

## Synthesis and characterization of new metallophthalocyanines containing $O_4S_2$ mixed-donor substituted macrocyclic groups

Meltem Betül KILIÇASLAN, Halit KANTEKİN\*

Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon, Turkey

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**Abstract:** New phthalocyanine compounds containing mixed-donor substituted macrocyclic groups were synthesized. The complexes of metal phthalocyanines **3-5** were prepared by the reaction of **2** to get dinitrile derivative complexes by means of the corresponding anhydrous metal salts.

Structures of the new compounds were characterized by IR,  $^1H$  NMR,  $^{13}C$  NMR, elemental analysis, and MS spectral data.

**Key words:** Phthalonitrile, cyclotetramerization, dicarbonitrile, phthalocyanine

### 1. Introduction

Phthalocyanines (Pcs) comprise 2-dimensional, well-conjugated, planar macrocyclics with a delocalized  $18\pi$  electron system.<sup>1</sup> This structure provides them with strong nonlinear optical properties and numerous application areas. Phthalocyanines emit a visible light and so the blue and green colors, because of these properties, are often used as colorants.<sup>2-4</sup> Initially known as dye compounds, phthalocyanines are now used in many branches of industry, and in particular in many areas of medicine such as photodynamic therapy (PDT) of cancer.<sup>5-8</sup> They exhibit very interesting features in terms of molecular spectroscopy. Furthermore, the optical, photochemical, and photobiological as well as crystal properties of these compounds are interesting and important. These photochromic materials are investigated in such advanced technology, e.g., speed data transfer and high-capacity data storage applications, nonlinear optics, solar cells, and liquid crystals<sup>9-16</sup> Phthalocyanines have been applied as photoconducting agents in photocopiers and laser printers.

Industrial development is associated with emission of toxic substances, such as pesticides, toxic organic compounds, and heavy metals, and inevitably air pollution.<sup>17</sup> Keeping air pollution under control, especially in terms of environmental quality, and continuous monitoring of changes are vital in terms of any measures to be taken. In recent years, rates of toxic gases in the atmosphere have significantly increased and so it is very important to develop precise sensors for determination and continuous monitoring of these gases.<sup>18</sup> Metallophthalocyanines are very important in this respect. This class of compounds can be highly sensitive and selective to many poisonous gases. A further advantage of these compounds is that they allow for the synthesis of molecules with desired characteristics by replacing the metal atom or substituents. A recent study demonstrated that thin films produced from nickel phthalocyanines can behave as a good sensor against ozone in a wide temperature range.<sup>19-22</sup>

\*Correspondence: halit@ktu.edu.tr

The importance of phthalocyanine compounds is increasing and nowadays alternative synthetic methods for the synthesis of these compounds are being developed. One of them is the synthesis of phthalocyanine using microwave radiation.<sup>23</sup> Briefly the benefits of microwave radiation are as follows: a very fast reaction takes place, high purity products can be obtained, by-products can be reduced according to the methods of synthesis, and the classic products with high efficiency are achieved in less time and with less expenditure of energy.<sup>24,25</sup>

Optically active 1,1'-binaphthyl phthalocyanines bearing a crown ether unit were synthesized.<sup>26,27</sup> To date, few reports have explored the process of combining chiral binaphthol groups with a phthalocyanine core.<sup>28</sup> Since the first report on the use of chiral binaphthyl-based crown ethers as hosts for molecular recognition, chiral binaphthol has attracted much attention. Chiral macrocycles, metal complexes, linear oligomers, and polymers based on the 1,1'-binaphthyl structure have been synthesized for use in molecular recognition and asymmetric catalysis and as new functional materials.<sup>29</sup>

In the present study, we describe the synthesis and characterization of new 1,1'-binaphthyl phthalocyanines bearing O<sub>4</sub>S<sub>2</sub> macrocyclic moieties.

## 2. Experimental

### 2.1. Synthesis of 2,2'-[1,1'-Binaphthalene-2,2'-diyl bis(oxy)]diethanol (1)

1,1'-Binaphthalene-2,2'-diol (10 g, 35 mmol) was dissolved in 60 mL of absolute ethanol under a nitrogen atmosphere and NaOH (35 g, 87.5 mmol) was added. The mixture was heated at 50 °C and 2-chloroethanol (6 mL, 87.4 mmol) and 17 mL of absolute ethanol were added dropwise over 15 min. After the addition was completed, the reaction mixture was refluxed for 2 days under nitrogen. The reaction was controlled with a chloroform/methanol (9.5:0.5) solvent system and then ended. The cream-like mixture was cooled to room temperature and filtered before evaporating it to dryness under vacuum to obtain a viscous liquid product. This product was redissolved in chloroform (200 mL) after washing it with 10% NaOH and water, consecutively. The combined organic extracts were dried with anhydrous MgSO<sub>4</sub> and evaporated to dryness. The product was isolated as a cream-like solid following recrystallization of the crude residue from ethanol. Yield: 7 g (54%). mp: 100–102 °C. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>: C: 77.01; H: 5.88. Found: C: 77.20; H: 5.76%. IR (KBr tablet),  $\nu_{max}/\text{cm}^{-1}$ : 3516–3240 (OH), 3055 (Ar–H), 2917 (Aliph. C–H), 1619, 1456, 1242 (Ar–O–C), 1141–1082 (–OCH<sub>2</sub>), 972. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ( $\delta$ : ppm): 8.06–7.87 (m, 4H, ArH), 7.47–7.11 (m, 8H, ArH), 4.19–4.03 (m, 4H, O–CH<sub>2</sub>), 3.57 (br s, 4H, O–CH<sub>2</sub>), 2.29 (s, 2H, OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ( $\delta$ : ppm): 155.03, 134.02, 130.12, 129.87, 127.66, 126.92, 124.44, 123.69, 117.84, 111.14, 71.96, 61.46. MS (FAB) (m/z): 374 [M]<sup>+</sup>.

