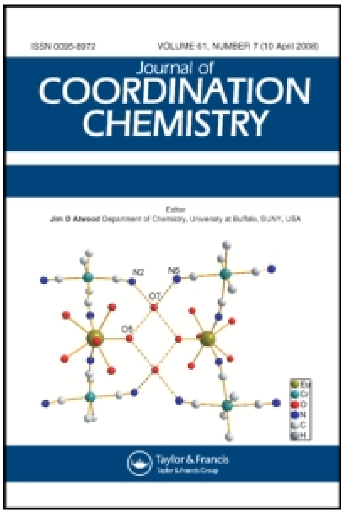

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Microwave-assisted synthesis and characterization of a new metal-free and metallophthalocyanines

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Microwave-assisted synthesis and characterization of a new metal-free and metallophthalocyanines

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Dinitrile monomer (**3**) was synthesized by nucleophilic aromatic substitution of 4-phenoxyphenol (**1**) with 4-nitrophthalonitrile (**2**). The metal-free phthalocyanine (**4**) was prepared by the reaction of dinitrile monomer (**3**) with DMAE. Ni(II), Co(II), and Zn(II) metallophthalocyanines were prepared by the reaction of **3** with chlorides of Ni(II), Co(II), and Zn(II) in DMAE. The new compounds were characterized by IR, ^{1}H- and ^{13}C-NMR, UV-Vis, elemental analysis, and MS specral data.

Keywords: Phthalocyanine; Microwave; Phthalonitrile

1. Introduction

Since their accidental synthesis in 1928, phthalocyanines (Pcs) have been used in dyes, paints, color for metal surface, fabrics, and plastics. Pcs are found in liquid crystals, catalysts, gas sensors, non-linear optics, photosensitizers for photodynamic therapy (PDT) of cancer, thin films, fibrous assemblies, and laser service substances [1–4]. Pcs are generally insoluble in common organic solvents, although their solubility can be improved by incorporation of substituents such as phenoxy, alkyl, or alkoxy of different chain lengths [5, 6] or branched system at peripheral positions [7–12]. The solubility of Pcs is very important for new technological applications as advanced materials, apart from their traditional use as industrial dyes and pigments.

Microwave-promoted organic reactions can accelerate chemical processes with reaction time and energy input reduced in reactions that are run for a long time at high temperatures [13]. Microwave-assisted synthesis of Pcs is rare [14–16].

We previously synthesized Pcs containing long-chain substituents [17] and new soluble metal Pcs containing macrocycle units on the periphery [18]. In this article, we prepare metal-free and metallophthalocyanines bearing phenoxy groups on peripheral positions by microwave irridation and describe the characterization of the new compounds.

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2. Experimental

IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr pellets or NaCl discs. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$ and chemical shifts are reported relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quattro LC/ULTIMA LC–MS/MS spectrometer. Elemental analyses were determined using a LECO Elemental Analyser (CHNS O932) and a Unicam 929 AA spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected. Optical spectra in the UV-Vis region were recorded with a Varian Cary 50 Conc spectrophotometer using 1 cm path length cuvettes at room temperature. 4-Phenoxy-phenol (**1**) [19] and 4-nitrophthalonitrile (**2**) [20] were synthesized according to reported procedures. Commercially available solvents were dried and purified by conventional procedures [21].

2.1. *Preparation of 4-(4-phenoxy-phenoxy)phthalonitrile (3)*

4-Phenoxy-phenol (**1**) (0.75 g, 4.02 mM) was dissolved in dry DMF (15 mL) under N_2 and 4-nitrophthalonitrile (**2**) (0.69 g, 3.90 mM) was added to the solution after stirring for 10 min; finely anhydrous K_2CO_3 (1.65 g, 12.06 mM) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50°C for 3 days. Then the solution was poured into ice water (165 mL) and stirred for 1 day. The precipitate formed was filtered off and dried in vacuum over P_2O_5. The crude product was crystallized from ethanol. Yield: 0.78 g (62%). m.p. 110–112°C. Anal. Calcd for $C_{20}H_{12}N_2O_2$ (%): C, 76.92; H, 3.84; N, 8.97. Found: C, 76.90; H, 3.87; N, 8.94. IR (KBr tablet) $V_{\max}$ (cm^{-1}): 3073 (Ar–H), 2923–2852 (Alip C–H), 2226 (C≡N), 1595, 1497, 1283, 1238, 1191, 875, 754. ^{1}H-NMR ($CDCl_3$) (δ : ppm) 7.75 (s, 1H, Ar–H), 7.40 (d, 1H, Ar–H), 7.26 (d, 1H, Ar–H), 7.08 (m, 6H, Ar–H), 6.95 (d, 3H, Ar–H). ^{13}C-NMR ($CDCl_3$), (δ : ppm): 154.43, 152.61, 133.85, 133.41, 128.99, 128.75, 127.87, 127.81, 126.03, 125.84, 124.75, 123.36, 122.25, 119.75, 118.30, 115.15. MS (FAB), (*m*/*z*): 313 $[M+1]^+$.

