



Far-red sensitizing octatrifluorobutoxy phosphorous triazatetrabenzocorrole: Synthesis, spectral characterization and aggregation studies

Gururaj M. Shivashimpi^{a,*}, Shyam S. Pandey^a, Azwar Hayat^a, Naotaka Fujikawa^a, Yuhei Ogomi^a, Yoshihiro Yamaguchi^b, Shuzi Hayase^a

^a Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu, Japan

^b Nippon Steel and Sumikin Chemical Company Limited, Nakabaru, Tobata, Kitakyushu, Japan

ARTICLE INFO

Article history:

Received 17 March 2014
Received in revised form 1 May 2014
Accepted 22 May 2014
Available online 2 June 2014

Keywords:

Far-red sensitizer
Phosphorous phthalocyanine
Aggregation studies
Solvent effect

ABSTRACT

Novel phosphorous triazatetrabenzocorrole (**4**) bearing non-peripheral octatrifluorobutoxy groups was successfully synthesized, with an aim to develop potential far-red sensitizer for dye sensitized solar cells. The dye was characterized by ¹H NMR, IR, mass, and UV–vis spectral techniques. It showed excellent solubility in majority of common organic solvents. Aggregation behavior of the dye **4** was investigated in several solvents with increasing dielectric constants. This dye-**4** was found to be adsorbed on the nanoporous TiO₂ via axial ligation. Further implication of structure of dye due to incorporation of –CF₃ group on the energy levels was evaluated by theoretical and experimental approaches. The intense far-red absorption of dye **4** including its excellent solubility and proper control of its energy levels makes it a promising candidate for its application as sensitizer in dye sensitized solar cells.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) and their derivatives are the stable macrocyclic planar complexes having intense light absorption. The absorption wavelength in this class of dyes can be tailored from far-red to infra-red region by judicious molecular design. They have gained the attention as versatile organic materials for various applications [1–5]. Triazatetrabenzocorroles (TBC), which are first reported by Fujiki et al. [6], are the contracted analogs of phthalocyanines in which one meso-nitrogen atom is missing. Peculiar characteristic of these compounds is the presence of both sorret and Q-bands which are red and blue shifted, respectively. In the recent past, several TBCs bearing phosphorous as central atom were synthesized and characterized by various research groups [7–11], but till date no efforts have been directed to design such class of dyes toward the application as sensitizer in the area of fast growing field of dye-sensitized solar cells (DSSCs).

Recently, due their high molar extinction co-efficient and chemical stability, phthalocyanines have been utilized as challenging

photosensitizing materials in the next generation photovoltaics like DSSCs [12,13]. These phthalocyanine based sensitizers can be adsorbed on nanoporous semiconductor surface via several ways of bonding like covalent bonding and hydrophobic or electrostatic interactions [14]. In majority of reports on phthalocyanines based DSSCs, phthalocyanine dyes bearing peripheral anchoring groups are being utilized [15]. However, the demerit of phthalocyanines bearing peripheral anchoring groups is inter-dye interaction due to molecular aggregation on surface of semiconductors which leads to poor electron injection and recombination. To overcome this, new phthalocyanine dyes which can coordinate with semiconductor (TiO₂ and SnO₂) surface through their axial substituents were designed and synthesized. Unfortunately, overall photovoltaic performance of the DSSCs bearing phthalocyanine dyes having axial anchoring groups was found to be very poor. Further, in an interesting report by Park et al. [16] it was found that phthalocyanine dyes with axial anchoring groups did not show promising adsorption on well known nanoporous titania semiconductor surface. Recently, a report by Gratzel and co-workers [17] showed that the unsymmetrical zinc phthalocyanine bearing phosphonic acid group can also anchor on TiO₂ surface much better than its carboxy counterpart. In this regard, we envisaged that, the phosphorous TBCs bearing central P–OH group could be a challenging sensitizers for DSSCs ligating axially on to the surface of nanoporous TiO₂.

