



## Metal-free and metallophthalocyanines appending with eight 12-crown-4 ethers

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### ARTICLE INFO

#### Article history:

Received 30 November 2009

Received in revised form

5 April 2010

Accepted 18 April 2010

Available online 24 April 2010

#### Keywords:

Crown Ether

Thermal Stability

Phthalocyanine

Synthesis

Phthalonitrile

Microwave

### ABSTRACT

The metal-free phthalocyanine **2** was synthesized from the 4,5-bis(1,4,7,10-tetraoxacyclododecan-2-ylmethoxy)phthalonitrile **1** in the presence of a strong base in *n*-pentanol. The synthesis of metallo derivatives [Ni(II), Co(II), Cu(II)] of phthalocyanines obtained from corresponding phthalonitrile derivative **1** and in the presence of the anhydrous divalent metal salts (NiCl<sub>2</sub>, CoCl<sub>2</sub> and CuCl<sub>2</sub>) were described. The thermal stabilities of the metal-free and metallophthalocyanines were determined by thermogravimetric analysis. These phthalocyanines were good soluble in organic solvents such as chloroform, dichloromethane, tetrahydrofuran and DMF. The products were characterized by elemental analysis, IR, <sup>1</sup>H NMR, UV–vis and MS spectral data.

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## 1. Introduction

Since their accidental synthesis in Scotland in 1928, phthalocyanines have enjoyed considerable industrial importance for use in dyestuffs, paints, colors for metal surfaces, fabrics and plastics [1]. Phthalocyanines have been found to be important in applications in material science [2], medicine [3], optical storage [4] and photocatalysis [5]. Owing to their large conjugated molecular structure, together with strong  $\pi$ – $\pi$  interactions between aromatic rings, phthalocyanine derivatives have also been used as staple building blocks for ordered molecular systems [6,7].

One of the most extensively studied class of functional organic materials are phthalocyanines due to their catalytic, structural, electronic and optical properties in addition to their wide spread use as dyes and pigments [8].

The solubility of phthalocyanines is very important for the investigation of their chemical and physical characteristics [9]. A common means for preparing soluble phthalocyanines is to attach functional groups like tertiary butyl groups, amide groups and carboxylic acid groups [10,11], bulky and crown ether groups [12–16], azo groups [17], etc. at the peripheral and axial positions of phthalocyanine ring. In the case of soluble products in apolar organic

solvents, these substituents are long alkyl or alkoxy chains, bulky substituents or macrocyclic groups such as crown ether.

