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A new unsymmetrical phthalocyanine with a single *o*-carborane substituent

Nilgün Özgür, Ilgın Nar, Ahmet Gül, Esin Hamuryudan*

Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

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ABSTRACT

Unsymmetrical zinc phthalocyanine carrying a single *o*-carborane substituent on the peripheral position was synthesized in a multistep reaction sequence. At the first step, metal-free phthalocyanine **3** was prepared by cyclotetramerization of 4,5-di(hexylthio)phthalonitrile and 4-(2-hydroxyethylthio)phthalonitrile in pentanol in the presence of lithium; and zinc phthalocyanine **4** was prepared by insertion of Zn(II) salt. After esterification of phthalocyanine **4** with 4-pentynoic acid, terminal alkynyl bearing precursor phthalocyanine **5** was obtained. At the last step, reaction of decaborane with phthalocyanine **5** yielded phthalocyanine **6** with the desired o-carborane moiety. The new phthalocyanine compounds were characterized by elemental analysis, NMR, FT-IR, UV–vis and mass spectral data. Aggregation behaviour and electrochemical properties of these newly synthesized unsymmetrical phthalocyanine derivatives were also reported.

Introduction

Multifaceted electrochemical and spectroscopic properties of phthalocyanines have attracted a great deal of attention from researchers in diverse fields [1] such as catalysis [2], nonlinear optics [3], photovoltaic cells, solar energy conversion [4], chemical sensors [5,6], photodynamic cancer therapy [7,8], etc. The peripheral or nonperipheral substituents of phthalocyanines such as alkyl chains or bulky groups increase the solubility properties of corresponding phthalocyanines and make them beneficial in different application areas [9,10]. However, there are some limitations of using symmetrical phthalocyanines. Hence, recently, researchers have been interested in low symmetrical phthalocyanines which enrich the specifications and make them usable in a more controlled manner [11–15].

In addition, the boron containing cluster systems have recently become an extensively studied class of compounds due to their three-dimensional structure: aromaticity, high chemical and thermal stability and incorporation into various organic molecules as substituents [16].

Boron containing cluster systems such as carborane, cobalt bis dicarballide and dodecaborate anion are used in substitution of phthalocyanines and these phthalocyanine derivatives are potential sentisizers for photodynamic therapy (PDT) and boron neutron capture therapy (BNCT) [17–24]. Furthermore, substitution of phthalocyanines with *o*-carborane group enhances the properties of the compound as it displays a rich chemistry. The substituted *o*-carboranes are electrochemically more powerful. The redox activity of phthalocyanine may improve when it is substituted with *o*-carborane group due to the high stability, electrochemistry and ease of functionalization related to *o*-carborane [25–29].

In this study, we have synthesized an unsymmetrical phthalocyanine carrying a single *o*-carborane unit on the periphery through a multistep reaction sequence. We also report spectroscopic characterization, aggregation behaviour and electrochemical properties of these newly synthesized unsymmetrical phthalocyanine derivatives.

Experimental section

Materials and equipment

Precursor phthalonitriles 4,5-di(hexylthio)phthalonitrile (**1**) and 4-(2-hydroxyethylthio) phthalonitrile (**2**) were prepared according to the literature [30,31]. All necessary reagents and solvents were of reagent grade quality obtained from commercial sources. Silica gel (Kieselgel 60, 200–400 mesh) was chosen as stationary phase for column chromatography. FT-IR spectra were

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* Corresponding author. Tel.: +90 212 285 68 26.
E-mail address: esin@itu.edu.tr (E. Hamuryudan).

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obtained on a Perkin Elmer Spectrum One FT-IR spectrophotometer. ^1H and ^{11}B NMR spectra were taken in $CDCl_3$ and pyridine *d*5 solutions, recorded on Agilent VNMRS 500 MHz spectrometer. Electronic spectra were measured on Scinco LabProPlus UV/vis spectrophotometer and mass spectra were performed on Bruker microflex LT MALDI-TOF mass spectrometer.

Electrochemical measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat. Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed in a three-electrode cell with a platinum disk (0.071 cm^2 surface area) working, a platinum wire counter and a saturated calomel reference electrodes. Saturated calomel electrode (SCE) was connected to the solution through a bridge. Dichloromethane (DCM) containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte.

In situ UV–vis absorption spectra were measured by an Ocean Optics HR2000 + diode array spectrophotometer. For in situ spectroelectrochemical measurements, an optically transparent thin layer quartz cell of path length 1 mm was employed, in which a platinum gauze electrode, a platinum wire and a SCE were used for the working, counter and reference electrodes, respectively.

