Journal of Organometallic Chemistry 749 (2014) 18–25

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Crown ether-substituted water soluble phthalocyanines and their aggregation, electrochemical studies

Zekeriya Bıyıklıoğlu*, Volkan Çakır, Dilek Çakır, Halit Kantekin

Department of Chemistry, Faculty of Science, Karadeniz Technical University, 61080 Trabzon, Turkey

ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form
27 July 2013
Accepted 31 July 2013

Keywords:
Phthalocyanine
Quaternization
Aggregation
Water-soluble
UV–Vis spectra
Cyclic voltammetry

ABSTRACT

The synthesis of a new metal-free, zinc (II), cobalt phthalocyanines and their water soluble quaternized derivatives **5a**, **6a** substituted with four crown ether groups are described. The aggregation behavior of these compounds was investigated in different concentrations of DMSO. The effect of solvents on absorption spectra was studied in various organic solvents. Water soluble phthalocyanines **5a** and **6a** were investigated for their aggregation behavior in DMSO, DMF, water and in various DMSO/water mixtures by comparing their UV–Vis spectra. Water soluble phthalocyanines in DMSO and in up to 50 vol.% DMSO/water are nonaggregated. But increasing amounts of water leads to higher aggregation ratios. Electrochemical properties of phthalocyanines were investigated by cyclic and square wave voltammetry. While cobalt phthalocyanine displayed metal and ring-based redox processes, the other phthalocyanines displayed only ring-based redox processes.

1. Introduction

Phthalocyanines have found a great number of important technological applications for example gas sensors [1], non-linear optical devices [2], electrochromism [3], photochromic materials [4,5], catalysis [6], liquid crystal [7], photodynamic therapy and nanotechnology [8–10]. The solubility of phthalocyanines is important for many applications. When plausible functional groups such as crown ethers, alkyl, alkoxy, alkylthio, tertiary butyl groups and amide groups bound in the peripheral benzene rings of the Pc structure, solubility of phthalocyanines can improve in protic or non-protic solvents [11–19]. Water solubility plays important role in PDT applications because the blood itself is a hydrophilic system. The water-soluble drug can be injected into the patient's blood stream [20–22]. Water-soluble phthalocyanines consist of sulfonates [23], carboxylates [24,25] and quaternized amino groups [26–28] on the peripheral and non-peripheral positions.

Phthalocyanines have a high trend to aggregate particularly in aqueous solutions, whereby commonly H-type aggregates are formed which is indicated by their broad Q-bands in the UV–Vis spectra. By aggregation, the photosensitizing skill of the phthalocyanines is decreased by self-quenching. Bulky, crown ether, *tert*-butyl groups and water solubilizing groups for example carboxylates, quaternized amino, sulfonates have been introduced in peripheral positions of metal phthalocyanines to minimize their aggregation skill [29].

The industrial application of phthalocyanines is related to their redox properties [30–36]. In order to define redox properties of phthalocyanines, generally voltammetric methods such as cyclic voltammetry, square wave voltammetry are used. Due to our interest in the synthesis of crown ether and phthalocyanines, we report the synthesis, characterization, aggregation behavior and UV–Vis spectra of water soluble metal-free and metallophthalocyanines bearing four 2-[2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl) ethoxy] groups which enabled the molecules to dissolve in a number of organic solvents and water, to minimize aggregation. A combination of these two potentially promising units [phthalocyanine and 2-[2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)ethoxy] groups] may improve their solubility in organic solvents, water and applications in PDT.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried as described by reported procedure [37] before use. 2-[2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)ethoxy]ethanol **1** [38] and 4-nitrophthalonitrile **2** [39] were prepared according to the literature procedure.

* Corresponding author. Tel.: +90 462 377 76 39; fax: +90 462 325 31 96.
E-mail address: zekeriya_61@yahoo.com (Z. Bıyıklıoğlu).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.07.079

2.2. Equipment

The IR spectra were taken on a Perkin Elmer 1600 FT-IR Spectrophotometer (400–4000 cm^{-1}) with the samples prepared as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$ and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Optical spectra in the UV–Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. The MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. Methanol, chloroform were used as solvents in mass analysis and all mass analysis were conducted in positive ion mode.

MALDI-MS of complexes were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932).