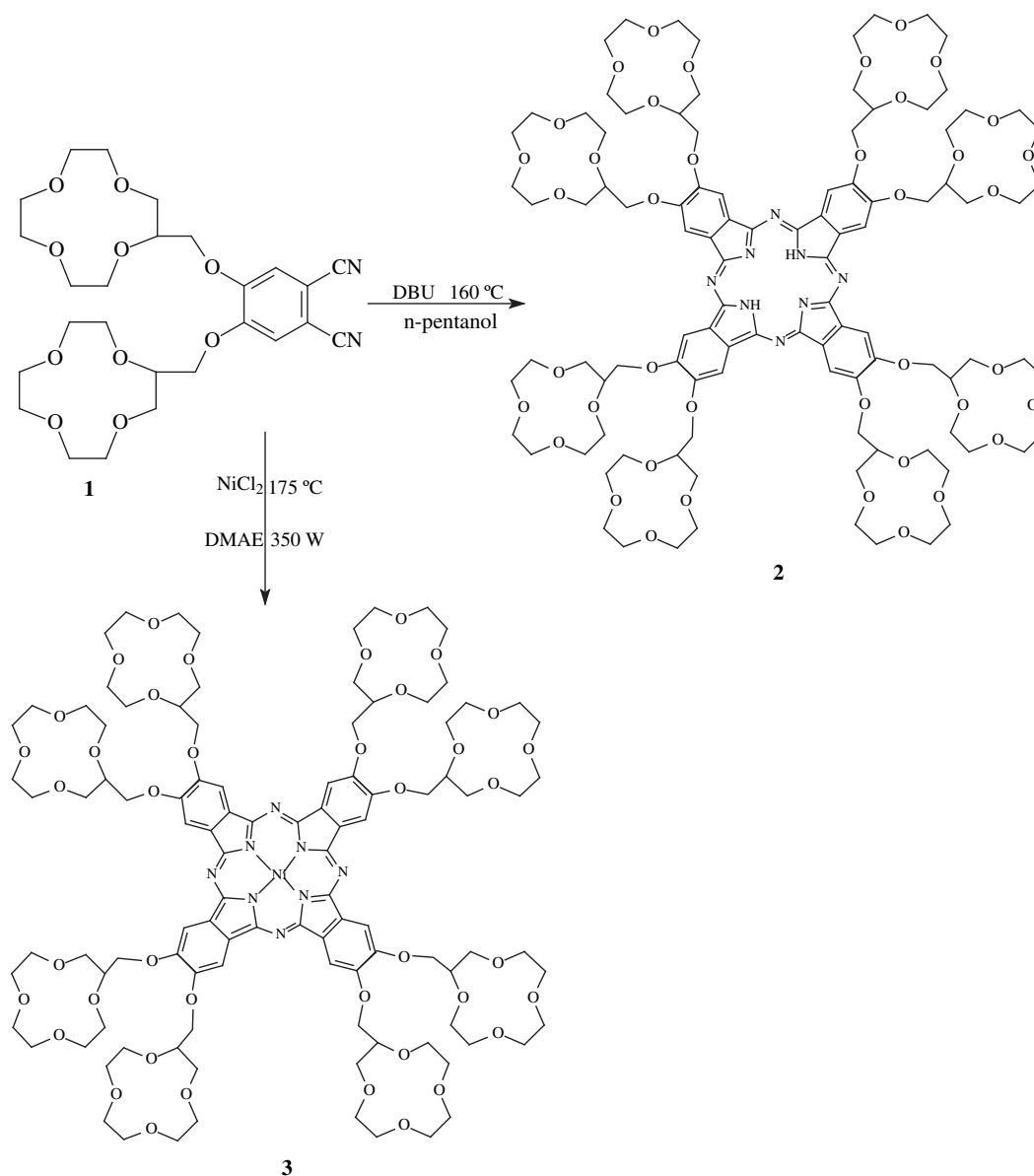
Microwaves have been previously used for the synthesis of phthalocyanines and include a wider range of references on the topic [18–21]. Microwave-assisted synthesis reduces chemical reactions times from hours to minutes, and also, reduces side reactions, increases the yield, and improves reproducibility. So, many academic and industrial research groups are already using microwave-assisted synthesis for the efficient synthesis of new chemical reactivity [22]. In the present work, the objective is the preparation and characterization of metal-free **2** and metallophthalocyanines **3–5** (Ni, Co, Cu) containing octakis-flexible 12-crown-4 ether moieties by microwave irradiation. Moreover the thermal stabilities of the metal-free and metallophthalocyanines were determined by thermogravimetric analysis.

## 2. Results and discussion

### 2.1. Synthesis and characterizations

Starting from 4,5-bis(1,4,7,10-tetraoxacyclododecan-2-ylmethoxy)phthalonitrile **1** general synthetic route for the synthesis of new metal-free and metallophthalocyanines is given in Schemes 1 and 2. The structures of novel compounds were characterized by

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**Scheme 1.** The synthesis of the metal-free and nickel(II) phthalocyanines.

