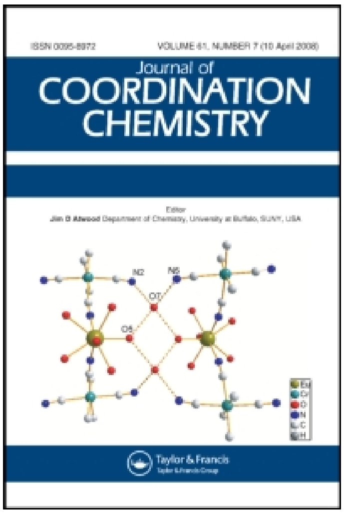

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Synthesis and characterization of octakis(4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy})- substituted metal-free and metallophthalocyanines

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Synthesis and characterization of octakis(4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy})-substituted metal-free and metallophthalocyanines

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The synthesis of octakis(4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}) metal-free (**4**) and metallophthalocyanines (**5**–**8**) were carried out by the cyclotetramerization of a 4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (**3**). Newly substituted octakisphthalocyanines showed enhanced solubility in organic solvents. The new compounds were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and MS spectral data.

Keywords: Synthesis; Cyclotetramerization; 4,5-Dichlorophthalonitrile; Microwave irradiation

1. Introduction

Phthalocyanines with high chemical and thermal stability [1, 2] are used in solar energy conversion [3], electrochromic displays, chemical sensors [4], organic laser materials [5], and optical data storage [6, 7]. In addition, phthalocyanines have been particularly studied in photodynamic therapy (PDT) of cancer [8–12].

Phthalocyanines have a major disadvantage of low solubility in common organic solvents or water [13–15]. Solubility may be enhanced by adding long alkyl, alkoxy, or crown ether groups into peripheral and non-peripheral positions of the phthalocyanine framework [16, 17]. Because of the lower degree of order in the solid state, tetra-substituted phthalocyanines are more soluble than the corresponding octa-substituted ones [17].

Microwave irradiation has been used for the synthesis of phthalocyanines to decrease the reaction time and increase the reaction yield [18–21]. In this article, we describe the synthesis and characterization of metal-free phthalocyanine **4** accomplished in 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) and *n*-pentanol in a Schlenk tube under N_2 and metallo phthalocyanines **5–8** by microwave irradiation containing 4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}-substituents.

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2. Experimental

2-[2-(1-Naphthyloxy)ethoxy]ethanol (**1**) [22] and 4,5-dichlorophthalonitrile (**2**) [23] were prepared according to the literature. All reagents and solvents were of reagent grade, obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [24]. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets. ^{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 internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. 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.

2.1. *Preparation of 4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (3)*

2-[2-(1-Naphthyloxy)ethoxy]ethanol (**1**) (2 g, 8.61 mmol) was dissolved in dry DMF (15 mL) under N_2 and 4,5-dichlorophthalonitrile (**2**) (0.85 g, 4.30 mmol) was added to the solution. After stirring for 15 min, finely ground anhydrous K_2CO_3 (2.07 g, 15.05 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50°C for 72 h and then poured into ice-water (150 mL), and the aqueous phase was extracted with chloroform (3×50 mL). The combined extracts were dried over anhydrous sodium sulfate. The crude product was crystallized from ethanol. Yield: 1.39 g (55%), m.p.: 90–92°C. Anal. Calcd (%) for $C_{36}H_{32}N_2O_6$: C, 73.45; H, 5.48; N, 4.76. Found (%): C, 73.49; H, 5.43; N, 4.75. IR (KBr tablet), ν_{max} (cm^{-1}): 3052 (Ar–H), 2927-2873 (Aliph. C–H), 2232 (C$\equiv$N), 1587, 1495, 1462, 1395, 1312, 1270, 1240, 1131, 1101, 1052, 896, 794, 772, 529. ^{1}H-NMR ($CDCl_3$), (δ: ppm): 8.14 (d, 2H, Ar–H), 7.81 (d, 2H, Ar–H), 7.55 (s, 2H, Ar–H), 7.49–7.35 (m, 8H, Ar–H), 6.80 (d, 2H, Ar–H), 4.32 (t, 8H, CH_2–O), 4.09 (t, 8H, CH_2–O). ^{13}C-NMR ($CDCl_3$), (δ: ppm): 157.93, 154.18, 128.77, 127.56, 126.52, 125.85, 125.38, 125.19, 121.95, 121.72, 117.08, 115.25, 114.53, 104.78, 70.31, 70.03, 69.62, 67.87. MS (ESI$^+$), (m/z): 588 $[M]^+$.

