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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, ^{1}H, ^{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. ^1H 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. ^1H 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. ^1H 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. ^1H 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.

*2.4. Tetrakis[11,12:13,14-di(1′,2′-phenyl)-1,4,7,10,15,18hexaoxacycloeicosa-2,11,13-trieno]phthalocyanine (**6**)*

A mixture of dicyano compound (**4**) (0.83 g, 1.71 mmol) and (*N*,*N*-dimethylamino) ethanol (3 ml) was placed in a Schlenk tube under nitrogen, gently heated, and subsequently heated at 125 °C for 23 h. After cooling to room temperature, the solvent was evaporated to dryness under reduced pressure. The pale green solid product was purified by column chromatography on silica gel with ethanol:chloroform (3:7, volume ratio) as the eluent. The solvent was concentrated under reduced pressure about 5 ml and then cooled to −18 °C. A dark green solid product was obtained which was filtered off, washed with cold ethanol and diethyl ether and dried in vacuo. The product was recrystallized from ethanol to yield the dark green solid (0.2 g, 24.1%), mp. 136−137 °C. IR: ν_{max}/cm^{-1} 3380 (N-H), 3068 (Ar-H), 2918−2867 (C-H), 1618 (C=N), 1603 (N-H), 1594, 1493, 1442, 1305, 1217, 1127, 1061. ^{1}H NMR (DMSO-d_6): δ 3.61 (m, 32H, OCH$_2$), 4.04 (m, 32H, ArOCH$_2$), 6.99 (m, 16H, Ar-H), 7.12 (m, 16H, Ar-H), 7.28 (m, 8H, Ar-H). ^{13}C NMR (DMSO-d_6): δ 156.91, 145.19, 144.87, 132.42, 131.52, 130.25, 128.56, 128.03, 119.13, 115.95. FAB-MS: *m*/*z* (%) 1947 $[M+1]^+$. UV−visible (chloroform) λ_{max}/nm (log[dm^3 mol^{-1} cm^{-1}]) 681.0 (3.94), 641 (3.79), 629 (3.65), 404 (3.65), 343 (4.78), 282.0 (5.17), 244 (5.27). Anal. calcd. for $C_{112}H_{106}O_{24}N_8$ (1946): C, 69.06; H, 4.45; N, 5.56. Found: C, 69.35; H, 5.29; N, 5.98.

2.5. Tetrakis[11,12:13,14-di(1′,2′-phenyl)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-trieno]-phthalocyaninato nickel(II) (7)

A mixture of anhydrous NiCl$_2$ (0.0072 g, 0.054 mmol), dry quinoline 1.5 ml and (**6**) (0.07, 0.036 mmol) was placed in a Schlenk tube under nitrogen and heated at 183 °C for 6 h. The reaction mixture was cooled to room temperature, diluted with methanol, diethyl ether (2:1) and filtered. The dark green solid was then washed with water, methanol, then dried in vacuo. The product was purified by column chromatography on silica gel with chloroform to give the product as a dark green solid (0.02 g, 28.57%), 161−162 °C. IR: ν_{max}/cm^{-1} 3049 (Ar-H), 2923−2868 (C-H), 1629 (C=N), 1596, 1477, 1440, 1385, 1339, 1279, 1212, 1157, 1107. ^{1}H NMR (DMSO-d_6): δ 3.56 (m, 32H, OCH$_2$), 4.20 (m, 32H, ArOCH$_2$), 7.39 (m, 16H, Ar-H), 7.53 (m, 32H, Ar-H), 7.76 (m, 8H, Ar-H). FAB-MS: *m*/*z* (%) 2021 $[M+H_2O]^+$. UV−visible (chloroform) λ_{max}/nm (log[dm^3 mol^{-1} cm^{-1}]) 671 (4.03), 640 (3.81), 608 (3.85), 398 (4.73), 311 (4.88), 275 (5.19), 248 (5.27). Anal. calcd. for $C_{112}H_{104}O_{24}N_8Ni$ (2003): C, 67.11; H, 5.19; N, 5.59; Ni, 2.93. Found: C, 67.39; H, 5.41; N, 5.83; Ni, 2.71.