### 2.2. Synthesis of 6,7,9,10,25,26,28,29-Octahydrobenzo[h]dinaphtho [1,2-s:2',1' - $\alpha$ ] [1,4, 13,16,7,10] tetraoxacyloicosine-2,3-dicarbonitrile (2)

Compound **1** (3 g, 8.02 mmol), 192 mL of dry acetonitrile, anhydrous K<sub>2</sub>CO<sub>3</sub> (5.58 g, 40.08 mmol), NaI (6.12 g, 40.08 mmol), and 1,2-bis(2-iodoethyl mercapto)-4,5-dicyanobenzene (4.08 g, 8.16 mmol)<sup>30–32</sup> were refluxed under nitrogen atmosphere for 7 days. The reaction was controlled with chloroform/methanol (9.5:0.5) solvent system and then ended. The yellow-orange mixture was cooled to room temperature and filtered. Then it was evaporated to dryness under vacuum to obtain a viscous liquid product. This product was redissolved in chloroform (200 mL) and washed with water. The combined organic extracts were dried with anhydrous MgSO<sub>4</sub> and until 10 mL were evaporated and filtered. The product was isolated as a yellow solid following

recrystallization of the crude residue from ethanol. Yield: 4.27 g (66%). mp: 124–126 °C. Anal. Calcd for  $C_{36}H_{30}N_2O_4S_2$ : C: 69.90; H: 4.85; N: 4.53. Found: C: 70.00; H: 4.81; N: 4.46%. IR (KBr tablet),  $\nu_{max}/cm^{-1}$ : 3065 (Ar–H), 2923–2852 (Aliph. C–H), 2231 ( $C\equiv N$ ), 1619, 1462, 1260 (Ar–O–C), 1120–1085 ( $-OCH_2$ ), 749.  $^1H$  NMR ( $CDCl_3$ ), ( $\delta$ : ppm): 8.05–7.87 (m, 6H, ArH), 7.55–7.15 (m, 8H, ArH), 4.22–4.02 (m, 12H,  $-OCH_2$ ), 3.34–3.19 (m, 4H,  $-SCH_2$ ).  $^{13}C$  NMR ( $CDCl_3$ ), ( $\delta$ : ppm): 153.74, 142.85, 138.35, 134.05, 130.97, 129.89, 128.43, 127.02, 124.43, 123.53, 120.53, 117.61, 115.42, 112.82, 71.95, 71.33, 70.41, 32.70. MS (FAB) (m/z): 618  $[M]^+$ .

### 2.3. Co(II) phthalocyanine (3)

A mixture of **2** (0.5 g, 0.8 mmol) and anhydrous  $CoCl_2$  (0.052 g, 0.4 mmol) was ground in a microwave oven and 2-(dimethylamino)ethanol (5 mL) was added. The reaction mixture was irradiated in a microwave reaction oven at 175 °C and 350 W for 6 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and washed with hot ethanol and dried under vacuum. The solid product was purified by preparative thin layer chromatography (TLC) using an ethanol/ethyl acetate (10.0:0.5) solvent system. Yield: 0.26 g (51%) mp: >300 °C. Anal. Calc. for  $C_{144}H_{120}N_8O_{16}S_8Co$ : C: 68.27; H: 5.10; N: 4.43. Found: C: 68.31; H: 5.16; N: 4.40%. IR (KBr tablet),  $\nu_{max}/cm^{-1}$ : 3035 (Ar–H), 2922–2851 (Aliph. C–H), 1464, 1266 (Ar–O–C), 1121–1071 ( $-OCH_2$ ), 964, 751. UV-vis (chloroform):  $\lambda_{max}/nm$ :  $[(10^{-5} \text{ } \epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$ : 701 (5.20), 656 (5.00), 320 (5.12). MS (FAB) (m/z): 2553  $[M+Na-H]^+$ .

### 2.4. Cu(II) phthalocyanine (4)

A mixture of **2** (0.5 g, 0.8 mmol) and anhydrous  $CuCl_2$  (0.054 g, 0.4 mmol) was ground in a microwave oven and 2-(dimethylamino)ethanol (5 mL) was added. The reaction mixture was irradiated in a microwave reaction oven at 175 °C and 350 W for 7 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and washed with hot ethanol and dried under vacuum. The solid product was purified by preparative TLC using a chloroform/methanol (7:3) solvent system. Yield: 0.21 g (41%) mp: >300 °C. Anal. Calc. for  $C_{144}H_{120}N_8O_{16}S_8Cu$ : C: 68.15; H: 4.73; N: 4.42. Found: C: 68.02; H: 4.75; N: 4.50%. IR (KBr tablet),  $\nu_{max}/cm^{-1}$ : 3043 (Ar–H), 2918–2862 (Aliph. C–H), 1378, 1283 (Ar–O–C), 1075–1068 ( $-OCH_2$ ), 745. UV-vis (chloroform):  $\lambda_{max}/nm$ :  $[(10^{-5} \text{ } \epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$ : 713 (5.27), 659 (5.03), 341 (5.02). MS (FAB) (m/z): 2535  $[M]^+$ .