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

4,5-Bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (**3**) (200 mg, 0.34 mmol), DBU (four drop) and dry *n*-pentanol (2.5 mL) were added into a Schlenk tube and then heated and stirred at 160°C for 24 h under N_2. After the reaction mixture cooled, the product was precipitated by adding ethanol. Solid product was filtered and washed with ethanol, water, and diethyl ether. The green product was chromatographed on silica gel with chloroform as eluent. Yield: 70 mg (35%). Anal. Calcd (%) for $C_{144}H_{130}N_8O_{24}$: C, 73.39; H, 5.56; N, 4.75. Found (%): C, 73.42; H, 5.40; N, 4.89. IR (KBr tablet) ν_{max} (cm^{-1}): 3296 (N–H), 3049 (Ar–H), 2923–2846 (Aliph. C–H), 1593, 1580, 1508, 1463, 1397, 1269, 1103, 771, 740. ^{1}H-NMR ($CDCl_3$), (δ: ppm): 8.21 (d, 8H, Ar–H), 7.65 (m, 8H, Ar–H), 7.45–7.32 (m, 40H, Ar–H), 6.53 (d, 8H, Ar–H), 4.31 (m, 32H, CH_2–O), 4.11 (m, 32H, CH_2–O). UV-Vis (chloroform): λ_{max} (nm): $[(10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1})]$: 295 (5.18), 619 (4.75), 637 (4.77), 669 (5.04), 705 (5.07). MS (ESI$^+$), (m/z): 2410 $[M + 3H_2O]^+$.

2.3. *General procedure for metallophthalocyanine derivatives (5–8)*

A mixture of 4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (**3**) (200 mg, 0.34 mmol), anhydrous metal salts [$NiCl_2$ (22 mg), $Zn(CH_3COO)_2$ (31 mg), $CoCl_2$ (22 mg), $CuCl_2$ (23 mg)] and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175°C, 350 W for 10 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 P_2O_5. The obtained green solid product was purified by column chromatography on silica gel with chloroform as eluent.

2.4. *Nickel(II) phthalocyanine (5)*

Yield: 139 mg (68%). Anal. Calcd (%) for $C_{144}H_{128}N_8O_{24}Ni$: C, 71.67; H, 5.35; N, 4.64. Found (%): C, 71.89; H, 5.39; N, 4.72%. IR (KBr) ν_{max} (cm^{-1}): 3049 (Ar–H), 2923–2851 (Aliph. C–H), 1593, 1580, 1468, 1444, 1393, 1349, 1267, 1241, 1135, 1102, 1076, 909, 791, 771. ^{1}H-NMR ($CDCl_3$), (δ: ppm): 8.26 (d, 8H, Ar–H), 7.72 (m, 8H, Ar–H), 7.43–7.30 (m, 40H, Ar–H), 6.72 (d, 8H, Ar–H), 4.28 (m, 32H, CH_2–O), 4.05 (m, 32H, CH_2–O). UV-Vis (chloroform): λ_{max} (nm): [($10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1}$)]: 301 (5.00), 623 (4.60), 673 (5.03). MS (ESI^+), (*m*/*z*): 2414 $[M+H]^+$.

2.5. *Zinc(II) phthalocyanine (6)*

Yield: 148 mg (72%). Anal. Calcd (%) for $C_{144}H_{128}N_8O_{24}Zn$: C, 71.47; H, 5.33; N, 4.63. Found (%): C, 71.30; H, 5.25; N, 4.75. IR (KBr) ν_{max} (cm^{-1}): 3052 (Ar–H), 2923–2873 (Aliph. C–H), 1595, 1577, 1506, 1434, 1391, 1341, 1268, 1171, 1102, 897, 771. ^{1}H-NMR ($CDCl_3$), (δ:ppm): 8.19 (d, 8H, Ar–H), 7.66 (m, 8H, Ar–H), 7.47–7.36 (m, 40H, Ar–H), 6.79 (d, 8H, Ar–H), 4.24 (m, 32H, CH_2–O), 4.03 (m, 32H, CH_2–O). UV-Vis (chloroform): λ_{max} (nm): [($10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1}$)]: 345 (4.95), 629 (4.55), 683 (5.02). MS (ESI^+), (*m*/*z*): 2443 $[M+Na]^+$.