3. Results and discussion

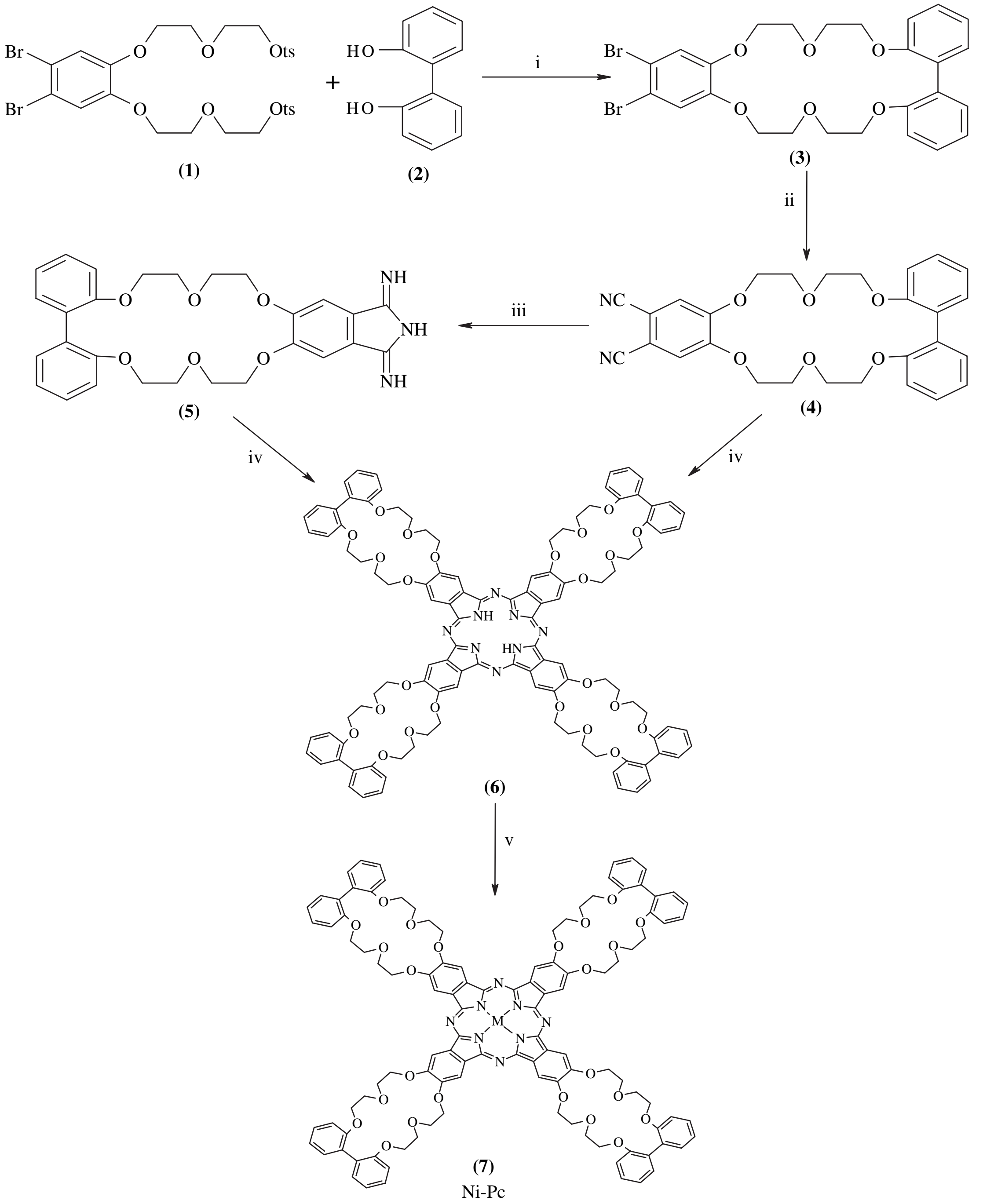
The compound (**3**) was a synthesized reaction of 2,2′-dihydroxy-1,1′-biphenyl (**1**) with 1,2-bis[2′-(2″-(*p*-toluenesulfonyloxy)ethoxy]-4,5-dibromobenzene (**2**) [16] in the presence of NaOH as a template agent and in *n*-butanol at reflux temperature under argon atmosphere. Dibromo compound (**3**) was obtained in 68.7% yield after being purified by column chromatography on silica gel using chloroform as eluent. Formation of the macrocycle (**3**) was verified by the $[M]^+$ peak at $m/z = 594$ $[M]^+$ which was obtained by fast atom bombardment mass spectroscopy.