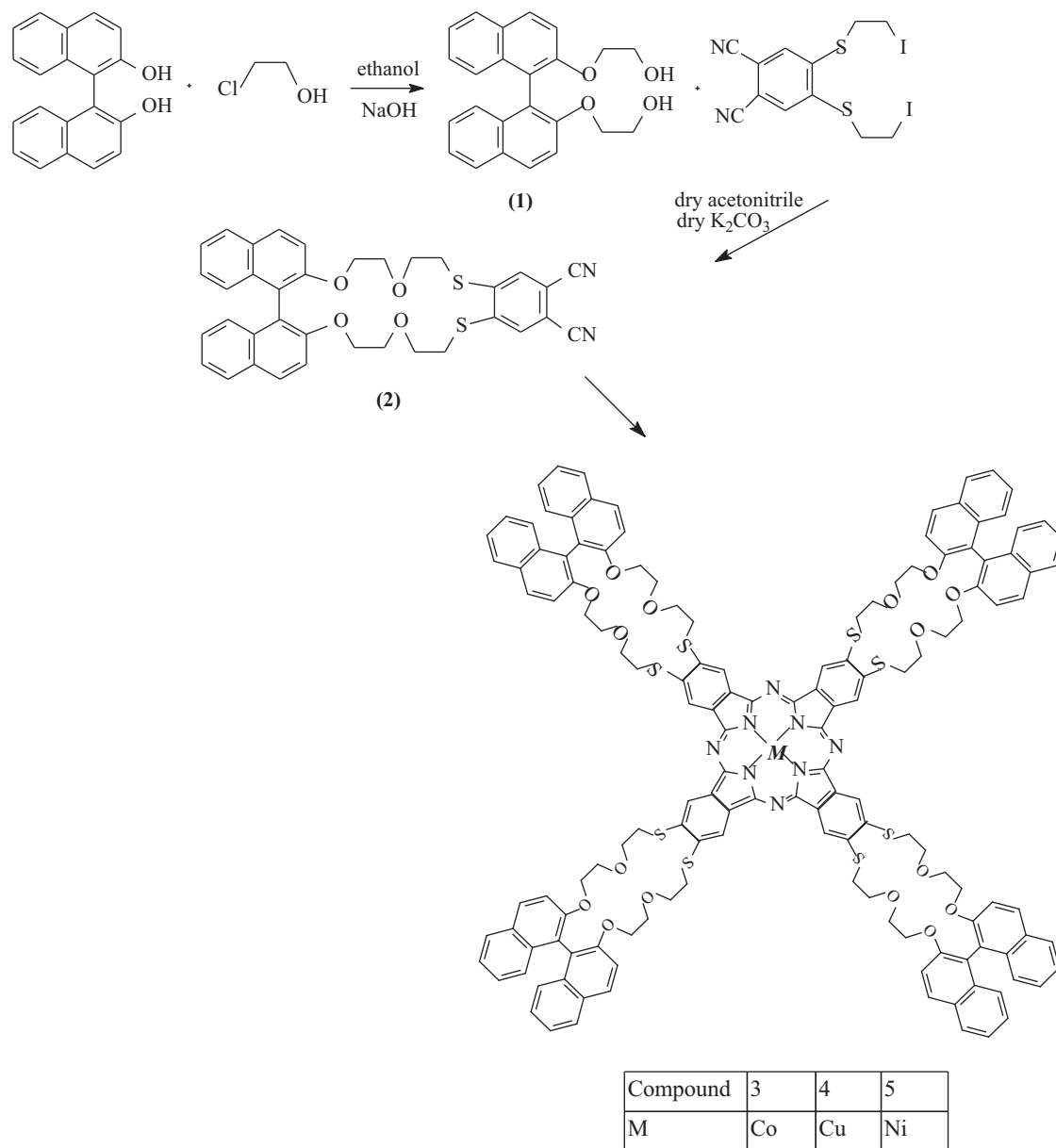
### 2.5. Ni(II) phthalocyanine (5)

A mixture of **2** (0.5 g, 1 mmol) and anhydrous  $NiCl_2$  (0.051 g, 0.4 mmol) was ground in a microwave oven and 2-(dimethylamino)ethanol (5 mL) was added. The reaction mixture was irradiated in a microwave reaction oven at 175 °C and 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and washed with hot ethanol and dried under vacuum. The solid product was purified by preparative TLC using a chloroform/acetone (8:2) solvent system. Yield: 0.18 g (35%) mp: >300 °C. Anal. Calc. for  $C_{144}H_{120}N_8O_{16}S_8Ni$ : C: 68.27; H: 4.74; N: 4.43. Found: C: 68.19; H: 4.70; N: 4.38%. IR (KBr tablet),  $\nu_{max}/cm^{-1}$ : 3087 (Ar–H), 2919–2875 (Aliph. C–H), 1413, 1268 (Ar–O–C), 1126–1072 ( $-OCH_2$ ), 743.  $^1H$  NMR ( $CDCl_3$ ), ( $\delta$ : ppm): 7.68–7.64 (m, 28H, Ar–H), 7.49–7.30 (m, 28H, Ar–H), 4.03–4.00 (m, 48H,  $-OCH_2$ ), 3.73–3.66 (m, 16H,  $-SCH_2$ ).  $^{13}C$  NMR ( $CDCl_3$ ), ( $\delta$ : ppm): 167.94,

152.53, 144.99, 133.87, 132.58, 131.18, 130.01, 129.08, 124.56, 122.04, 118.89, 111.14, 105.00, 101.28, 72.03, 70.98, 69.40, 32.87. UV-vis (chloroform):  $\lambda_{max}/nm$ :  $[(10^{-5}\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$ : 707 (4.96), 650 (4.89), 314 (5.04). MS (FAB) (m/z): 2570  $[M+K]^+$ .