2.2. *Preparation of metal-free Pcs (4)*

A mixture of **3** (0.3 g, 0.97 mM), 0.45 mL *n*-penthanol, 0.05 mL 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), and 0.03 mL dry pyridine was placed in a Schlenk tube under N_2 and degassed several times. The temperature was gradually increased to 160°C and stirred for 12 h. After cooling to room temperature, the reaction mixture was refluxed with ethanol (15 mL) to precipitate the product which was washed with hot ethanol and dried in vacuo. The green product was purified by preparative thin layer chromatography using chloroform : methanol (100 : 4) as the solvent system. Yield: 0.045 g (15%) m.p. > 300°C. Anal. Calcd for $C_{80}H_{50}N_8O_8$ (%): C, 76.80; H, 4.00; N, 8.96. Found: C, 76.82; H, 4.02; N, 8.99. IR (KBr tablet) $V_{\max}$(cm^{-1}): 3290 (N–H), 3043 (Ar–H), 2930–2859 (Alip C–H), 1219 (Ar–O–C), 1614, 1487, 1315. ^{1}H-NMR ($CDCl_3$) (δ : ppm) 8.02 (s, 4H, Ar–H), 7.75 (d, 4H, Ar–H), 7.56 (d, 4H, Ar–H), 7.24 (m, 24H, Ar–H), 7.18 (d, 12H, Ar–H). ^{13}C-NMR ($CDCl_3$), (δ : ppm): 158.24, 154.60, 150.12, 130.17, 128.20, 124.52, 123.48, 121.46, 120.98, 118.87, 115.28, 113.43, 110.32, 108.72, 107.88, 105.00. UV-Vis (chloroform): $\lambda_{\max}$ (nm): [$10^{-5}\,\epsilon$ (dm^3 mol^{-1} cm^{-1})]: 255

(5.09), 350 (5.02), 610 (4.48), 645 (4.67), 671 (5.06), 708 (5.12). MS (FAB), (*m*/*z*): 1273 $[M+Na]^+$.

2.3. *Preparation of nickel(II) Pc (5)*

Mixture of **3** (0.1 g, 0.320 mM), anhydrous $NiCl_2$ (0.013 g, 0.1 mM) and 2-(dimethylamino)ethanol (2 mL) were irradiated in a microwave oven at 175°C, 350 W for 5 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 in vacuum. The green solid was purified by preparative thin layer chromatography using chloroform : methanol (100 : 4) as the solvent system. Yield: 0.238 g (57%) m.p. >300°C. Anal. Calcd for $C_{80}H_{48}N_8O_8Ni$ (%): C, 73.50; H, 3.67; N, 8.58. Found: C, 73.58; H, 3.72; N, 8.63. IR (KBr tablet) $V_{max}(cm^{-1})$: 3064 (Ar–H), 2925–2824 (Alip C–H), 1488–1223 (Ar–O–C), 1093, 872, 691. ^{1}H-NMR ($CDCl_3$) (δ : ppm): 7.39 (s, 4H, Ar–H), 7.26 (d, 4H, Ar–H), 7.07 (d, 4H, Ar–H), 7.05 (m, 24H, Ar–H), 7.18 (d, 12H, Ar–H). ^{13}C-NMR ($CDCl_3$), (δ : ppm): 158.01, 157.88, 153.10, 135.66, 130.24, 130.05, 124.62, 124.21, 123.19, 123.27, 122.27, 121.34. 120.78, 120.59, 119.47, 118.63. UV-Vis (chloroform): λ_{max} (nm): $[10^{-5}\ \varepsilon\ (dm^3\ mol^{-1}\ cm^{-1})]$: 242 (5.25), 302 (4.76), 623 (4.96), 677 (5.28). MS (FAB) (*m*/*z*): 1329 $[M+Na]^+$.