2.6. *Cobalt(II) phthalocyanine (7)*

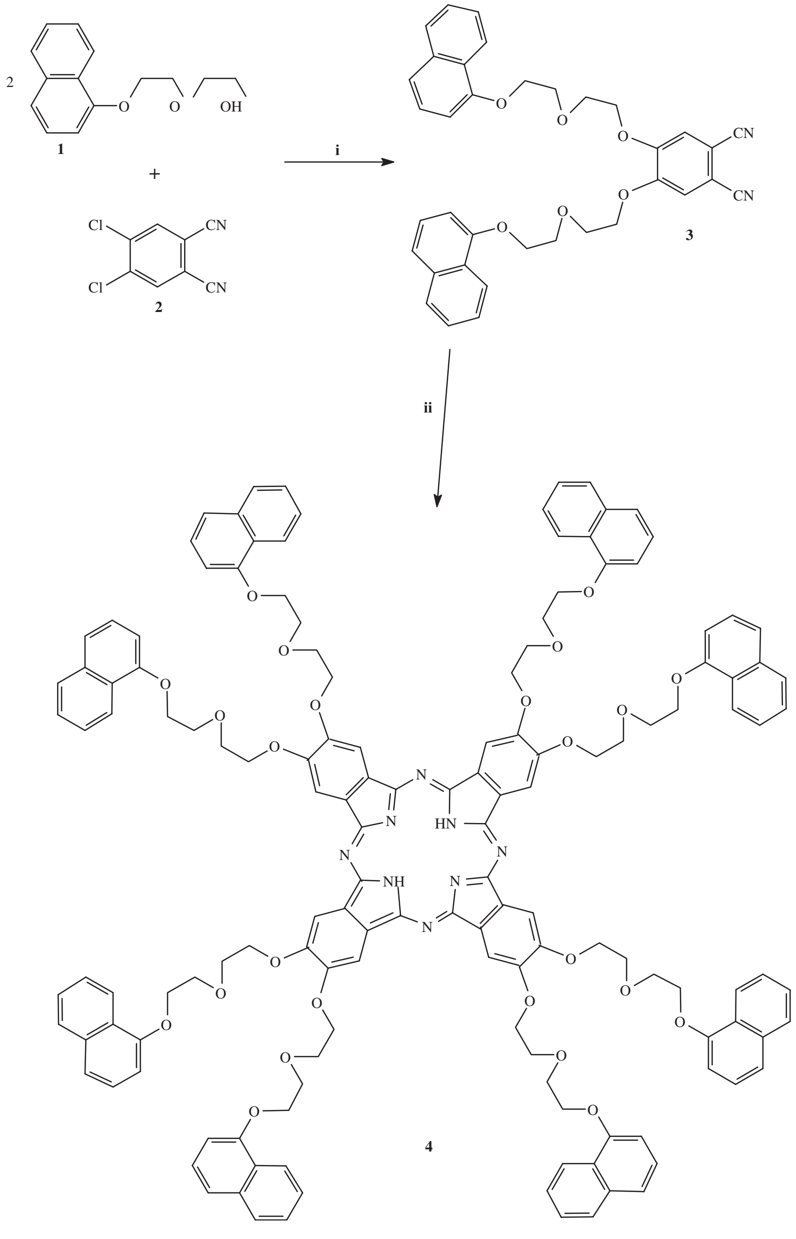
Yield: 125 mg (61%). Anal. Calcd (%) for $C_{144}H_{128}N_8O_{24}Co$: C, 71.66; H, 5.35; N, 4.64. Found (%): C, 71.17; H, 5.30; N, 4.78. IR (KBr) ν_{max} (cm^{-1}): 3049 (Ar–H), 2923–2851 (Aliph. C–H), 1595, 1574, 1519, 1416, 1390, 1265, 1237, 1086, 1073, 964, 886, 750. UV-Vis (chloroform): λ_{max} (nm): [($10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1}$)]: 321 (4.92), 619 (4.59), 675 (4.96). MS (ESI^+), (*m*/*z*): 2414 $[M+H]^+$.

2.7. *Copper(II) phthalocyanine (8)*

Yield: 113 mg (55%). Anal. Calcd (%) for $C_{144}H_{128}N_8O_{24}Cu$: C, 71.52; H, 5.34; N, 4.63. Found (%): C, 71.62; H, 5.26; N, 4.74. IR (KBr) ν_{max} (cm^{-1}): 3052 (Ar–H), 2923–2857 (Aliph. C–H), 1593, 1577, 1464, 1382, 1341, 1264, 1240, 1086, 1064, 946, 842, 768. UV-Vis (chloroform): λ_{max} (nm): [($10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1}$)]: 305 (4.89), 611 (4.57), 677 (4.94). MS (ESI^+), (*m*/*z*): 2419 $[M+H]^+$.