### 3. Results and discussion

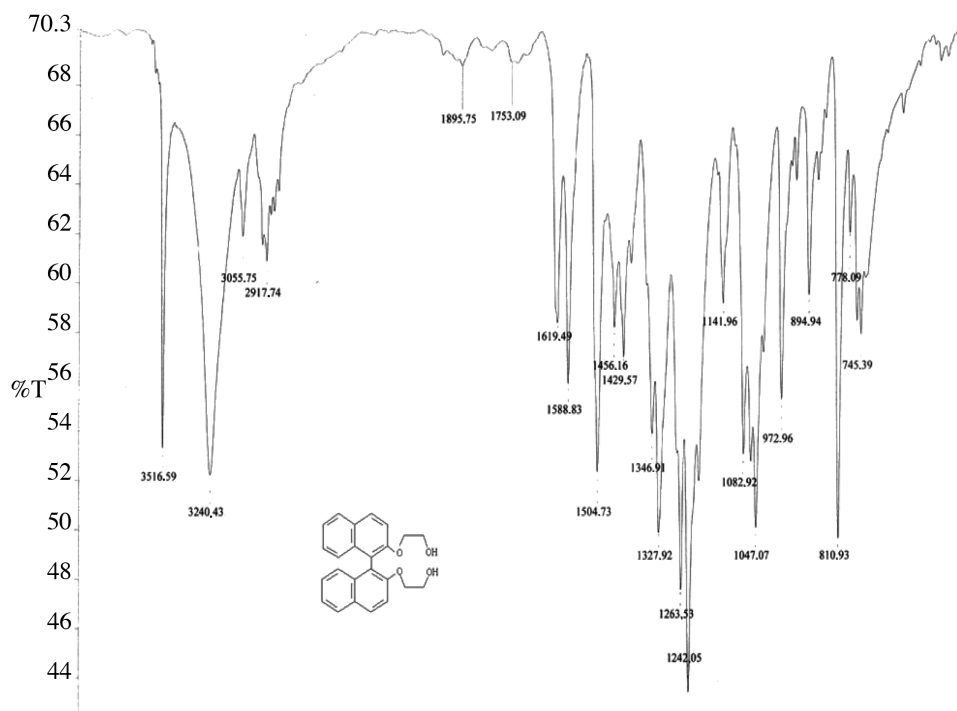
1,2-Bis(2-iodoethylmercapto)-4,5-dicyanobenzene was synthesized according to the literature.<sup>30-32</sup> The preparation of **1**, **2**, CoPc (**3**), CuPc (**4**), and NiPc (**5**) is shown in Figure 1.



**Figure 1.** The synthesis of the metallophthalocyanines.

Compound **1** was prepared with 1,1'-binaphthalene-2,2'-diol and 2-chloroethanol reaction at 95 °C in absolute ethanol and the yield was 54%. In the IR spectrum (Figure 2) of **1** stretching vibrations of the O–H

band at 3516–3240  $\text{cm}^{-1}$  seemed to shift after the reaction. In addition, stretching vibrations of O–CH<sub>2</sub> were observed at 1141–1047  $\text{cm}^{-1}$ . A singlet peak at  $\delta = 5.00$  ppm of OH protons of compound 1,1'-binaphthalene-2,2'-diol was seen at  $\delta = 2.29$  ppm for compound **1** and it disappeared after addition of D<sub>2</sub>O. The <sup>1</sup>H NMR spectrum of **1** indicated aromatic protons at 8.06–7.87 and 7.47–7.11 and aliphatic protons at 4.19–4.03 and 3.57 ppm. The <sup>13</sup>C NMR spectrum of **1** indicated the presence of carbon resonance at  $\delta = 71.96$  and  $\delta = 61.46$  ppm. The MS spectrum of **1** displayed the [M]<sup>+</sup> parent ion peak at  $m/z = 374$ , confirming the structure. The elemental analysis was satisfactory.



**Figure 2.** IR spectrum of compound **1**.

Compound **2** was prepared with 2,2'-[1,1'-binaphthalene-2,2'-diyl bis(oxy)]diethanol and 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene reaction at 85 °C in dry acetonitrile and the yield was 66%. In the IR spectrum (Figure 3) of **2** stretching vibrations of the –OH band at 3516–3240  $\text{cm}^{-1}$  disappeared and C≡N groups were observed at 2231  $\text{cm}^{-1}$ . In the <sup>1</sup>H NMR spectrum (Figure 4) of **2**, signals belonging to OH groups at  $\delta = 2.29$  ppm disappeared to give the proposed structure. In addition, the <sup>1</sup>H NMR spectrum of **2** indicated aromatic protons at 8.05–7.87 and 7.55–7.15 ppm and aliphatic protons at 4.22–4.02 (–OCH<sub>2</sub>) and 3.34–3.19 (–SCH<sub>2</sub>) ppm. The <sup>13</sup>C NMR spectrum of **2** indicated the presence of nitrile carbon atoms (C≡N) in **2** at 115.42 ppm. The MS spectrum (Figure 5) of **2** displayed the [M]<sup>+</sup> parent ion peak at  $m/z = 618$ , confirming the structure. The elemental analysis was satisfactory.

