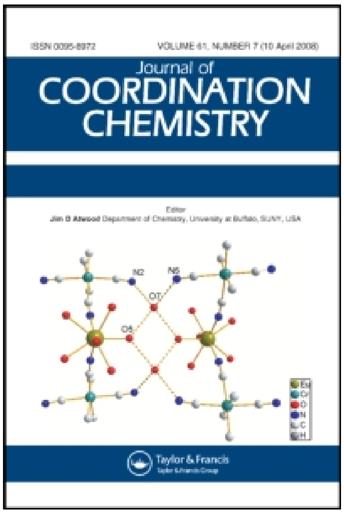

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The synthesis and characterization of new metal-free and metallo phthalocyanines substituted with four dithiatetraoxa macrocyclic moieties

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First published on: 18 June 2007

To cite this Article Kantekın, Halıt , Rakap, Murat , Misir, Mıraç Nedım , Gök, Halıl Zekı and Acar, İrfan(2007) 'The synthesis and characterization of new metal-free and metallo phthalocyanines substituted with four dithiatetraoxa macrocyclic moieties', Journal of Coordination Chemistry, 60: 18, 1965 — 1972, First published on: 18 June 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701217412

URL: http://dx.doi.org/10.1080/00958970701217412

Journal of Coordination Chemistry
Vol. 60, No. 18, 15 September 2007, 1965–1972

Taylor & Francis
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The synthesis and characterization of new metal-free and metallo phthalocyanines substituted with four dithiatetraoxa macrocyclic moieties

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(*Received 7 March 2006; revised 13 July 2006; in final form 18 July 2006*)

New metal-free phthalocyanine (**7**) fused symmetrically in peripheral positions with four dithiatetraoxa macrocycles, has been synthesized by cyclotetramerization of the isoindolinediimine derivative of macrocyclic **6**. Metallophthalocyanine (**8**) was synthesized by reaction of phthalonitrile derivative (**5**) with anhydrous nickel(II) chloride. The new compounds were characterized by elemental analysis, ^{1}H and ^{13}C-NMR, IR UV–Vis and mass spectroscopies.

Keywords: Isoindolinediimine, Nickel(II) phthalocyanine; Mixed-donor macrocycle; Template effect

1. Introduction

Strong interactions between molecules with extended π-electron systems contribute to the exceptional stability of various supramolecular assemblies. Due to their particular properties, they may be referred to as *aromatic* or $\pi \rightarrow \pi$ interactions [1, 2]. They have been important industrial dyes and pigments since their synthesis at the beginning of last century [3]. Many applications are expected for these molecular materials which have high thermal and chemical stability, for instance as oxidation catalysts [4], solar cell functional materials [5], gas sensors [6], nonlinear optical limiting devices [7], photodynamic therapy agents [8], antimycotic material [9], and corrosion inhibitors [10].

Owing to their architectural and functional plasticity, macropolycyclic systems are especially attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic substrates [11]. In the past decade, the preparation of various peripherally substituted derivatives has generated interesting physical and chemical properties for many different applications in materials science. Since crown ethers were first recognized by Pedersen as having selective metal-ion binding properties [12, 13],

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701217412

various crown ethers have been prepared and their complexation behavior studied extensively.

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 [14] and macrobicyclic moieties [15]. In this study, we report for the first time a generalizable procedure for the preparation and characterization of a macrocyclic phthalonitrile (**5**) which contains S_2O_4 mixed donors and we discuss the synthesis, characterization and structural investigation of the symmetrical metal-free phthalocyanine (**7**) and Ni(II) phthalocyanine (**8**).