* Corresponding author. Tel.: +81 93 695 6044; fax: +81 93 695 6005.

E-mail addresses: shivashimpi@life.kyutech.ac.jp, gururaj.shivashimpi@gmail.com (G.M. Shivashimpi).

Along with molecular aggregation, insolubility of phthalocyanines in common polar organic solvents is another stumbling block toward their application particularly in the area of DSSCs as light harvesting materials. Therefore, finding a suitable solvent in which phthalocyanines are easily soluble and show minimum aggregation is the immediate need for DSSC application. Apart from this, control of the energetics of the dye under investigation with respect to the oxide semiconductor and redox electrolyte are crucial for the functioning of the DSSCs. Recently fluorinated phthalocyanines bearing peripheral fluoro-alkyl [18,19] and aryl [20,21] substituents have received a great deal of attentions due to their interesting electron transfer properties and high solubility in polar as well as aprotic solvents. In our previous report we found that, fluoroalkylated substituents play an important role in controlling the energy level of sensitizers, which is also a crucial factor in designing a photosensitizer for DSSCs [22].

Based on these reports, for the first time, we designed and synthesized the phosphorous 3,6,10,13,17,20,24,27-octatrifluorobutoxy-triazatetrabenzocorrole **4** (Scheme 1) incorporated with non-peripherally (α , α') substituted octatrifluorobutoxy groups. The non-peripheral trifluoroalkoxy groups not only increase the solubility of phthalocyanines in various polar solvents, but at the same time (α , α') substitution of alkoxy groups leads to red-shifted absorption maxima also [23,24], making them potential near infrared (NIR) sensitizers for DSSC applications. In the present work, we report the synthesis, characterization and detailed investigation of the solvent effect on aggregation behavior of phosphorous triazatetrabenzocorrole **4**. We also report the investigation pertaining to the implication of incorporating $-\text{CF}_3$ groups on the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels by theoretical and experimental methods.

2. Experimental

2.1. Materials, instruments and methods

All the chemicals for synthesis or solvents are of analytical or spectroscopic grade and used as received without further purification. Flash chromatography was performed using silica gel 60 (230–400 mesh) eluting with solvents as indicated. Purity of all compounds including intermediates and final products were confirmed by high performance liquid chromatography (JASCO). Mass of the intermediates as well as final dyes was confirmed by MALDI-TOF mass (Applied Biosystems) or fast ion bombardment mass (FAB-MS) and high resolution mass (HR-MS) spectra on a JEOL JMS-SX 102A instrument. Nuclear magnetic resonance (NMR) spectrum was recorded on a JEOL JNM A (500 MHz) spectrometer in CDCl_3 or DMSO-d_6 solvents with reference to tetramethyl silane (TMS) for structural elucidation. All proton NMR signal shifts are given in parts per millions (s = singlet; d = doublet; t = triplet; m = multiplet). Electronic absorption spectroscopic investigations in solution and thin film adsorbed on TiO_2 surface were conducted using UV–visible spectrophotometer (JASCO model V550). The HOMO energy level was measured using photoelectron spectroscopy in air (Riken, model AC3). On the other hand LUMO energy level was determined from the edge of optical absorption considering it as optical band gap (Eg) using the relation $\text{LUMO} = \text{HOMO} + \text{Eg}$. Optimized geometries of the final dye along with the energies of HOMO and LUMO were calculated without any symmetry restriction at B3PW91/6-311G level of calculation using Gaussian 09 program package [25].

2.2. Synthesis

2.2.1. Synthesis of 3,6-bis-(trifluorobutoxy)-1,2-benzenedinitrile [2]

To a slurry of 2,3-dicyano hydroquinone (**1**) (1.8 g, 11.3 mmol) and K_2CO_3 (3.9 g, 28.30 mmol) in DMF (30 mL) was added 1-iodo-4,4,4-trifluorobutane (4.4 mL, 34 mmol), and the solution was heated at 60–70 °C for 12 h. After completion of the reaction, reaction mixture was poured into water (1 L) and the solution was stirred vigorously for 30 min. The precipitated white solid was filtered under suction and the residue washed with methanol to yield phthalonitrile **2** as white solid **2** (3 g, 88.5%). HR-FAB mass m/z : calcd. for $\text{C}_{16}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_2$, 380.0959; found, 381.1034 $[\text{M}+1]^+$.