The metallophthalocyanines of CoPc (**3**), CuPc (**4**), and NiPc (**5**) were obtained from anhydrous metal salts (CoCl<sub>2</sub>, CuCl<sub>2</sub>, NiCl<sub>2</sub>) in 2-(dimethylamino)ethanol by microwave irradiation. We used a 350-W domestic oven at 175 °C for synthesis of **3–5**.

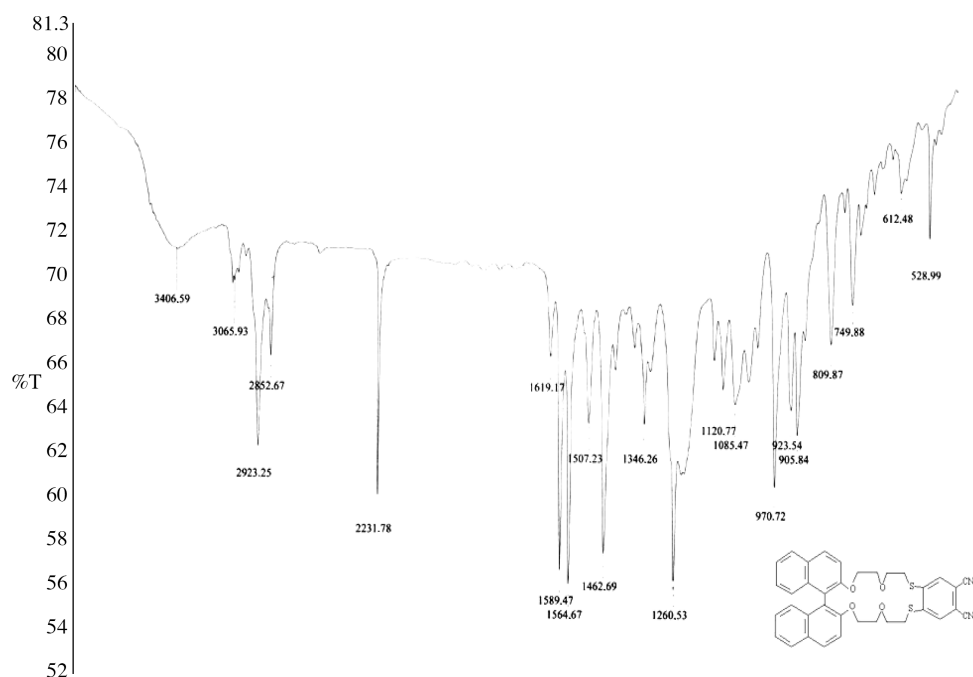


Figure 3. IR spectra of compound 2.

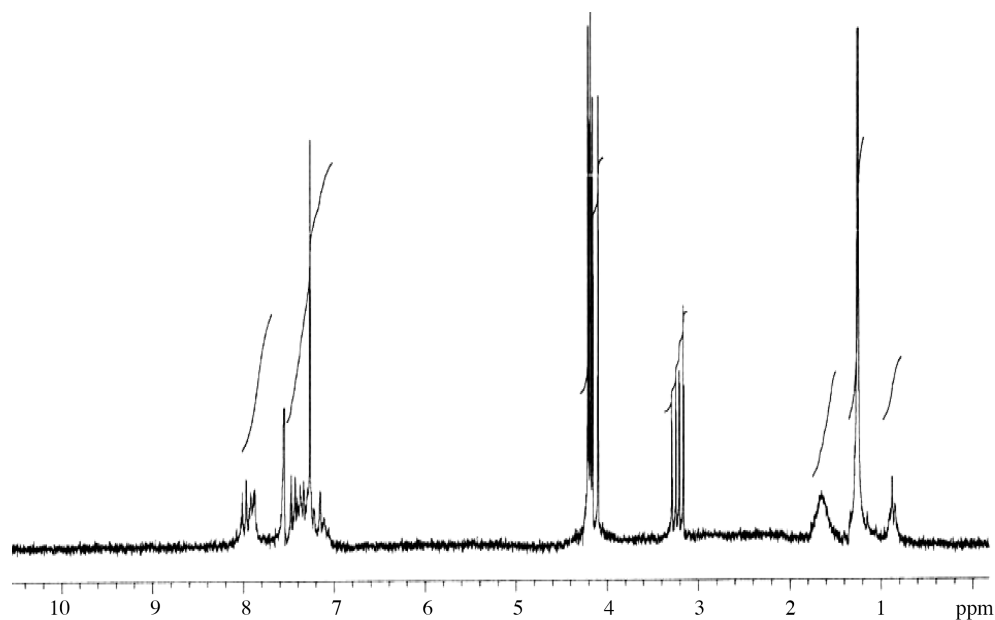


Figure 4.  $^1\text{H}$  NMR spectrum of compound 2.