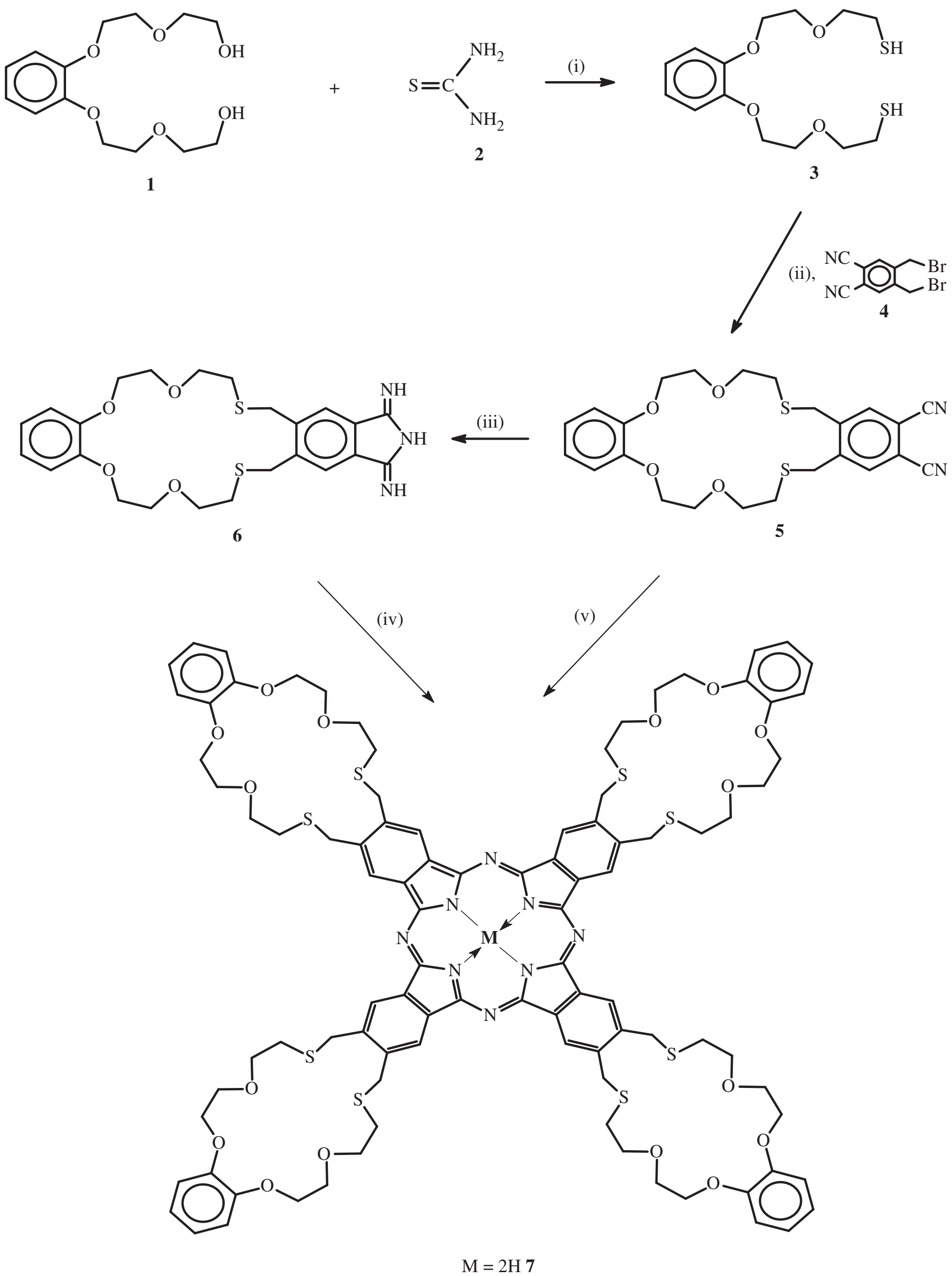
2. Results and discussion

Preparations of the target metal-free **7** and nickel(II) metallophthalocyanine (**8**) are shown in scheme 1. The structures were identified by a combination of elemental analysis, ^{1}H and ^{13}C-NMR, IR, UV–Vis and mass spectral data. We prepared **1** by using the known procedure [16]. This compound was converted to dithiol compound **3** in fuming HCl.

Similarity of the IR spectra of these compounds is expected for the vibrations of the OH and SH containing methylene groups. In the ^{1}H and ^{13}C-NMR spectra of **3**, the characteristic signals of the aromatic protons and carbons are very similar to those of **1**. In the ^{1}H NMR spectrum of **1**, the signal belonging to OH protons at $\delta = 2.58$ ppm in the precursor compound **1** disappears after the formation of compound **3**. The singlet at $\delta = 3.80$ ppm and triplets at $\delta = 3.89$ and 2.95 ppm correspond to H_2C–SH H_2C–O, and H_2C–S groups, respectively. The SH protons are also identified easily by deuterium exchange. The aromatic protons are at $\delta = 7.58$ and 7.45 ppm. Proton decoupled ^{13}C-NMR spectrum of this compound shows signals for the new CH_2–SH, CH_2–O and aromatic carbon atoms at $\delta = 32.26$, 70.28-68.62, 148.55, 142.52, 132.49 ppm, respectively, clearly suggesting compound formation has occurred. Compound **3** displays the expected molecular ion peak at $m/z = 319$ $[M+1]^+$ in its mass spectrum, as found using the (EI) technique. The mass spectrum (EI) and elemental analysis data of this compound also support the proposed structure.

