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Synthesis and characterization of new metal-free and phthalocyanine nickel(II) complex containing macrocyclic moieties

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Abstract

A new metal-free and metallophthalocyanine carrying four 1,1′-biphenyl crown ether units on peripheral positions have been synthesized. Metal-free phthalocyanine was prepared by the reaction of 2,3-(4′,5′-dicyanobenzo)-11,12:13,14-di(1′,2′-biphenyl)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-triene with dry 2-(*N*,*N*-dimethylamino)ethanol under reflux. Metal derivative of phthalocyanine was also synthesized by the anhydrous $NiCl_2$ and metal-free phthalocyanine in dry quinoline under reflux. The target symmetrical phthalocyanines were separated by column chromatography and characterized by elemental analysis, ^1H, ^{13}C NMR, IR, UV–visible and FAB mass spectroscopies.

Keywords: Macrocycle; Phthalocyanine; Template effect; Metallophthalocyanine; Crown ether; Aggregation

1. Introduction

Phthalocyanine, which was first developed as a pigment, has found widespread applications in materials science. To name a few, this compound and its substituted analogues can be used as semiconductors, photoconductors, electrochromic displays, optical recording materials, and gas sensors [1]. Phthalocyanines, in particular their readily soluble peripherally substituted derivatives, possess a wide range of chemical and physical properties that make them interesting building blocks for a number of applications and materials. Apart from their important contributions in materials science, this class of functional dyes also has potential applications in the treatment of a range of cancers, infectious diseases [2], and eye and neurodegenerative diseases [3], most of which are related to the photocyctotoxic effects of these compounds.

Among these properties are the presence of highly conjugated π-electron systems, high absorptivity in the near IR region, the ability to exhibit varying conductivity upon doping and photocatalytic effects [4]. In order to make use of these properties, it is usually favorable to incorporate the pc unit with base materials, such as polymeric groups, biomaterials or inorganic surfaces [5]. For the medical applications, it is desirable that the macrocycles can be substituted with biocompatible moieties which can only not enhance the solubility of these compounds in biological media, but also promote cellular recognition and maintain the photoactivity of the phthalocyanine core by preventing its self-association [6]. To date, phthalocyanines conjugated with biological molecules are rare and only a few examples containing monosaccharides [7], amino acids [8], and anti-bodies [9] have been described. Although porphyrin nucleo base and nucleoside conjugates have been studied extensively owing to their potential applications in molecular recognition, energy and electron transfer processes, and antiviral and anticancer therapies [9], up to now few reports have explored the process of combining chiral biphenyl groups with a phthalocyanine core [10]. Chiral macrocycles, metal complexes, linear oligomers and polymer based on the 1,1′-binaphthyl structure have been synthesized for use in molecular recognition, asymmetric catalysis and as new functional materials [11]. Metal phthalocyanines

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played a key role in the dyes and pigments industry because of their tinetorial power, brilliance and beauty of shades. They have an outstanding stability to light, heat, acids and alkalis. The class of compounds was insoluble in water and most of the organic solvents and was extensively used in the manufacturing of printing inks, paints, coatings and plastics [12].

We have previously described the synthesis of metal-free and metal phthalocyanines which contain four 20-membered diazatetraoxa macrocycles each attached to a 15-crown-5 unit [13] and macrobicyclic moieties [14]. In the present paper, we have discussed the synthesis, characterization and structural investigation of these novel symmetrical phthalocyanine and its nickel(II) derivative.

2. Experimental

The IR spectra were recorded on a Perkin Elmer 1600 FTIR Spectrophotometer, using potassium bromide pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in DMSO-d_6, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. Elemental analysis and metal contents of these compounds were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. UV–visible absorption spectra were measured by a Unicam UV–visible spectrometer. Melting points were measured on an Electrothermal apparatus. Commercially available pure solvents were dried and purified by conventional procedure [15].

*2.1. Synthesis of 2,3-(4′,5′-dibromobenzo)-11,12:13,14-di(1′,2′-phenyl)-1,4,7,10,15,18-hexaoxacycloeicosan-2,11,13-triene (**3**)*