In the IR spectrum of metallophthalocyanines **3** (Figure 6)–**5**, phthalocyanines **3**–**5** were confirmed by the disappearance of the sharp  $\text{C}\equiv\text{N}$  vibration at  $2231\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectra of **3**–**5** were almost identical, except for broad signals of **3**–**5**, from aggregation of planar phthalocyanines at the high concentration used for NMR measurements, and the  $^1\text{H}$  NMR spectra of CoPc (**3**) and CuPc (**4**) were precluded owing to their paramagnetic nature. The  $^1\text{H}$  NMR spectrum (Figure 7) of **5** indicated aromatic protons at 7.68–7.64 and 7.49–7.30 and aliphatic protons at 4.03–4.00 and 3.73–3.66 ppm. The inner core protons N–H of this compound

**5** could not be observed because of the probable strong aggregation of the molecule. The  $^{13}\text{C}$  NMR spectrum of NiPc (**5**) was confirmed by the disappearance of the sharp  $-\text{C}\equiv\text{N}$  vibration at **5** at 115.42 ppm ( $\text{C}\equiv\text{N}$ ). The MS spectra of **3** (Figure 8), **4** (Figure 9), and **5** (Figure 10) show molecular ion peaks at  $m/z = 2553$   $[\text{M}+\text{Na}-\text{H}]^+$ , 2535  $[\text{M}]^+$ , and 2070  $[\text{M}+\text{K}]^+$ , respectively, confirming the proposed structure. The elemental analysis data were satisfactory.<sup>32,33</sup>

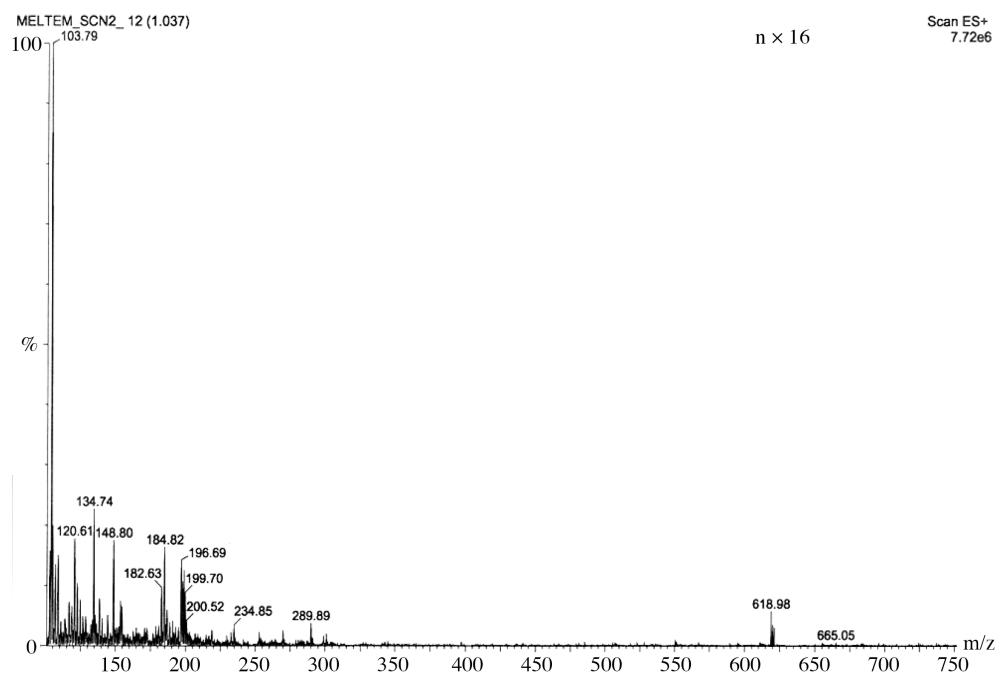


Figure 5. Mass spectrum of compound **2**.

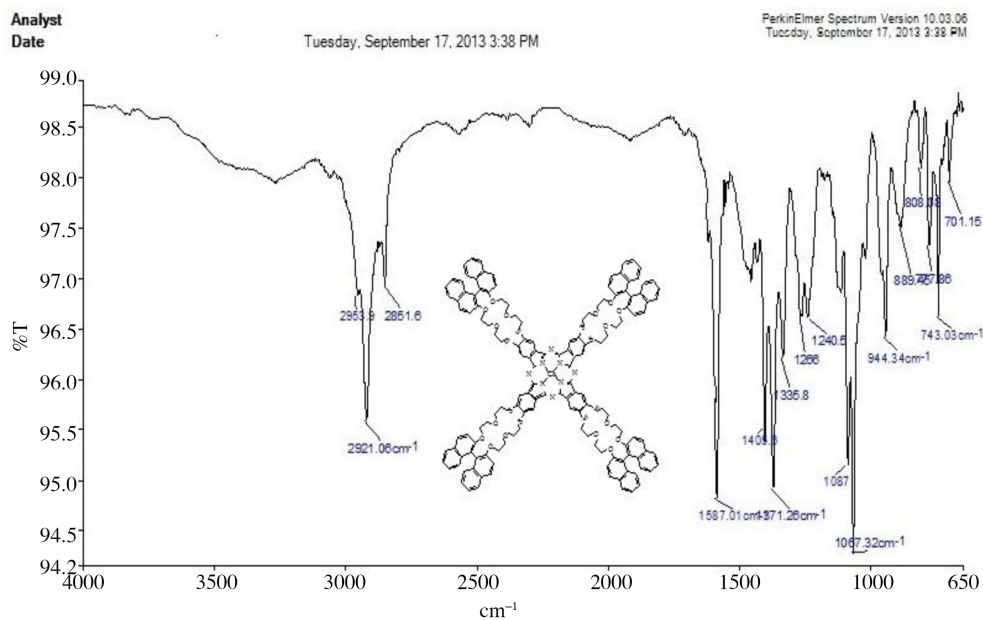


Figure 6. IR spectrum of compound **3**.