Compound **5** was prepared by reaction of **3** with 1,2-*bis*(bromomethyl)-4,5-dicyanobenzene **4** [17]. IR spectrum of **5** was easily verified with the disappearance of SH at 2566 and presence of C≡N stretching vibrations at 2233 cm^{-1}. In the ^{1}H-NMR spectrum of **5**, the singlet belonging to aromatic protons neighboring C≡N appear at $\delta = 7.88$ ppm. The other aromatic proton signals appear at $\delta = 7.64$ and 7.52 ppm. The protons belonging to CH_2–S–CH_2, and S–CH_2 groups appear at $\delta = 3.09$ and 2.99 ppm, respectively. The proton decoupled ^{13}C-NMR spectrum of this compound has signals for the cyano groups and aromatic carbon atoms at $\delta = 116.82$ and 149.58 ppm, respectively. Compound **5** displays the expected molecular ion peak at $m/z = 471$ $[M+1]^+$ in its mass spectrum (EI technique).

The dicyano compound containing the macrocyclic moiety **5** reacted with anhydrous ammonia in the presence of sodium methoxide in refluxing dry methanol [18–20] to give the corresponding isoiminoindoline derivative **6** as the first precursor in 43.12% yield. The C≡N stretching vibrations of **5** disappeared after conversion of **5** to isoiminoindolinediimine **6** which shows absorptions at 3298, 3182 and 1642 cm^{-1} for the N–H and C=N groups, respectively. The ^{1}H-NMR spectra of **5** and **6** are quite



M = 2H **7**
M = Ni **8**

Scheme 1. (i) Fuming HCl, reflux; (ii) dry THF, NaH, reflux, N_2; (iii) dry methanol, NH_3(g), CH_3ONa; (iv) (*N*,*N*-dimethylamino)ethanol, 125°C, N_2; (v) anhydrous $NiCl_2$, dry quinoline, 185°C, N_2.

similar, but the spectrum of **6** indicates the presence of deuterium-exchangeable N–H imino groups observed as a broad signal at $\delta = 8.52$ ppm. When the proton-decoupled ^{13}C-NMR spectra of **6** were compared with that of **5** the characteristic feature is the disappearance of nitrile carbon chemical shifts at $\delta = 116.82$ ppm. The mass spectrum of **6** showed a peak at $m/z = 487$ [M + 1], which supports the structure of the proposed structure.

The condensation of four molecules of the isoiminoindoline derivative **6** into the metal-free phthalocyanine **7** was carried out in a standard Schlenk tube in 2-(dimethylamino)ethanol at reflux for 30 h under argon to afford the target compound in 35.5% yield. Metal-free phthalocyanine was obtained as a crystalline dark green solid after purification by chromatographic separation on silica gel [ethanol : chloroform (2 : 8)]. The IR spectrum of **7** is similar to that of **6** and contains characteristic vibrations of aromatic and aliphatic groups. The absorptions at 3375 and 1604 cm^{-1} belong to N–H resonances. In the ^{1}H NMR spectrum of **7**, signals from the internal NH protons could not be observed. The signals of aromatic and aliphatic protons of the macrocycles and phthalocyanine skeleton gave the significant characteristic of the proposed structure, closely resembling that of the precursor **6** as expected. A distinct difference encountered in the ^{1}H NMR spectrum of **7** when compared with the ^{1}H NMR spectrum of **8** is the sharp signals, which indicates a lower tendency to aggregate even at high concentration used for proton NMR measurements [21]. A close investigation of the fast atom bombardment (FAB) mass spectrum of metal-free phthalocyanine at $m/z = 1881$ $[M + 1]^+$ is in accord with the proposed formulation. With the desired anhydrous metal salts in hand, it became possible to convert the metal-free phthalocyanine into metallo derivates. For this purpose, Ni(II) chloride has been used in a high boiling point solvent (e.g quinoline) to prepare the nickel(II) phthalocyanine in 26.83% yield. In the IR spectrum of this compound, the stretching vibrations from C=N, Ar–OCH$_2$ and OCH$_2$–CH$_2$ groups appear at 1645 (C=N), 1249–1213 (Ar–OCH$_2$), 1129–1048 (CH$_2$–OCH$_2$) cm^{-1}. The structure proposed for this new compound is consistent with the data obtained from elemental analysis, IR, UV–Vis, ^{1}H NMR spectra and mass spectra. The nickel(II) phthalocyanine content is in accord with its calculated analysis.