Synthesis

*2,3,9,10,16,17-Hexakis(hexylthio)-23-hydroxyethylthiophthalocyanine (**3**)*

A mixture containing 0.432 g (1.2 mmol) of 4,5-di(hexylthio) phthalonitrile **1** and 0.08 g (0.4 mmol) of 4- (2-hydroxyethylthio) phthalonitrile **2** in 3 ml pentanol was heated and stirred at 140 °C under N_2 in a sealed tube. After 15 min, 0.015 g (2 mmol) lithium metal was added to the mixture and refluxed for 4 h. The reaction mixture was cooled to ambient temperature and then poured into 25 ml methanol and acidified with acetic acid until the crude product precipitated. In this mixture, lithium phthalocyanine derivatives were converted into metal free phthalocyanines. The precipitate was centrifuged and washed several times with hot methanol to remove unreacted materials. Finally, the green residue was chromatographed on silica gel using dichloromethane: methanol as the eluent, changing from 150:1 to 75:1 (v/v), to result in **3** as a green solid on the second fraction. Yield: 0.13 g (26%); m.p. > 200 °C. IR υ (cm^{-1}): 3300 (–OH), 3290 (–NH), 2950–2850 (alkyl –CH); ^1H NMR ($CDCl_3$) δ ppm: 8.42–7.57 (m, 9H, Ar–H), 4.71 (s, H, OH), 4.19 (m, 2H, OCH_2), 3.68 (m, 2H, SCH_2), 3.56–3.24 (m, 12H, SCH_2), 2.03–1.26 (m, 48H, $-CH_2$), 1.05 (m, 18H, CH_3), –4.3 (br, 2H, N–H); UV–vis λ_{max} (nm) in THF: 342, 694, 725; MALDI-TOF MS (matrix DHB) *m*/*z*: 1287.85 $[M]^+$; anal. calcd. for $C_{70}H_{94}N_8OS_7$; C, 65.28; H, 7.36; N, 8.70; found: C, 65.17; H, 7.45; N, 8.78%.

*[2,3,9,10,16,17-Hexakis(hexylthio)-23-hydroxyethylthiophthalocyaninato]zinc(II) (**4**)*

A solution of 0.1 g (0.08 mmol) **3** and 0.044 g (0.24 mmol) anhydrous $Zn(CH_3COO)_2$ was refluxed in 2 ml of 1-pentanol with stirring for 4 h under N_2 atmosphere. The resulting suspension was cooled to ambient temperature and then poured into 20 ml methanol. The precipitate was filtered off, washed successively with water, hot methanol, hot aceton and hot hexane. The purification was carried out by column chromatography on silica gel using dichloromethane: methanol (50:1) as the eluent to result in **4** as a green solid. Yield: 0.10 g (94.4%); m.p. > 200 °C. IR υ (cm^{-1}): 3360 (–OH), 2950–2850 (alkyl –CH); ^1H NMR ($CDCl_3$ + 1 drop pyridine *d*5) δ ppm: 9.10–8.82 (br, 5H, Ar–H), 8.55 (s, 1H, Ar–H), 8.03 (m, 2H, Ar–H), 7.62 (s, 1H, Ar–H), 4.64 (s, H, OH), 4.15 (m, 2H, OCH_2), 3.84 (m, 2H, SCH_2), 3.44–2.86 (m, 12H, SCH_2), 2.02–1.72 (m, 24H, CH_2), 1.44–1.22 (m, 24H, CH_2), 0.96 (m, 18H, CH_3); UV–vis λ_{max} (nm) in THF: 361, 629, 699; MALDI-TOF MS (matrix DHB) *m*/*z*: 1352.52 $[M + H]^+$; anal. calcd. for $C_{70}H_{92}ZnN_8OS_7$; C, 62.21; H, 6.86; N, 8.29; found: C, 62.25; H, 6.77; N, 8.35%.