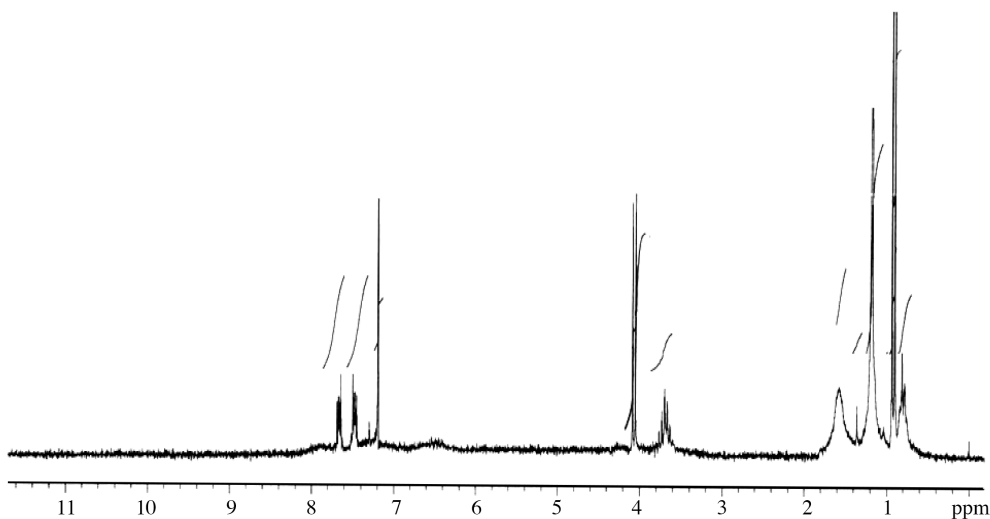


Figure 7.  $^1\text{H}$  NMR spectrum of compound **5**.

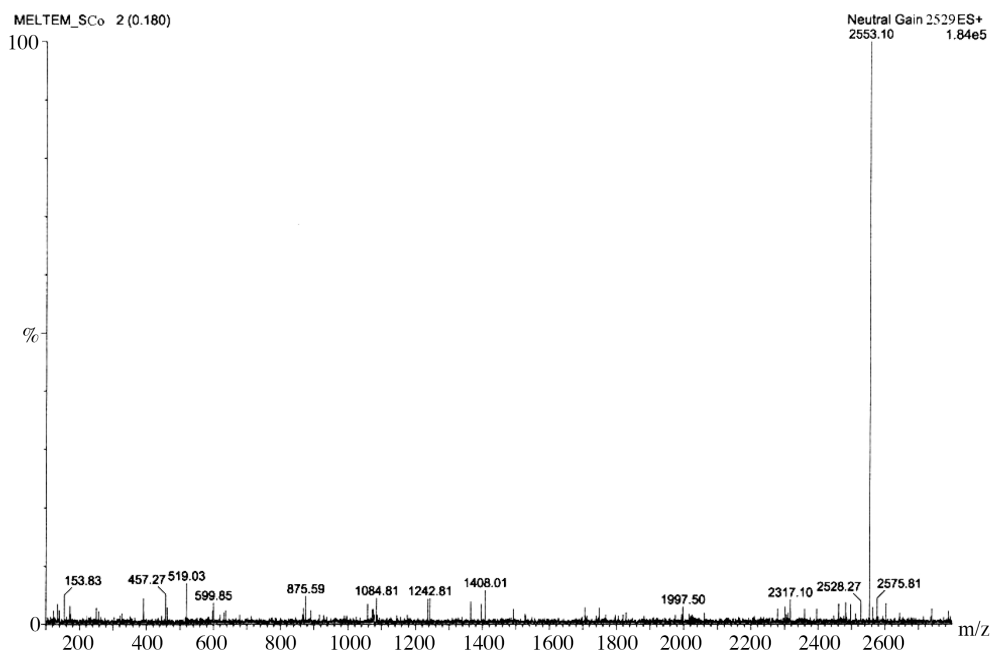


Figure 8. Mass spectrum of compound **3**.

The spectra of metallophthalocyanines complexes consist of an intense absorption band in the visible region traditionally near 670 nm called the Q band and a generally weaker band near 340 nm called the Soret or B band, both being  $\pi - \pi^*$  transitions. Metalation, which maintains the planarity of the molecule, increases the symmetry  $D_{4h}$ .<sup>35,36</sup> The introduction of a metal ion inside the cavity results in a slightly blue shift in the wavelength of the Q band as the introduction of a metal ion reduces electron density. It has been demonstrated that a more electronegative metal ion in the phthalocyanine cavity causes a greater blue shift for the wavelength of the Q band of phthalocyanines.<sup>35,36</sup>

The UV-vis absorption spectra of **3–5** in chloroform at room temperature are shown in Figure 11. The UV-vis absorption spectra of metallophthalocyanines **3–5** had intense Q band absorptions at  $\lambda_{max} = 701, 713,$



and 707 nm, respectively, with weaker absorptions at  $\lambda_{max} = 656, 659,$  and  $650$  nm, respectively. The single Q band in metallo derivatives **3–5** was characteristic. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with  $D_{4h}$  symmetry.<sup>35,36</sup> The other bands (B) in the UV region for **3–5** were observed at  $\lambda_{max} = 320, 341,$  and  $314$  nm due to transition from deeper  $\pi$  levels to the LUMO.