2.4. *Preparation of cobalt(II) Pc (6)*

A mixture of **3** (0.1 g, 0.320 mM), anhydrous $CoCl_2$ (0.013 g, 0.1 mM), and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175°C, 350 W for 5 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate product, which was filtered off, washed with hot ethanol and dried in vacuum. The green product was purified by the preparative thin layer chromatography using chloroform : methanol (100 : 4) as the solvent system. Yield: 0.192 g (46%) m.p. > 300°C. Anal. Calcd for $C_{80}H_{48}N_8O_8Co$ (%): C, 73.45; H, 3.67; N, 8.57. Found: C, 73.50; H, 3.70; N, 8.60. IR (KBr tablet) V_{max} (cm^{-1}): 3060 (Ar–H), 2917–2869 (Alip C–H), 1487, 1327, 1221 (Ar–O–C), 1094, 868, 751, 690. UV-Vis (chloroform): λ_{max} (nm): $[10^{-5}\ \varepsilon\ (dm^3\ mol^{-1}\ cm^{-1})]$: 245 (5.00), 326 (4.67), 608 (4.35), 677 (4.89). MS (FAB), (*m*/*z*): 1308 $[M+2]^+$.

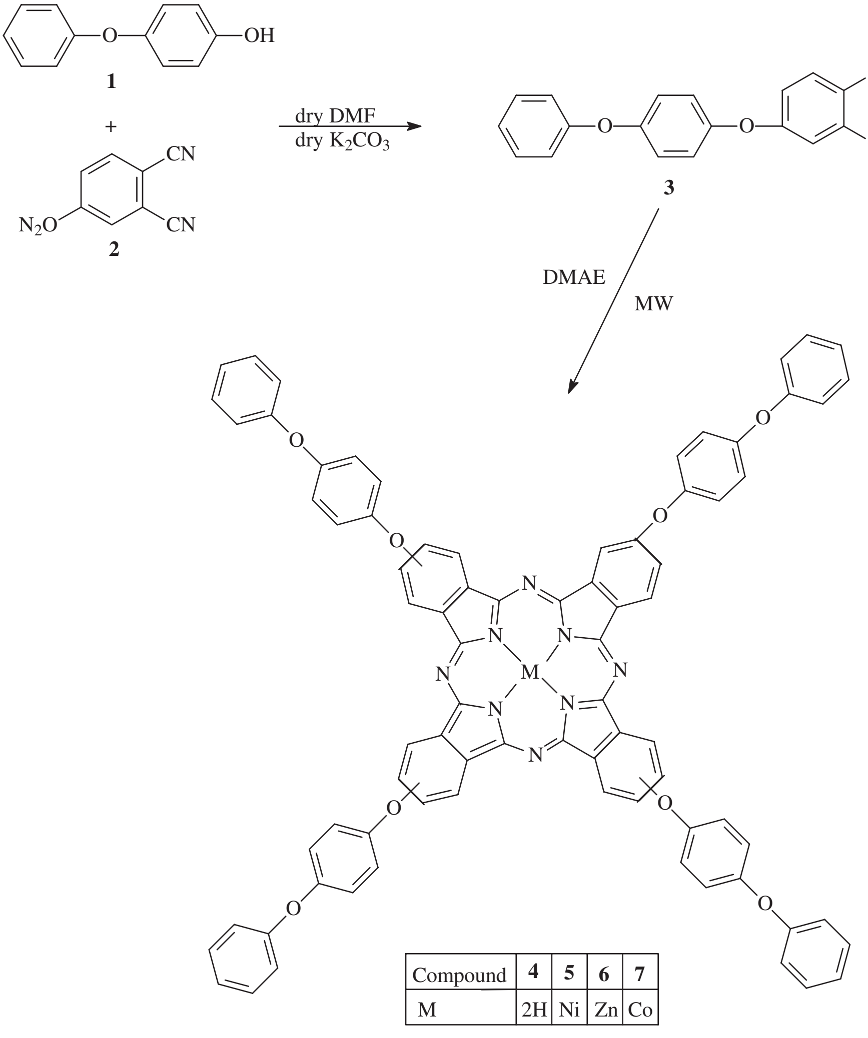
2.5. *Preparation of zinc(II) Pc (7)*

A mixture of **3** (0.1 g, 0.320 mM), anhydrous $ZnCl_2$ (0.013 g, 0.1 mM), and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175°C, 350 W for 5 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate product, which was filtered off, washed with hot ethanol and dried in vacuum. Then the green product was purified by preparative thin layer chromatography using chloroform : methanol (100 : 4) as the solvent system. Yield: 0.2815 g (67%) m.p. > 300°C. Anal. Calcd for $C_{80}H_{48}N_8O_8Zn$ (%): C, 73.11; H, 3.65; N, 8.53. Found: C, 73.20; H, 3.72; N, 8.58. IR (KBr tablet) V_{max} (cm^{-1}): 3038 (Ar–H), 2924–2873 (Alip C–H), 1498, 1487, 1219 (Ar–O–C), 1091, 1043, 945, 744, 690. ^{1}H-NMR ($CDCl_3$) (δ : ppm) 7.36 (s, 4H, Ar–H), 7.29 (d, 4H, Ar–H), 7.25

(m, 24H, Ar–H), 7.01 (d, 12H, Ar–H). ^{13}C-NMR (CDCl$_3$), (δ : ppm): 158.00, 157.61, 157.55, 157.49, 152.88, 151.85, 149.76, 137.10, 129.76, 124.42, 123.05, 122.98, 120.81, 120.40, 118.34, 118.28. UV-Vis (chloroform): $\lambda_{\max}$ (nm): [$10^{-5}\,\varepsilon$ (dm^3 mol^{-1} cm^{-1})]: 245 (4.98), 284 (4.73), 371 (4.66), 617 (4.90), 692 (5.10). MS (FAB), (*m*/*z*): 1314 [M + 1]$^+$.

3. Results and discussion