2.2.2. Synthesis of 3,6,10,13,17,20,24,27-octatrifluorobutoxy phthalocyanine [3]

To a solution of phthalonitrile **2** (3 g, 10 mmol) in butanol (20 mL) was added lithium (500 mg, 70 mmol). The reaction mixture was refluxed for 2 h under argon atmosphere. The crude reaction mixture was passed through a short silica gel column, using chloroform as eluent to yield the metal free phthalocyanine (**3**) as green powder (600 mg, 4%). FAB-MS m/z : calcd. for $\text{C}_{64}\text{H}_{58}\text{F}_{24}\text{N}_8\text{O}_8$, 1522.39; found, 1522.28 $[\text{M}]^+$.

2.2.3. Phosphorous 3,6,10,13,17,20,24,27-octatrifluorobutoxy-triazatetrabenzocorrole [4]

To a solution of metal free phthalocyanine **3** (600 mg, 0.4 mmol) in pyridine (15 mL) in a two necked flask fitted with condenser and gas inlet, was added PBr_3 (1.5 mL, 16 mmol) drop wise. The reaction mixture was refluxed for 2–2.5 h under argon atmosphere. After the completion of reaction, the reaction mixture was allowed to cool to room temperature and poured onto the crushed ice and allowed to stand overnight to precipitate. The crude product that is settled down as precipitate was filtered and washed thoroughly with water. Finally, the crude product was purified by silica gel chromatography using chloroform:methanol solvent mixture as eluent to yield 200 mg (32%) of dark green powder. HR-FAB MS, observed $[\text{M}]^+$ 1554.3662 for $\text{C}_{64}\text{H}_{57}\text{F}_{24}\text{N}_7\text{O}_9\text{P}$ (calcd 1554.3572). ^1H NMR (500 MHz, CDCl_3): δ = 7.39–7.65 (m, 8H, Ar-H), 4.54–4.87 (m, 16H, $-\text{O}-\text{CH}_2-$), 2.29–2.71 (m, 16H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.42–1.83 (m, 16H, $-\text{CH}_2-\text{CF}_3$). ^{31}P NMR (500 MHz, CDCl_3): δ = –106.09. FT-IR (KBr, cm^{-1}): 3431 (PO–H), 3053, 2959, 2880, 1725, 1590, 1508, 1386, 1332, 1284, 1249, 1153, 949, 812, 810, 734 and 659.

3. Results and discussion

3.1. Synthesis and characterization

Synthetic method for the preparation of phthalocyanines involves the synthesis of starting phthalonitrile or 1,3-diimino-1H-isoindole subunits with desired functionality substituted on their aromatic ring and final cyclotetramerization of the these phthalonitrile or 1,3-diimino-1H-isoindole derivatives in high boiling alcohols in the presence of catalytic DBU or lithium metal [26]. The synthetic route for the novel TBC analog **4** under investigation is shown in Scheme 1. In the first step, commercially available 2,3-dicyanohydroquinone (**1**) was O-alkylated using 1-iodo-4,4,4-trifluorobutane. The reaction was carried out in DMF solvent at 70 °C in the presence of potassium carbonate as a base, giving 3,6-bis(trifluorobutoxy)-1,2-dicyanobenzene (**2**) in quantitative yield. Li metal mediated cyclotetramerization of the phthalonitrile **2** was carried out by refluxing in 1-butanol under argon atmosphere giving octatrifluorobutoxy substituted metal-free phthalocyanine (**3**) in 5% yield. Lower yield

Download English Version:

<https://daneshyari.com/en/article/26565>

Download Persian Version:

<https://daneshyari.com/article/26565>

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