4,5′-Dicyano substituted macrocycle which synthesized by treating the dibromo compound (**3**) with three equivalents of CuCN according to Rosenmund von Braun reaction [17] in a moderately high-boiling solvent such as DMF at 145 °C under argon atmosphere. After this reaction, the desired compound (**4**) was purified by column chromatography on silica gel using ethyl acetate:petroleum ether (3:1) and (2:1) as eluent. Then the purification of compound (**4**) was completed by crystallization using the mixture of ethanol:chloroform (1:1) in 72.13% yield. In the IR spectrum of (**4**), the intense absorption band at 2228 cm^{-1} corresponds to the C≡N stretching vibrations. The ^{1}H NMR spectrum of (**4**) closely resembles that of the precursor compound (**3**) as expected. The ^{13}C NMR spectrum of (**4**) shows the presence of nitrile carbon atoms at $\delta = 115.50$ ppm which indicates the completion of conversion of (**3**) to (**4**). FAB mass spectrum and elemental analysis also confirm the formation of (**4**) $m/z = 487$ $[M+1]^+$.

The dicyano substituted macrocycle (**4**) was reacted with anhydrous ammonia in the presence of sodium methoxide in refluxing dry methanol under argon atmosphere over a period of 6 h [18] to give the corresponding *iso*-iminoindoline derivative (**5**). This compound was obtained as a pale green solid in 60.5% yield. The disappearance of the C≡N and the appearance of N−H and C=NH stretching vibrations in the IR spectrum of (**5**) suggest the formation of *iso*-iminoindoline derivative of macrocycle. There is a broad signal at $\delta = 8.65$ ppm due to the imino groups in the ^{1}H NMR spectrum of this compound. This signal can be attributed to the occurring of the proposed structure. The molecular ion peak observed at $m/z = 504$ $[M+1]^+$ as expected also confirms the proposed formulation.

Condensation of four molecules of the dinitrile derivative of macrocycle (**4**) into the metal-free phthalocyanine (**6**) was carried out at standard Schlenk tube in 2-(dimethylamino)ethanol at reflux temperature for 23 h under argon atmosphere and afforded the target compound in 24.1% yield as a crystalline dark green solid after purification on chromatographic separation on silica gel [ethanol:chloroform (3:7)]. The IR spectrum of (**6**) is closely similar to that of precursor compound (**5**) and contains characteristic vibrations of aromatic and aliphatic groups. The resonance came out at 3380 and 1603 cm^{-1} belonging to the significant N−H resonances. In the ^{1}H NMR spectrum of (**6**), the signals concerning the internal NH protons could not be observed. The signals related to aromatic and aliphatic protons of the macrocycles and phthalocyanine skeleton gave the significant characteristic of the proposed structure. This spectrum closely resembles that of the precursor compound (**5**) as expected. A distinct difference encountered in the ^{1}H NMR spectra of (**5**) and (**6**) when compared with previously obtained macrocycle substituted derivatives are the sharp signals, which indicate a lower tendency to aggregate even at the concentration used for proton NMR measurements [19]. A close investigation of the fast atom bombardment (FAB) mass spectrum of metal-free phthalocyanine at $m/z = 1947$ $[M + 1]^+$ is in accord with the proposed formulation.