The mode of preparation of the metal-free Pc (**4**) and metallophthalocyanines (**5–7**) are shown in scheme 1. Compound **3** was prepared by a base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile (**2**) with 4-phenoxy-phenol (**1**) [22].



Compound	**4**	**5**	**6**	**7**
M	2H	Ni	Zn	Co

Scheme 1. The synthesis of the metal-free Pc and metallophthalocyanines.

The reaction was carried out at 50°C in DMF with K_2CO_3 as the base, and the yield was 62%. Metal-free Pc (**4**) was synthesized 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 reflux under argon. The metallophthalocyanines (**5–7**) were obtained from anhydrous metal salts [$NiCl_2$, $CoCl_2$, and $ZnCl_2$] in 2-(dimethylamino)ethanol by microwave irradiation. We used a domestic oven synthesis of **5–7** including 350 W, 175°C.

The IR spectrum of **3** confirmed the disappearance of the NO_2 band of 4-nitrophthalonitrile at 1538 cm^{-1} and appearance of new absorptions at 1090–1020 cm^{-1} belonging to ether. In addition, the disappearance of the OH band at 3338 cm^{-1} gave support for the proposed structure and appearance of C≡N band at 2226 cm^{-1}. ^1H-NMR spectrum of **3** showed new signals at 7.75 (s, 1H, Ar–H), 7.40 (d, 1H, Ar–H), 7.26 (d, 1H, Ar–H), 7.08 (m, 6H, Ar–H), 6.95 (d, 3H, Ar–H) and OH group of **1** disappeared. The proton-decoupled ^{13}C-NMR spectrum of **3** indicated the presence of nitrile carbons in **3** at $\delta = 115$ ppm. The mass spectrum of **3**, which shows a peak at $m/z = 313$ $[M+1]^+$, supports the proposed formula. Elemental analysis confirmed the proposed structure of **3**.

We synthesized metal-free Pc (**4**) by a classical method, not by microwave irradiation. Template effect of metal ions plays an important role in formation of some Pcs [23]; **4** shows characteristic peaks for Pcs: 3290 cm^{-1} is characteristic N–H stretching, 2226 cm^{-1} (C≡N) and 1219 cm^{-1} (Ar–O–C) disappeared in the spectrum of **4**. The ^1H-NMR spectrum of **4** [24] indicates aromatic protons at 8.02, 7.75, 7.56, 7.24, and 7.18 ppm. The MS spectrum of **4** displayed the $[M+Na]^+$ parent ion peak at $m/z = 1273$, confirming the structure. The elemental analysis was satisfactory.