2.3. Electrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Interface 1000 potentiostat/galvanostat controlled by an external Pc and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade TBAP in extra pure DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

2.4. Synthesis

2.4.1. Synthesis of 4-{2-[2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)ethoxy]ethoxy}phthalonitrile (**3**)

2-[2-(1,4,7,10-Tetraoxa-13-azacyclopentadecan-13-yl)ethoxy] ethanol **1** (2.00 g, 6.64 mmol) was added to anhydrous DMF (15 ml) and nitrogen gas was transferred in this solution and then 4-nitrophthalonitrile **2** (1 g, 5.78 mmol) was added to reaction mixture. The mixture was stirred for 30 min at 60 °C, finely ground anhydrous K_2CO_3 (3.2 g, 2.3 mmol) was added portionwise within 2 h with efficient stirring. The reaction solution was stirred under N_2 at 60 °C for 5 days. At the end of this time, the solution was poured into ice-water (150 g) and stirred at room temperature for 2 h and aqueous phase was extracted with chloroform (3 × 50 ml). The combined extracts were dried over dry magnesium sulfate. Finally, the oily product was chromatographed on column chromatography which is placed aluminum oxide using $CHCl_3$:CH_3OH (99:1) as solvent system. Yield: 1.05 g (42%). IR (KBr tablet) ν_{max}/cm^{-1}: 3079(Ar–H), 2940–2865 (Aliph. C–H), 2230 (C≡N), 1597, 1562, 1452, 1310, 1254, 1120, 1087, 1041, 936, 838, 750, 663. ^1H NMR ($CDCl_3$), (δ: ppm): 7.59 (d, 1H, Ar–H), 7.17 (d, 1H, Ar–H), 7.09 (s, 1H, Ar–H), 4.06 (t, 2H, $-CH_2-O$), 3.76–3.68 (m, 4H, $-CH_2-O$), 3.58–3.39 (m, 16H, $-CH_2-O$), 2.60 (t, 6H, $-CH_2-N$). ^{13}C NMR ($CDCl_3$), (δ: ppm): 162.15, 135.51, 120.15, 119.78, 116.87, 115.96, 115.49, 106.72, 72.66, 70.69, 70.39, 69.97, 69.59, 68.81, 61.20, 55.84, 55.05. MS (ESI), (m/z): 434 $[M + H]^+$. $C_{22}H_{31}N_3O_6$: calcd. C 60.95, H 7.21, N 9.69%; found: C 60.77, H 7.03, N 9.94.

2.4.2. Synthesis of metal-free phthalocyanine (**4**)

A mixture of compound **3** (250 mg, 0.557 mmol) and 1.8-diazabicyclo[5.4.0]undec-7-ene (0.3 ml, 0.28 mmol) (DBU) in 2.5 ml of dry *n*-pentanol was heated and stirred at 160 °C in a glass sealed tube for 12 h under N_2. After cooling to room temperature the green crude product was precipitated with diethyl ether and then dried in vacuo. Finally, the solid product was chromatographed on column chromatography which is placed aluminum oxide using $CHCl_3$:CH_3OH (100:1) as solvent system. Green pure product obtained from eluents. Yield: 70 mg (28%). IR (KBr tablet) ν_{max}/cm^{-1}: 3292 (N–H), 3072 (Ar–H), 2919–2875 (Aliph. C–H), 1610, 1523, 1481, 1452, 1322, 1284, 1239, 1111, 1095, 1014, 946, 824, 745. ^1H NMR ($CDCl_3$), (δ: ppm): 8.38 (m, 4H, Ar–H), 7.80 (m, 4H, Ar–H), 7.21 (s, 4H, Ar–H), 4.46 (m, 8H, $-CH_2-O$), 4.14–3.87 (m, 16H, $-CH_2-O$), 3.71–3.62 (m, 64H, $-CH_2-O$), 2.94 (m, 24H, $-CH_2-N$), −4.11 (s, br, 2H, NH). UV–Vis (DMF): λ_{max}, nm (log ε): 704 (4.93), 671 (4.94), 643 (4.72), 614 (4.62), 336 (4.95). MALDI-TOF-MS m/z: 1737 $[M + H]^+$. $C_{88}H_{126}N_{12}O_{24}$: calcd. C 60.88, H 7.32, N 9.68%; found: C 60.57, H 7.05, N 9.86.