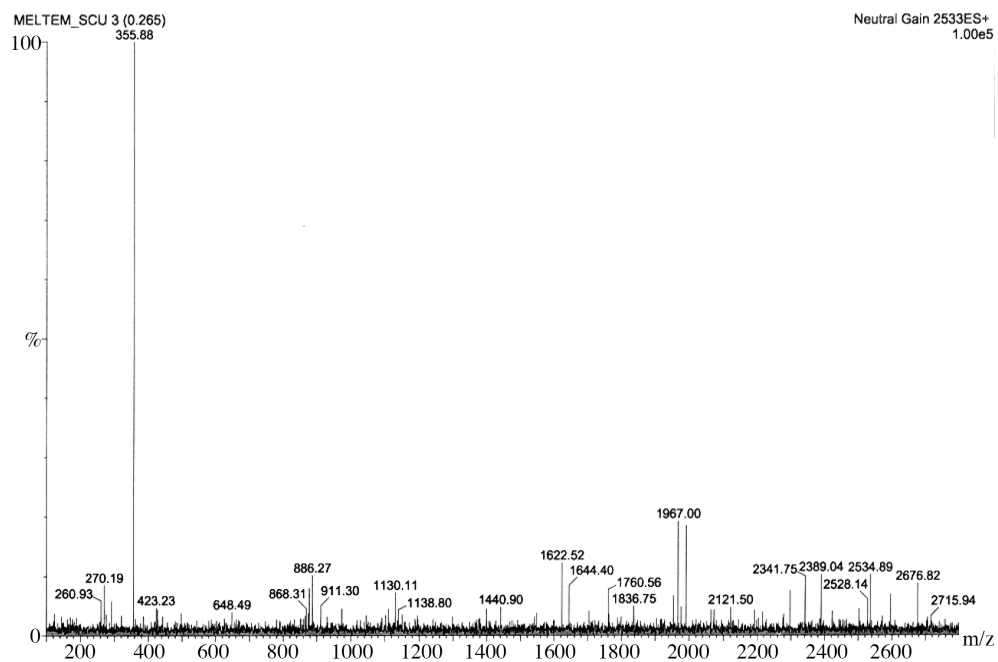


Figure 9. Mass spectrum of compound 4.

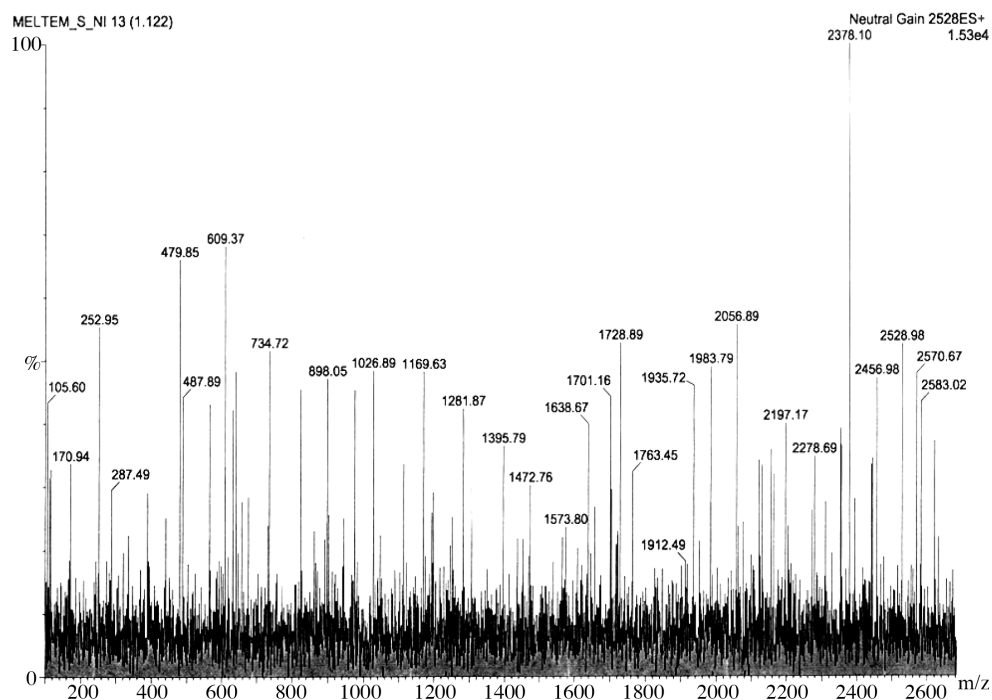
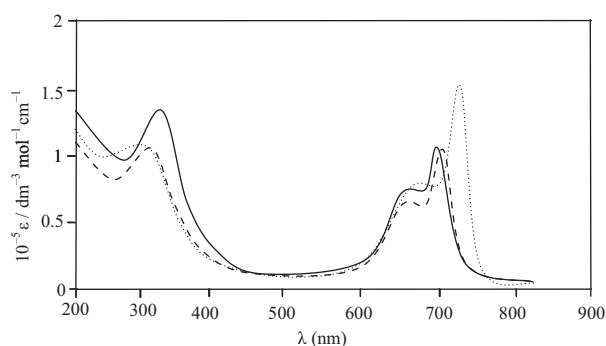


Figure 10. Mass spectrum of compound 5.



**Figure 11.** UV-vis spectra of compounds 3(-),4(—),5(-.-) in chloroform.

#### 4. Conclusion

We demonstrated the synthesis and characterization of new metallophthalocyanines **3–5** containing mixed-donor substituted macrocyclic groups.

Structures of the new compounds were characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, elemental analysis, and MS spectral data.

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