxyethyl) phthalonitrile (2): This compound was synthesized according to the procedure reported in the literature [13]. Elemental analysis

of C₁₉H₂₀N₂O₆ (calculated mass % in parentheses): C, 61.03 (61.28); H, 5.65 (5.41); N, 7.60 (7.52). EI-MS: *m/z* 373 [M]⁺. ¹H NMR (CDCl₃): δ , ppm 7.93 (s, 1H); 7.84–7.74 (q, 2H); 4.30–4.03 (m, 6H); 3.35 (s, 2H); 1.30–1.18 (m, 9H).

3: 3,6-bis-(butoxy)-1,2-dicyanobenzene (1) (2.195 g, 8.07 mmol), 4-(1,1,2-tricarboethoxyethyl)-phthalonitrile (2) (1.00 g, 2.69 mmol) and 100 mg of DBU were dissolved in 20 ml of dry 1-pentanol. The reaction mixture was refluxed for 20 h and the solvent 1-pentanol was removed under reduced pressure. The obtained solid material was subjected to silica gel column chromatography and eluted with CHCl₃. The second greenish color band was the desired triester phthalocyanine (3). The compound was recrystallized twice from CHCl₃–hexane (yield 11%). Elemental analysis of C₆₇H₈₂N₈O₁₂ (calculated mass % in parentheses): C, 67.40 (67.54); H, 7.00 (6.94); N, 9.36 (9.41). MALDI-MS: *m/z* 1192 [M]⁺.

4: Zinc metallation of free-base triester phthalocyanine (3) was achieved with zinc acetate in DMF solvent.

Synthesis of PCH003: This compound was synthesized by the hydrolysis of 4, using Na/ethanol. 100 mg of compound 4 was dissolved in 25 ml of ethanol. To this 1 g of Na was added. The resulting reaction mixture was stirred at room temperature for 7 days. The solvent was evaporated under reduced pressure. The obtained solid material was redissolved in ethanol and pH was adjusted to 3 by using dil. HCl. The precipitate was filtered and dried under reduced pressure. This phthalocyanine was characterized by ¹H NMR, UV–Vis, MALDI-TOF spectroscopies and elemental analysis. Elemental analysis of C₆₀H₆₈N₈O₁₀Zn (calculated mass % in parentheses): C, 63.80 (63.96); H, 6.15 (6.08); N, 10.01 (9.95). IR (KBr) cm⁻¹: 3434, 2924, 2858, 1835, 1630, 1458, 1275, 1188, 1073, 760. MALDI-TOF MS: C₆₀H₆₈N₈O₁₀Zn (1126.62): 1129 (5%), 1099 (10%), 1072 (85%). UV–Vis, (in ethanol, λ_{\max} , log ϵ): 697 (4.83), 636 (sh), 343 (4.69).

2.2. Characterization methods

The UV–Vis spectra were recorded with a Shimadzu model 1700 spectrophotometer and steady state fluorescence spectra were recorded using a Spex model Fluoromax-3 spectrofluorometer for solutions having optical density at the wavelength of excitation (λ_{ex}) \approx 0.11. MALDI-MS spectra were recorded on a TO-4X KOMPACT SEQ, KARTOS, UK, Mass spectrometer. Major fragmentations are given as percentages relative to the base peak intensity. ¹H NMR spectra were obtained at 300 MHz using a Bruker 300 Avance NMR spectrometer running X-WIN NMR software. The chemical shifts are relative to tetramethylsilane (TMS). The Fourier transform IR (FTIR) spectra of all the samples were measured using a Thermo Nicolet Nexus 670 spectrometer.

Cyclic-and differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. Cyclic voltammetric

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