The reaction of (**6**) in a high-boiling aprotic solvent such as quinoline with anhydrous $NiCl_2$ gave the metallophthalocyanine. A mixture of (**6**) and $NiCl_2$ in dry quinoline was heated and stirred at 183 °C under argon atmosphere in a sealed glass tube for 6 h. The product (**7**) was purified by column chromatography on silica gel by using chloroform as an eluent in 28.57% yield. The elemental analysis and mass spectra results agreed with the proposed structure. ^1H NMR spectrum of **7** is rather broad owing probably to the aggregation of phthalocyanine which is frequently encountered at the concentration used for proton NMR. The signals for the aliphatic, biphenyl and aromatic protons of the phthalocyanine core of this compound appear as expected at $\delta = 4.26$,



Scheme 1. Reagents and conditions: (i) *n*-butanol, NaOH, under nitrogen atmosphere at reflux temperature; (ii) dry DMF, CuCN, under nitrogen atmosphere; (iii) CH_3ONa, dry methanol, under nitrogen atmosphere, anhydrous ammonia; (iv) (*N*,*N*-dimethylamino)ethanol, under nitrogen atmosphere, at reflux temperature; (v) dry quinoline, anhydrous $NiCl_2$ at reflux temperature.

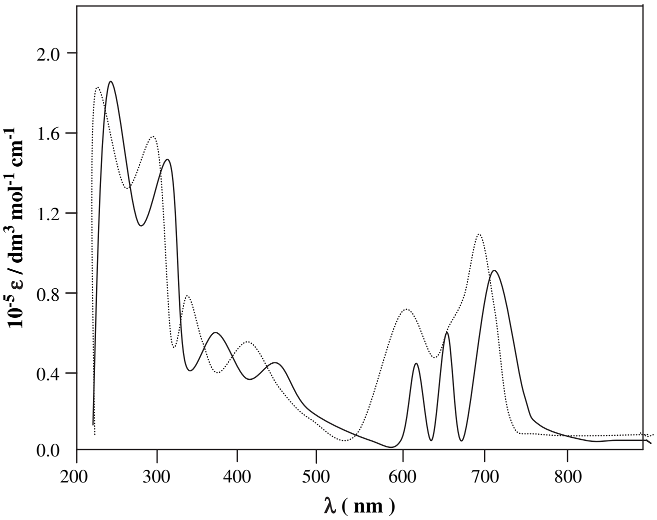


Fig. 1. UV–visible spectra of **6** (solid line) and **7** (dotted line) in pyridine.

7.79–7.53 and 7.10 ppm, respectively. The similarities in the IR spectra of the metal-free phthalocyanine and its nickel derivative were seen except the disappearance of N–H stretching vibrations concerning phthalocyanine core as expected. The mass spectrum of (**7**) obtained by the FAB technique is also in accord with expected value $(m/z) = 2021\ [M + H_2O]^+$. The reagents and conditions related to new compounds are illustrated in Scheme 1.

The electronic spectra of phthalocyanines (**6**) and (**7**) show the same typical B and Q bands of symmetrical 20-membered macrocycles substituted Pcs. The energy level location corresponding to those bands is illustrated in Fig. 1. In the UV–visible spectrum of metal-free phthalocyanine in chloroform, the characteristic split Q band was observed with absorptions at 681 and 641 nm which can be attributed to a_{1u} e_g transition [20]. The D_{2h} symmetry of the metal-free phthalocyanine (**6**) is verified by these two absorptions in the visible region [21]. However, the Q band of nickel(II) derivative of slightly shifted to the blue with respect to the parent metal-free compound [22]. The position of Q band of metallophthalocyanine (7) which is centered at around 670 nm without splitting changes due to the central nickel(II). This compound shows weak absorptions in the window region at 608 and 398 nm. These absorptions can be attributed to the intermolecular aggregation [23].

Acknowledgements

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