The best indications for phthalocyanine systems are given by their UV–Vis spectra in solution (figure 1). The electronic spectra of phthalocyanines (**7**), and (**8**) show the typical B and Q bands of symmetrical 20-membered dithiatetraoxa macrocycle substituted Pc. The energy level location corresponding to those bands is illustrated in figure 1. In the UV–Vis spectrum of metal-free phthalocyanine in chloroform, the characteristic split Q band was observed at 660–680 nm. These intense Q bands indicate monomeric species with D_{2h} symmetry (two intense absorptions around 700 nm) [22]. The lower absorption than the typical split Q band at 625 nm is due to dimeric association for higher aggregates [23]. Such split Q band absorptions are due to the $\pi \Rightarrow \pi^*$ transition from the HOMO to the LUMO of the phthalocyanine ring related to fully conjugated 18 π electron system. The presence of strong absorption bands in **7** in the UV region at $\lambda_{\max}$ 400 and 300 nm shows superimposed bands of the phthalocyanine due to the existence of Soret band of *Pc* which have been ascribed to the deeper $\pi \Rightarrow \pi^*$ levels of the LUMO transition [24]. However, in the Ni(II) derivative the average Q-bands are slightly shifted to the blue with respect to the metal-free compound [25]. The Q band position of metallo-phthalocyanine (**7**) changed due to the central Ni(II) without splitting and centered at around 670 nm. The single Q band in the

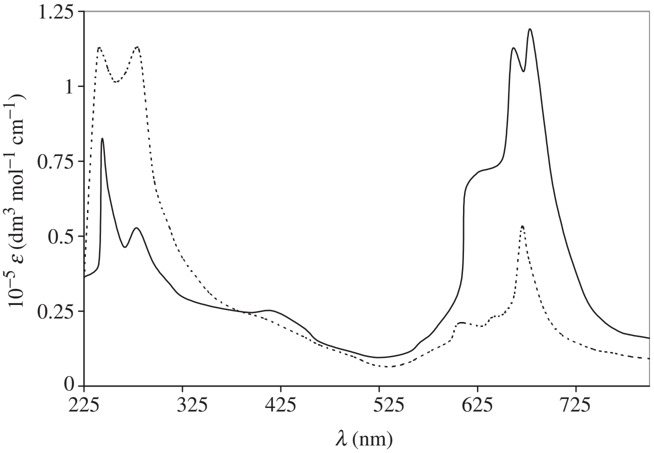


Figure 1. UV–Vis spectra of **7** (—) and **8** (····) in chloroform.

metallo derivative and its splitted form in its metal-free counterparts is characteristic [26]. Observed peaks as mentioned above indicate that the symmetry of the molecule has changed. This result is typical of metal complexes of substituted and unsubstituted *Pc* with D_{4h} symmetry [27].

3. Experimental

IR spectra were recorded on a Perkin–Elmer 1600 FTIR Spectrophotometer, using KBr pellets or NaCl disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts are reported (δ) relative to Me_4Si as the internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS MS spectrometer. Elemental analysis and metal content of these compounds were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. Electronic spectra were recorded on a Unicam UV–Vis spectrophotometer. Melting points were measured on an electrothermal apparatus and were uncorrected. Commercially available solvents were dried and purified by conventional procedures [28].