*[2,3,9,10,16,17-Hexakis(hexylthio)-23-1-pentynyloxyethylthiophthalocyaninato] zinc(II) (**5**)*

10 mg of 4-pentynoic acid (0.12 mmol) and 20 mL of anhydrous dichloromethane were added to a three-necked 50 mL flask. After the 4-pentynoic acid was solved, 150 mg (0.11 mmol) of **4** and 24 mg (0.12 mmol) of dicyclohexylcarbodiimide (DCC) were added. Then 7 mg (0.055 mmol) of N,N-dimethylaminopyridine (DMAP), dissolved in 1.5 mL of anhydrous dichloromethane, was added dropwise. The mixture was stirred for 48 h at room temperature under N_2 atmosphere. The solution was filtered and the filtrate was placed in the freezer for 30 min and then filtered again. Following the evaporation of the solvent, purification of the solid crude product **5** was accomplished by column chromatography with dichloromethane: methanol (50:1) as eluents to give a dark green solid. Yield: 95 mg (59.8%); m.p. > 200 °C. IR υ (cm^{-1}): 3310 (alkynyl –CH), 2950–2850 (alkyl –CH), 2202 ($-C\equiv CH$), 1720 ($-C{=}O$); UV–vis λ_{max} (nm) in THF: 360, 630, 698; MALDI-TOF MS (matrix DHB) *m*/*z*: 1432.47 $[M + H]^+$; anal. calcd. for $C_{75}H_{96}ZnN_8O_2S_7$; C, 62.93; H, 6.76; N, 7.83; found: C, 63.01; H, 6.71; N, 7.88%.

*[2,3,9,10,16,17-Hexakis(hexylthio)-23-1-(o-carboranyl) propanoxy ethylthio phthalocyaninato]zinc(II) (**6**)*

0.019 g (0.154 mmol) of decaborane ($B_{10}H_{14}$) was dissolved in a mixture of 10 mL dry toluene and 6 mL dry acetonitrile. The reaction mixture was heated to 90 °C. After 2 h, 0.20 g (0.140 mmol) phthalocyanine **5** was added. This mixture was heated to reflux for 48 h. After the reaction mixture was cooled to room temperature, it was filtered, and all solvents were evaporated. Purification of the solid crude product **6** was accomplished by column chromatography with THF as eluent to give a green solid. Yield: 0.086 g (40.0%); m.p. > 200 °C. IR υ (cm^{-1}): 2950–2850 (alkyl –CH), 2571 (-BH); ^1H NMR (pyridine *d*5): 9.73–9.45 (m, 6H, Ar–H), 8.97–8.38 (m, 3H, Ar–H), 4.74 (m, 2H, CH_2), 4.41 (s, H, CH), 3.92 (m, 2H, OCH_2), 3.80 (m, 2H, SCH_2), 3.56 (m, 12H, SCH_2), 3.22–1.10 (b, 10H, BH), 2.84 (m, 2H, $CH_2OC{=}O$), 2.13 (m, 2H, CCH_2), 2.03 (m, 12H, $SCCCH_2$), 1.70–1.30 (m, 24H, CCH_2), 0.93 (m, 18H, CH_3); ^{11}B NMR (pyridine *d*5): δ, ppm –2.34 (b, 1B); –5.34 (b, 1B), –9.18 (b, 3B), –11.21 (b, 5B).; UV–vis λ_{max} (nm) in THF: 361, 632, 700; MALDI-TOF MS (matrix DHB) *m*/*z*: 1551.72 $[M]^+$, 1352.090 $[M-C_5H_{17}B_{10}O]^+$; anal. calcd. for $C_{75}H_{108}B_{10}ZnN_8O_2S_7$; C, 58.05; H, 7.02; N, 7.22; found: C, 57.96; H, 6.93; N, 7.28%.

Results and discussion

Synthesis and characterization

4,5-Di(hexylthio)phthalonitrile (**1**) and 4- (2-hydroxyethylthio) phthalonitrile (**2**) were chosen as precursors and they were synthesized as reported in the literature [30,31]. Scheme 1 shows the synthetic pathway to 2,3,9,10,16,17-hexakis(hexylthio)-23-hydroxy ethylthiophthalocyanine (**3**) and [2,3,9,10,16,17-hexakis(hexylthio)-23-hydroxyethylthiophthalocyaninato]zinc(II) (**4**). A_3B type metal free phthalocyanine derivative **3** was synthesized in two steps. Preparation of the metal-free phthalocyanine begins with the lithium templated cyclotetramerization of hexylthio and hydroxyethylthio substituted phthalonitriles in a high boiling point solvent (1-pentanol) to obtain dilithium phthalocyanine [14,32]. In the second step, dilithium phthalocyanine was converted to metal-free phthalocyanine **3** by acidification with acetic acid. Column chromatography was used for the isolation of the A_3B type product with 26% yield. Metallation was achieved by refluxing **3** in 1-pentanol in the presence of zinc (II) acetate under N_2 atmosphere. The product