2,2′-Dihydrohxy-1,1′-biphenyl (**1**) (1.04 g, 5.58 mmol) was added dropwise to a mixture of 1,2-bis[2′-(2″-(*p*-toluenesulfonyloxy)ethoxy)ethoxy]-4,5-dibromobenzene (**2**) (4.20 g, 5.58 mmol) and NaOH (0.27 g, 6.68 mmol) in butanol (40 ml) under nitrogen atmosphere at reflux temperature for 30 min. After the addition, pale white crystals were formed in the flask for 2 h. The reaction mixture was refluxed under nitrogen atmosphere for 40 h. The end of the reaction was determined by thin-layer chromatography [ethylacetate–petroleum ether (60–90) (3:2)]. After cooling to room temperature, the solution was evaporated to dryness under reduced pressure. Water (10 ml) was added to this residue and extracted with methylene chloride. The combined organic layers were washed with water, dried over anhydrous magnesium sulphate and concentrated to about 2 ml under reduced pressure. The residue was purified by silica gel chromatography with chloroform as the eluent. The product was obtained as yellow oil (2.28 g, 68.7%). IR: ν_{max}/cm^{-1} 3080 (Ar-H), 2924 (C-H), 1582, 1484, 1201, 1129, 939, 857, 755. ^{1}H NMR ($CDCl_3$): δ 3.65 (m, 8H, OCH_2), 4.07 (t, 4H, $ArOCH_2$), 4.21 (t, 4H, $ArOCH_2$), 7.04 (m, 4H, Ar-H), 7.31 (m, H, Ar-H), 7.47 (s, 2H, Ar-H). FAB-MS: *m/z* (%) 594 $[M]^+$. Anal. calcd. for $C_{26}H_{26}O_6Br_2$ (594): C, 52.52; H, 4.38. Found: C, 52.84; H, 4.27.

*2.2. Synthesis of 2,3-(4′,5′-dicyanobenzo)-11,12:13,14-di(1′,2′-phenyl)-1,4,7,10,15,18-hexaoxacycloeicosan-2,11,13-trien (**4**)*

A mixture of (**3**) (2.24 g, 3.77 mmol) and CuCN (0.99 g, 11.31 mmol) in dry DMF (20 ml) in a Schlenk tube under nitrogen atmosphere was gently heated to reflux temperature. Then the reaction mixture was refluxed under nitrogen for 44 h. At the end of this period, the mixture was cooled to room temperature and then poured into aqueous ammonia. The mixture was stirred at room temperature for 6 h. Then the reaction mixture was extracted with methylene chloride. The combined organic layers were washed with water, dried over anhydrous sodium sulphate and then evaporated to about 5 ml. The yellow oil residue was purified by silica gel chromatography with 3:1, and 2:1 (v/v) ethylacetate–petroleum ether solvent systems. The combined same eluent fractions were concentrated to dryness under reduced pressure. Ethanol 10 ml was added to this section and then stirred at room temperature for 8 h. At the end of the time, the precipitation occurred. The resulting green precipitate was filtered off, washed with cold ethanol and diethyl ether and then dried in vacuo. The solid product was recrystallized from ethanol and chloroform (1:1) to yield green solid (1.32 g, 72.13%), mp. 196–198 °C. IR: ν_{max}/cm^{-1} 3072 (Ar-H), 2925 (C-H), 2228 ($C{\equiv}N$), 1591, 1484, 1441, 1271, 1219, 1129, 1056. ^{1}H NMR (DMSO-d_6): δ 3.66 (m, 8H, OCH_2), 4.11 (m, 8H, Ar-OCH_2), 7.13 (m, 4H, Ar-H), 7.32 (m, 4H, Ar-H), 7.45 (s, 2H, Ar-H). ^{13}C NMR (DMSO-d_6): δ 155.89, 154.55, 131.45, 128.46, 127.50, 125.32, 120.26, 118.50, 115.50, 112.36, 72.39–69.47. FAB-MS: *m/z* (%) 487 $[M+1]^+$. Anal. calcd. for $C_{28}H_{26}O_6N_2$ (486): C, 69.14; H, 4.35; N, 5.76. Found: C, 69.38; H, 5.57; N, 5.49.

*2.3. Synthesis of 2,3-(5′,8′-dihydro-5′,8′-diiminobenzo)-11,12:13,14-di(1′,2′-phenyl)-1,4,7,10,15,18-hexaoxacycloeicosan-2,11,13-trienisoiminoindolenine (**5**)*

Sodium methoxide (9.29 mg, 0.172 mmol) was added to a solution of (**4**) (0.42 g, 0.86 mmol) in dry methanol (25 ml) under nitrogen atmosphere. Anhydrous ammonia was bubbled through the mixture at reflux temperature for 6 h. At the end of the period, the reaction mixture was cooled to room temperature. The ammonia inlet was stopped and the volume of the solution reduced to 10 ml under reduced pressure. Then, methanol/acetone 1:1 (v/v) was added to this solution. The product was obtained as a pale green solid (0.26 g, 60.5%), mp. 152–153 °C. IR: ν_{max}/cm^{-1} 3414 (N-H), 3068 (Ar-H), 2918–2849 (C-H), 1637 (C=N), 1617, 1597, 1483, 1442, 1281, 1212, 1126, 1058. ^{1}H NMR (DMSO-d_6): δ 3.56 (m, 8H, OCH_2), 4.22 (m, 8H, $ArOCH_2$), 7.10 (m, 4H, Ar-H), 7.28 (m, 4H, Ar-H), 7.34 (s, 2H, Ar-H), 8.65 (br, 3H, NH). FAB-MS: *m/z* (%) 504 $[M+1]^+$. Anal. calcd. for $C_{28}H_{29}N_3O_6$ (503): C, 66.8; H, 5.77; N, 8.34. Found: C, 66.52; H, 5.95; N, 8.13.