3.1. *1,2-bis[2′-(2″-Mercapto)ethoxy]benzene (3)*

The mixture of 1,2-bis[2′-(2″-hydroxy)ethoxy]benzene (**1**) (5.72 g, 20 mmol), thiourea (**2**) (3.04 g, 40 mmol) and 5.26 mL of fuming HCl was refluxed for 16 h in a flask. The mixture was cooled to room temperature and KOH (6.72 g, 120 mmol) in 20 mL of water was added dropwise. After that, the mixture was refluxed for 3 h and two phases formed. This lower phase was removed and the upper phase acidified with dilute HCl and extracted with ether. The ether solution was combined with the oily lower phase and dried over sodium sulfate. The mixture was filtered and the solution was evaporated under vacuum. The product was isolated by two successive column chromatographic separations [silica gel; chloroform : petroleum ether (2 : 1)]. Pale yellow oily product was obtained. Yield: 2.64 g (41.5%). ^{1}H-NMR ($CDCl_3$): δ 2.95 (t, 4H, SCH_2), 3.80 (s, 2H, SH), 3.89 (t, 12H, CH_2–O), 7.45 (d, 2H, Ar–H), 7.58 (t, 2H, Ar–H). ^{13}C-NMR ($CDCl_3$): δ 32.18, 36.26, 68.62–70.28, 132.49, 142.52, 148.55. IR (KBr pellets, cm^{-1}): 3087 (Ar–H), 2929–2872 (C–H), 2566 (S–H), 1594–1503 (C=C), 1255 (Ar–OCH_2) 1123-1052 CH_2–OCH_2. Anal. Calcd for $C_{14}H_{22}O_4S_2$(%): C, 52.83; H, 6.92. Found: C, 52.35; H, 6.85. MS (EI): $m/z = 319$ $[M + 1]^+$.

3.2. *6,7,9,10,12,17,19,20,22,23-Decahydrodibenzo[e,o][1,4,7,10,13,18]tetra oxadithia–cycloicosine-14,15-dicabonitrile (5)*

1,2-bis[2′-(2″-Mercapto)ethoxy]benzene (**3**) (1.84 g, 5.79 mmol) was dissolved with 30 mL of dry THF into a 500 mL two-neck flask. NaH (0.1409 g, 5.8 mmol) was added to the solution; the system was purged and refluxed for 4 h. The reaction mixture was cooled to room temperature and solid 1,2-*bis*(bromomethyl)-4,5-dicyanobenzene (**4**) (0.91 g, 2.9 mmol) was added to the mixture. The reaction system was purged again and stirred for 4 h. at room temperature. The reaction mixture was filtered giving a brown solution, which was evaporated to dryness. Pale brown oily crude product was dissolved in chloroform and extracted with water. Combined chloroform phases were dried over $MgSO_4$. The mixture was filtered and the solution evaporated under vacuum. Yield: 1.77 g (65.19%). ^{1}H-NMR ($CDCl_3$): δ 2.99 (t, 4H, CH_2CH_2S), 3.09 (s, 4H, SCH_2), 4.13 (t, 8H, CH_2–O), 4.19 (t, 4H, $ArOCH_2$), 7.52 (t, 2H, Ar–H), 7.64 (d, 2H, Ar–H), 7.88 (s, 2H, Ar–H). ^{13}C-NMR ($CDCl_3$): δ 34.13, 36.26, 68.60-70.55, 116.81, 134.45, 141.32, 149.58. IR (KBr pellets, cm^{-1}): 3083 (Ar–H), 2926-2868 (C–H), 2233 (C≡N), 1591-1500 (C=C), 1254 (Ar–OCH_2) 1124–1048 CH_2–OCH_2. Anal. Calcd for $C_{24}H_{26}O_4S_2N_2$(%): C, 61.27; H, 5.53; N, 5.96. Found: C, 61.10; H, 5.48; N, 5.88. MS (EI): $m/z = 471$ $[M + 1]^+$.

3.3. *5,7,8,10,11,18,19,21,22,24-decahydro-1H-[1,4,15,18,7,12]benzotetraoxadithia-cycloicosino [9,10-f]isoindole-1,3(2H)-diimine (6)*