2.4.3. Synthesis of zinc(II) phthalocyanine (**5**)

Synthesized similarly to **4** from **3** by using anhydrous $Zn(CH_3COO)_2$ (42 mg, 0.23 mmol). Yield: 117 mg (56%). IR (KBr tablet) ν_{max}/cm^{-1}: 3067 (Ar–H), 2921–2859 (Aliph. C–H), 1605, 1487, 1449, 1393, 1336, 1284, 1236, 1114, 1087, 1055, 939, 832, 747. ^1H NMR ($CDCl_3$), (δ: ppm): 7.78 (m, 4H, Ar–H), 7.58 (m, 4H, Ar–H), 7.09 (s, 4H, Ar–H), 4.58 (m, 8H, $-CH_2-O$), 4.10–4.02 (m, 16H, $-CH_2-O$), 3.85–3.57 (m, 64H, $-CH_2-O$), 2.80 (m, 24H, $-CH_2-N$). UV–Vis (DMF): λ_{max}, nm (log ε): 680 (4.95), 613 (4.38), 353 (4.74). MALDI-TOF-MS m/z: 1800 $[M + H]^+$. $C_{88}H_{126}N_{12}O_{24}Zn$: calcd. C 58.74, H 6.95, N 9.34%; found: C 58.48, H 6.64, N 9.68.

2.4.4. Synthesis of cobalt(II) phthalocyanine (**6**)

Synthesized similarly to **4** from **3** by using anhydrous $CoCl_2$ (30 mg, 0.23 mmol). Yield: 94 mg (45%). IR (KBr tablet) ν_{max}/cm^{-1}: 3070 (Ar–H), 2933–2861 (Aliph. C–H), 1608, 1522, 1452, 1409, 1348, 1283, 1240, 1115, 1094, 1064, 935, 836, 751. UV–Vis (DMF): λ_{max}, nm (log ε): 668 (4.73), 610 (4.34), 324 (4.72). MALDI-TOF-MS m/z: 1793 $[M + H]^+$. $C_{88}H_{126}N_{12}O_{24}Co$: calcd. C 58.95, H 6.97, N 9.37%; found: C 58.71, H 6.51, N 9.60.

2.4.5. Synthesis of quaternized zinc(II) phthalocyanine (**5a**)

Zinc(II) phthalocyanine **5** (40 mg, 0.02 mmol) was dissolved in 3 ml of chloroform and 2.5 ml methyl iodide was added to this solution. The reaction mixture was stirred at room temperature for 4 days. The green precipitate was filtered off, washed with chloroform, acetone and diethyl ether, respectively. Finally, water-soluble quaternized phthalocyanine derivatives were dried in vacuo. Yield: 12 mg (23%). IR (KBr Tablet), ν/cm^{-1}: 3016 (Ar–H), 2922–2868 (Alif. C–H), 1606, 1522, 1452, 1407, 1338, 1284, 1238, 1116, 1092, 1062, 957, 828, 750. UV–Vis (DMF), λ_{maks}(log ε) nm: 681 (5.15), 613 (4.53), 357 (4.91). MALDI-TOF-MS m/z: 465 $[M - 4I + 1]^{+4}$. $C_{92}H_{136}I_4N_{12}O_{24}Zn$: calcd. C 46.68, H 5.79, N 7.10%; found: C 46.88, H 5.48, N 7.46.

2.4.6. Synthesis of quaternized cobalt(II) phthalocyanine (**6a**)

Synthesized similarly to **5a** from **6**. Yield: 10 mg (20%). IR (KBr Tablet), ν/cm^{-1}: 3019 (Ar–H), 2926–2868 (Alif. C–H), 1606, 1521, 1453, 1408, 1340, 1283, 1238, 1117, 1093, 1063, 928, 959, 828, 751. UV–Vis (DMF), λ_{maks}(log ε) nm: 673 (4.89), 608 (4.41), 333 (4.72). MALDI-TOF-MS m/z: 464 $[M - 4I + 1]^{+4}$. $C_{92}H_{136}I_4N_{12}O_{24}Co$: calcd. C 46.81, H 5.81, N 7.12%; found: C 47.07, H 5.41, N 7.44.

3. Results and discussion

3.1. Syntheses and characterization

The synthesis route for the new compounds are given in Figs. 1 and 2. The sequence begins with the reaction of the commercially available 4-nitrophthalonitrile **2** with 2-[2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)ethoxy]ethanol **1** to give 4-{2-[2-