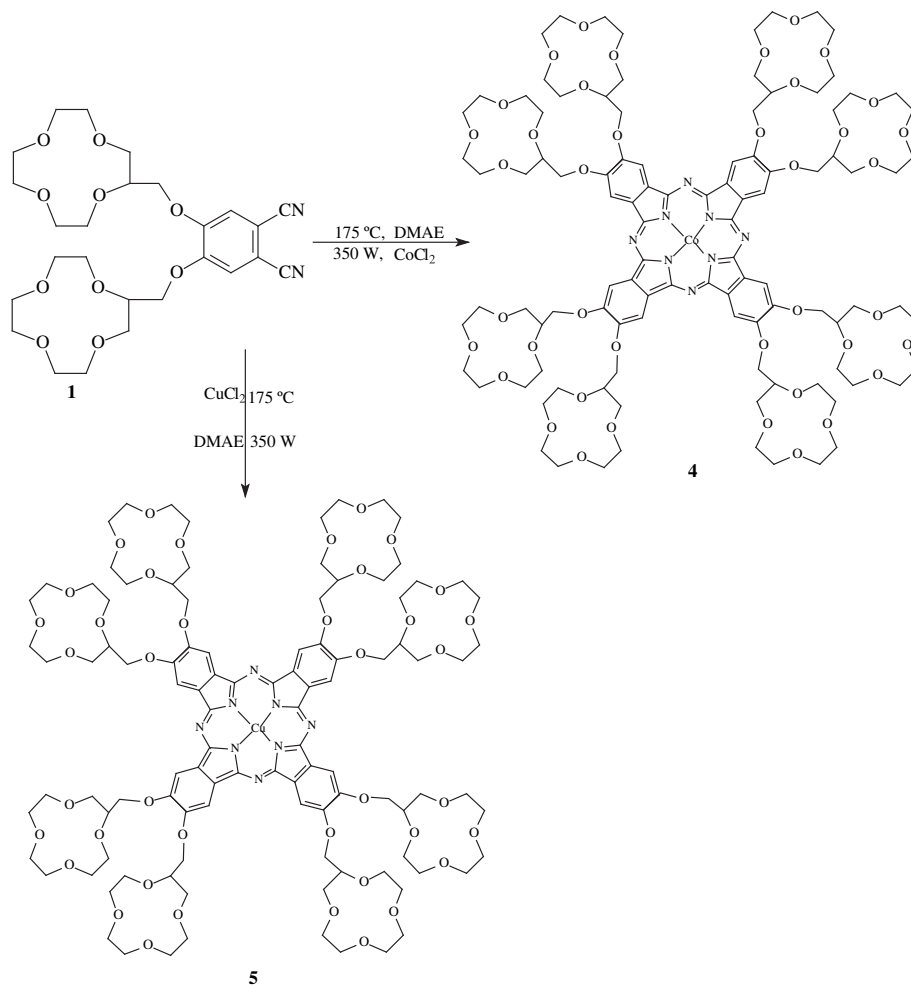
a combination of <sup>1</sup>H NMR, IR, UV–vis and MS spectral data. The solubility of phthalocyanines is summarized in Table 1.

Cyclotetramerization of the phthalonitrile derivative **1** to the metal-free phthalocyanine **2** was accomplished in n-pentanol in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at 160 °C in sealed tube. The IR spectra of metal-free **2** and metallophthalocyanines **3–5** are very similar. The significant difference is the presence of N–H vibrations of the inner phthalocyanine core which are assigned to a weak vibration at 3290 cm<sup>-1</sup> in the metal-free compound. After conversion of the dinitrile derivative **1** into the metal-free **2** and metallophthalocyanines **3–5**, the sharp peak for the C≡N vibration around 2235 cm<sup>-1</sup> disappeared. The <sup>1</sup>H NMR spectrum of compound **2** indicates the aromatic proton at δ7.25 and the aliphatic ether protons at δ4.07–3.82 ppm. A common feature of this spectrum is the broad absorptions caused by the aggregation of the phthalocyanines [23].

The NH-protons of compound **2** could not be observed owing to the probable strong aggregation of the molecules [24]. Also, the lack of NH-proton NMR-signals could also be caused by chemical

exchange (broad signals) or the dynamic range; (136 protons of crown ether vs. 2 NH-protons). <sup>1</sup>H NMR measurement of the cobalt(II) and copper(II) phthalocyanine **4, 5** was precluded owing to its paramagnetic nature. In the mass spectrum of metal-free **2**, Ni(II) **3**, Co(II) **4** and Cu(II) **5** phthalocyanines, the presence of molecular ion peaks at *m/z* = 2148 [M]<sup>+</sup>, 2204 [M]<sup>+</sup>, 2228 [M + Na]<sup>+</sup> and 2209 [M]<sup>+</sup>, respectively, confirmed the proposed structures.