In IR spectra of metallophthalocyanines (**5–7**) the disappearance of strong C≡N stretching vibration of **3** is the evidence for the formation of **5–7**. The rest of the IR spectra of metallophthalocyanines are very similar to those of **4**. ^1H-NMR spectrum of

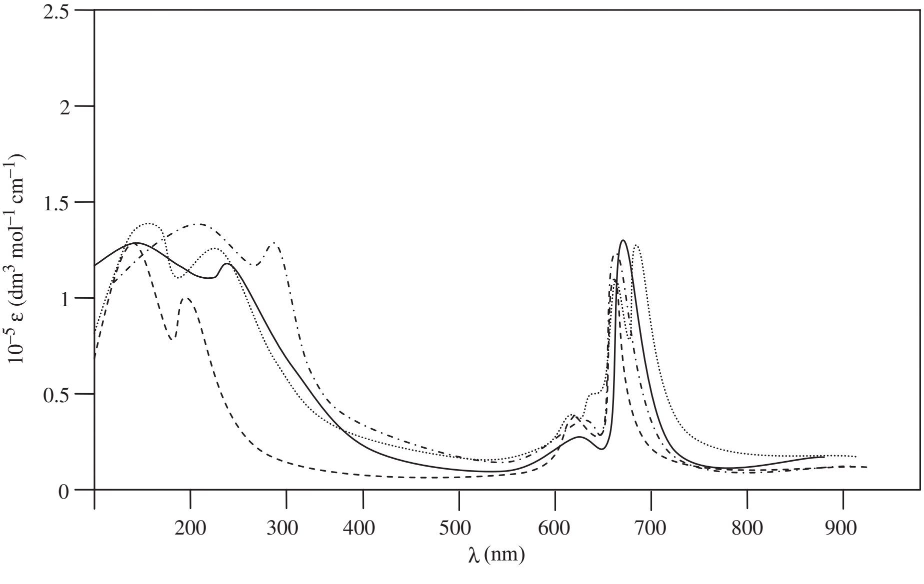


Figure 1. UV-Vis spectra of **4** (. . .), **5** (-···-·), **6** (- - -), and **7** (—) in chloroform.

5–7 are almost identical to those of **4**, except for broad signals in **5** and **7**, from aggregation of planar Pcs at the high concentration used for NMR measurements. ^{1}H-NMR measurement of the cobalt(II) Pc (**6**) was precluded owing to its paramagnetic nature. The mass spectra of Ni(II), Co(II) and Zn(II) Pcs show molecular ion peaks at $m/z = 1329$ $[M + Na]^+$, 1308 $[M + 2]^+$ and 1314 $[M + 1]^+$, respectively, confirming the proposed structures.

In general, Pcs show electronic spectra with two strong absorption regions, one in the UV region at 300–500 nm related to the B band and the other in the visible region at 600–700 nm related to the Q band [25]. Split Q bands in **4** were observed at 671–708 nm (figure 1). These Q-band absorptions show monomeric species with D_{2h} symmetry, due to the Pc ring being fully conjugated 18 π electron system [26, 27]. The UV-Vis absorption spectra of **5–7** (figure 1) show intense Q absorption at $\lambda_{max} = 677$, 677, and 692 nm, with weaker absorptions at 623, 608, and 617 nm, respectively. Single Q bands in **5–7** are characteristic for D_{4h} metallophthalocyanines [28]. Soret region B absorptions of **5–7** were observed at $\lambda_{max} = (242$ and 302), (245 and 326), (245, 284, and 371), respectively.

4. Conclusion

We have prepared metal-free Pc (**4**) and metallophthalocyanines (**5–7**) containing phenoxy groups on peripheral positions. The new dinitrile **3** was obtained from 4-(4-phenoxy-phenoxy) reaction with 4-nitrophthalonitrile in dry DMF under N_2. The metal-free Pc (**4**) was obtained from the reaction of **3** with *n*-penthanol and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The new Ni(II), Co(II), and Zn(II) metallophthalocyanines were prepared by the reaction of **3** with chlorides of Ni(II), Co(II), and Zn(II). The compounds were characterized by elemental analysis and ^{1}H-, ^{13}C-NMR, IR, UV-Vis, and mass spectroscopies.

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