Sodium methoxide (14.04 mg, 0.26 mmol) was added to a solution of **5** (0.6 g, 1.28 mmol) in dry methanol (30 mL) under nitrogen. Anhydrous ammonia was bubbled through the mixture at reflux temperature for 7 h and 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 : 2 (v/v) was added to this solution. The product was obtained as a pale green solid (0.27 g, 43.12.%); m.p.145–147°C. ^{1}H-NMR (DMSO-d_6): δ 3.01 (t, 4H, CH_2CH_2S), 3.09 (s, 4H, SCH_2), 4.08 (t, 8H, OCH_2) 4.15 (t, 4H, $ArOCH_2$), 7.48 (t, 2H, Ar–H), 7.59 (d, 2H, Ar–H), 7.66 (s, 2H, Ar–H), 8.52 (br, 3H, NH). IR (KBr pellets, cm^{-1}): 3374 (N–H), 3076 (Ar–H), 2928-2845 (C–H), 1642 (C=N), 1610 (NH), 1594–1480 (C=C), 1242–1214 (Ar–OCH_2), 1126-1058 (CH_2–OCH_2). Anal. Calcd for $C_{24}H_{29}O_4S_2N_3$(%): C, 59.14; H, 5.95; N,8.62. Found: C, 58.98; H, 5.82; N, 8.76. MS (FAB): $m/z = 487$ $[M + 1]^+$.

3.4. *Metal-free phthalocyanine (7)*

A mixture of **6** (0.21 g, 0.43 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 30 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 methanol : chloroform (2 : 5). The solvent was concentrated under reduced pressure to about 3 mL and then cooled to −15°C. A dark green solid 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 dark green solid (0.07, 35.5%); m.p. 176–178°C. ^{1}H–NMR ($CDCl_3$): δ 2.97 (t, 16H, CH_2CH_2S), 3.09 (s, 16H, CH_2S), 4.08 (t, 32H, OCH_2) 4.15 (t, 16H, $ArOCH_2$), 7.58–7.51 (m, 8H, Ar–H), 7.66 (d, 8H,Ar–H), 7.69 (s, 8H, Ar–H). ^{13}C–NMR ($CDCl_3$): δ 32.16, 35.72, 69.14–70.16, 112.95, 117.04, 127.44, 128.04, 130.15, 142.66, 147.22, 152.18. IR (KBr pellets, cm^{-1}): 3298 (N–H), 3087 (Ar–H), 2925–2876 (C–H), 1635 (C=N), 1611 (NH), 1590–1484 (C=C), 1245–1210 (Ar–OCH_2), 1128–1045 (CH_2–OCH_2). Anal. Calcd for $C_{96}H_{104}O_{16}S_8N_8$ (%): C, 61.28; H, 5.53; N, 5.95. Found: C, 60.98; H, 5.49; N, 5.82. UV–Vis (chloroform): λ (nm): [$(10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1})$]: 680 (4.07), 660 (4.04), 625 (3.87), 418 (3.39), 279 (4.72), 243 (4.92). MS (FAB): $m/z = 1881$ $[M+1]^+$.

3.5. *Nickel(II) phthalocyanine (8)*

A mixture of anhydrous $NiCl_2$ (0.026 g, 0.212 mmol), dry quinoline 4.0 mL and (**5**) (0.4g, 0.85 mmol) was placed in a Schlenk tube under nitrogen and heated at 185°C for 8 h. The reaction mixture was cooled to room temperature, diluted with methanol: diethyl ether (3 : 1) and filtered. The dark green solid was washed with water and methanol, and then dried *in vacuo*. The product was purified by column chromatography on silica gel with chloroform : ethanol (2 : 1) to give the product as a dark green solid (0.11 g, 26.83%); m.p. > 300°C. ^{1}H-NMR (DMSO-d_6): δ 3.01 (t, 16H, CH_2CH_2S), 3.09 (s, 16H, CH_2S), 3.56 (m, 32H, OCH_2), 4.20 (m, 16H, Ar OCH_2) 7.61–7.72 (m, 16H, Ar–H), 7.76 (s, 8H,Ar–H). IR (KBr pellets, cm^{-1}): 3095 (Ar–H), 2929-2879 (C–H), 1645 (C=N), 1598–1480 (C=C), 1249–1213 (Ar–OCH_2), 1129–1048 (CH_2–OCH_2). Anal. Calcd for $C_{96}H_{102}O_{16}S_8N_8Ni$(%): C, 59.41; H, 5.36; N, 5.78; Ni, 3.04 Found: C, 59.28; H, 5.45; N, 5.62; Ni, 2.98. UV–Vis (chloroform): λ (nm): [$(10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1})$]: 670 (3.72), 640 (3.36), 606 (3.32), 281 (5.05), 239 (5.05).

Acknowledgements

This work supported by the Research Fund of Karadeniz Technical University, Project No. 2002.111.002.6 (Trabzon/Turkey).

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