The best indications for phthalocyanine systems are given by their UV–vis spectra in solution (Fig. 1). The phthalocyanines **2–5** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 330 nm (B band) and the other in the visible part of the spectrum around 600–700 nm (Q band). A typical spectrum of the metal-free phthalocyanine **2** in chloroform showed a doublet in the Q band region at 703 and 669 nm, and a B band region at 333 and 293 nm; while the metallophthalocyanines each gave an intense single Q band at 677, 667 and 689 nm, B band 340, 301 and 354 nm for the corresponding compounds **3, 4** and **5**, respectively.



**Scheme 2.** The synthesis of the cobalt(II) and copper(II) phthalocyanines.

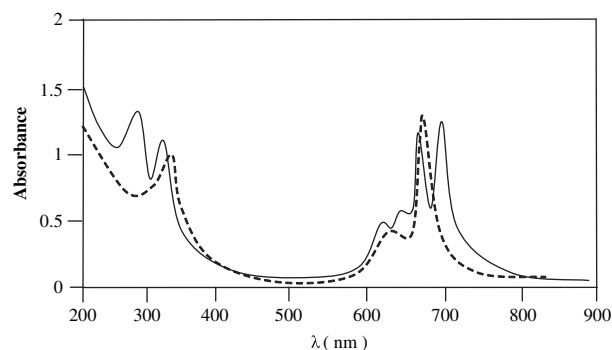
Tetra-substituted phthalocyanines are more soluble than the symmetrically octa-substituted ones because of the formation of four positional isomers in the case of tetra-substituted analogues [25]. When we compared with solubility of these octa-substituted phthalocyanines (Table 1) with tetra substituted ones [14], we observed high solubility in tetra substituted ones. Through the introduction of crown ether groups into peripheral positions of phthalocyanines, the solubility in organic solvents increases. With the current coating technology in the fabrication of optical disks, a good solubility of phthalocyanine in alcohols and other organic solvents is becoming more important [26]. Solvent soluble macrocycles are of interest to the energy research community due to their potential application in the preparation of sensor, electrode coating, catalysts and oxygen transporting agents [27]. So, good solubility of phthalocyanine in organic solvents is occurring important for technological materials.

**Table 1**  
The solubility of phthalocyanines in different solvents.

Compound	Solubility in mg/ml			
	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	THF	DMF
$\text{H}_2\text{-Pc}$ <b>2</b>	7.3	7.8	8.4	9.7
Ni-Pc <b>3</b>	7.4	7.6	8.3	9.6
Co-Pc <b>4</b>	7.6	7.9	8.5	9.8
Cu-Pc <b>5</b>	7.3	7.6	8.4	9.6

## 2.2. Thermal Gravimetric Analysis (TG/DTA)

The phthalocyanines are resistant to thermal oxidation. Also, the thermal stabilities of phthalocyanines are well known. The thermal stabilities of the metal-free **2** and metallophthalocyanines **3–5** were evaluated by the thermogravimetric analysis at a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  in a nitrogen flow (Fig. 2). Although the thermal stabilities of phthalocyanines are well known, the phthalocyanines compounds are not stable above  $310\text{ }^\circ\text{C}$ . The initial and main decomposition temperatures are given in Table 2. The initial



**Fig. 1.** UV-vis spectra of compounds **2** (—) and **3** (---) in chloroform.

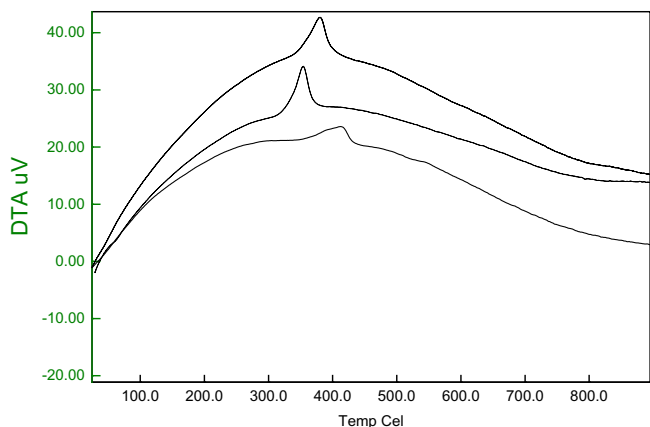


Fig. 2. DTA thermograms of compounds 2 (—), 3 (···) and 4 (---).

decomposition temperature decreased in the order: **2** > **3** > **4** > **5**. DTA curves exhibited exothermic changes for all phthalocyanines (2–5) in the region investigated [28], the curves do not show melting points.

### 3. Experimental

4,5-bis(1,4,7,10-Tetraoxacyclododecan-2-ylmethoxy)phthalonitrile **1** was prepared by reported procedure [29]. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [30]. The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in  $\text{CDCl}_3$  chemical shifts were reported ( $\delta$ ) relative to  $\text{Me}_4\text{Si}$  as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. A Seiko II Exstar 6000 thermal analyzer was used to record DTA curves under nitrogen atmosphere with a heating rate of  $20^\circ\text{C min}^{-1}$  in the temperature range  $30\text{--}900^\circ\text{C}$  using platinum crucibles. Melting points were measured on an electrothermal apparatus and are uncorrected. Optical spectra in the UV–vis region were recorded with a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature.

#### 3.1. Metal-free phthalocyanine (2)

A mixture of 4,5-bis(1,4,7,10-tetraoxacyclododecan-2-ylmethoxy)phthalonitrile **1** (0.25 g, 0.46 mmol) and 0.46 mmol of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.3 ml) in 2.5 ml of dry n-pentanol was heated and stirred at  $160^\circ\text{C}$  for 24 h under  $\text{N}_2$  and after that the reaction mixture was cooled precipitated by adding ethanol. The precipitated green solid product was filtered off, and then dried in vacuo over  $\text{P}_2\text{O}_5$ . The obtained green solid product was purified from the column chromatography which is placed aluminium oxide using only chloroform as solvent system. Yield:

Table 2  
Thermal properties of the phthalocyanine.

Compound	M	Initial decom. temp. ( $^\circ\text{C}$ )	Main decom. temp. ( $^\circ\text{C}$ )
<b>2</b>	2H	350	413
<b>3</b>	Ni	341	380
<b>4</b>	Co	321	354
<b>5</b>	Cu	310	351

80 mg (34%). Anal. Calcd for  $\text{C}_{104}\text{H}_{146}\text{N}_8\text{O}_{40}$ : C, 58.14; H, 6.85; N, 5.22%. Found: C, 57.94; H, 6.98; N, 5.06. IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3290 (N–H), 3060 (Ar–H), 2922–2853 (Aliph. C–H), 1606, 1500, 1462, 1446, 1378, 1265, 1134, 1104, 1077, 1022, 912, 884, 741.  $^1\text{H}$  NMR. ( $\text{CDCl}_3$ ), ( $\delta$ :ppm): 7.25 (s, 8H, Ar–H), 4.07–3.82 (m, 136H,  $\text{CH}_2\text{--O}$ ). UV–vis (chloroform):  $\lambda_{\text{max}}/\text{nm}$ : [( $10^{-5}$   $\epsilon$   $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 293 (5.14), 333 (5.06), 617 (4.72), 637 (4.77), 669 (5.09), 703 (5.11)]. MS ( $\text{ES}^+$ ), ( $m/z$ ): 2148 [ $\text{M}$ ] $^+$ .

#### 3.2. Nickel(II) phthalocyanine (3)

A mixture of 4,5-bis(1,4,7,10-tetraoxacyclododecan-2-ylmethoxy)phthalonitrile **1** (200 mg, 0.37 mmol), anhydrous  $\text{NiCl}_2$  (12 mg) and 2-(dimethylamino)ethanol (2.5 ml) was irradiated in a microwave oven at  $175^\circ\text{C}$ , 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 dried in vacuo over  $\text{P}_2\text{O}_5$ . The obtained green solid product was purified from the column chromatography which is placed aluminium oxide using only chloroform:methanol (100:1) as solvent system. Yield: 116 mg (57%). Anal. Calcd for  $\text{C}_{104}\text{H}_{144}\text{N}_8\text{O}_{40}\text{Ni}$ : C, 56.65; H, 6.58; N, 5.08%. Found: C, 56.78; H, 6.71; N, 5.18. IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3076 (Ar–H), 2917–2851 (Aliph. C–H), 1603, 1517, 1444, 1399, 1347, 1264, 1132, 1100, 883, 749.  $^1\text{H}$  NMR. ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 7.26 (s, 8H, Ar–H), 4.09–3.80 (m, 136H,  $\text{CH}_2\text{--O}$ ). UV–vis (chloroform):  $\lambda_{\text{max}}/\text{nm}$ : [( $10^{-5}$   $\epsilon$   $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 340 (5.00), 621 (4.67), 677 (5.11)]. MS ( $\text{ES}^+$ ), ( $m/z$ ): 2204 [ $\text{M}$ ] $^+$ .

#### 3.3. Cobalt(II) phthalocyanine (4)

The reaction was carried out by the compound **3** procedure using compound **1** (200 mg, 0.37 mmol) anhydrous  $\text{CoCl}_2$  (13 mg) and 2-(dimethylamino)ethanol (2.5 ml). The obtained green solid product was purified from the column chromatography which is placed aluminium oxide using only chloroform:methanol (100:1) as solvent system. Yield: 106 mg (52%). Anal. Calcd for  $\text{C}_{104}\text{H}_{144}\text{N}_8\text{O}_{40}\text{Co}$ : C, 56.64; H, 6.58; N, 5.08%. Found: C, 56.52; H, 6.40; N, 5.25. IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3082 (Ar–H), 2917–2858 (Aliph. C–H), 1603, 1517, 1443, 1415, 1344, 1264, 1132, 1102, 1072, 886, 750. UV–vis (chloroform):  $\lambda_{\text{max}}/\text{nm}$ : [( $10^{-5}$   $\epsilon$   $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 301 (5.07), 625 (4.69), 667 (5.09)]. MS ( $\text{ES}^+$ ), ( $m/z$ ): 2228 [ $\text{M} + \text{Na}$ ] $^+$ .

#### 3.4. Copper(II) phthalocyanine (5)

The reaction was carried out by compound **3** procedure using compound **1** (200 mg, 0.37 mmol) anhydrous  $\text{CuCl}_2$  (13 mg) and 2-(dimethylamino)ethanol (2.5 ml). The obtained green solid product was purified from the column chromatography which is placed aluminium oxide using only chloroform:methanol (100:1) as solvent system. Yield: 102 mg (50%). Anal. Calcd for  $\text{C}_{104}\text{H}_{144}\text{N}_8\text{O}_{40}\text{Cu}$ : C, 56.53; H, 6.57; N, 5.07%. Found: C, 56.43; H, 6.39; N, 5.24. IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3038 (Ar–H), 2923–2851 (Aliph. C–H), 1602, 1511, 1456, 1440, 1382, 1344, 1262, 1131, 1097, 1031, 834. UV–vis (chloroform):  $\lambda_{\text{max}}/\text{nm}$ : [( $10^{-5}$   $\epsilon$   $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 354 (5.00), 619 (4.68), 689 (5.079)]. MS ( $\text{ES}^+$ ), ( $m/z$ ): 2209 [ $\text{M}$ ] $^+$ .

### 4. Conclusion

In this work, we describe the synthetic procedure and characterization of new metal-free and metallophthalocyanines substituted with 4,5-bis(1,4,7,10-tetraoxacyclododecan-2-ylmethoxy)phthalonitrile. The target symmetrical phthalocyanines were separated by column chromatograph and characterized by

a combination of IR,  $^1\text{H}$  NMR, elemental analysis and MS spectral data. Also, thermal properties of the phthalocyanines were examined by thermogravimetric analysis. Compound **2** indicated the highest stability as compared to other compounds. The solubility in organic solvents increased, because of introducing of crown ether groups into peripheral positions of phthalocyanines. So, good solubility of phthalocyanine in organic solvents is occurring important for technological materials.

### Acknowledgement

This study was supported by the Research Fund of Karadeniz Technical University, project no: 2006.111.002.1, (Trabzon-Turkey).

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