3. Results and discussion

Usually substituted phthalocyanines are synthesized by the cyclotetramerization of substituted phthalonitrile. Starting from 2-[2-(1-naphthyloxy)ethoxy]ethanol (**1**) and 4,5-dichlorophthalonitrile (**2**), the general synthetic routes for the synthesis of new metal-free and metallophthalocyanines are given in schemes 1 and 2. The synthesis

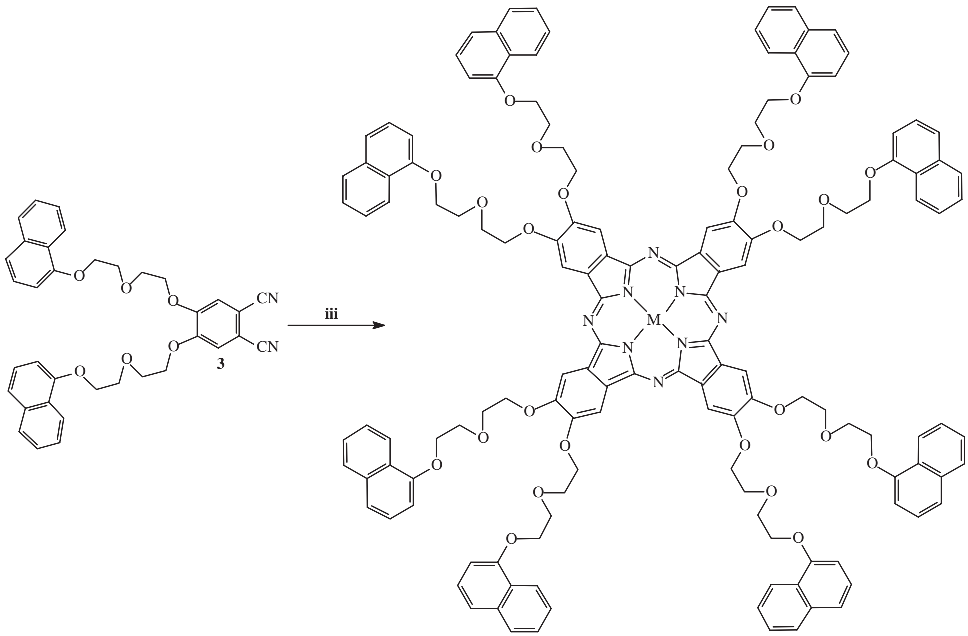


Scheme 1. The synthesis of the metal-free phthalocyanine (**4**). Reagents and conditions: (i) K_2CO_3, N_2, DMF, 50°C, 72 h; (ii) *n*-pentanol, DBU, 160°C, 20 h.

of 4,5-bis{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (**3**) is based on the reaction of 2-[2-(1-naphthyloxy)ethoxy]ethanol (**1**) with 4,5-dichlorophthalonitrile (**2**) (in dry DMF in the presence of dry K_2CO_3 as base, at 50°C in 72 h). The cyclotetramerization of the phthalonitrile derivative **3** to the metal-free phthalocyanine **4** was accomplished in *n*-pentanol in the presence of a few drops of DBU as a strong base at 160°C in a sealed tube. The metallophthalocyanines **5**–**8** were obtained from anhydrous metal salts [$NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$] in 2-(dimethylamino)ethanol by microwave irradiation. The structures were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and MS spectral data.

In the IR spectra, the formation of dinitrile derivative **3** was clearly confirmed by the disappearance of the OH band at 3448 cm^{-1} and the appearance of the C≡N band at 2232 cm^{-1}. The IR spectra of metal-free **4** and metallophthalocyanines **5**–**8** are very similar. The significant difference is the presence of N–H vibrations of the inner phthalocyanine core assigned as a weak vibration at 3296 cm^{-1} in the metal-free compound. After conversion of **3** into the metal-free **4** and metallophthalocyanines **5**–**8**, the sharp peak for the C≡N vibration at 2232 cm^{-1} disappeared.

In the ^{1}H-NMR spectrum of **3**, the signal corresponding to the O–H proton in precursor **1** disappeared as expected. Also, the ^{1}H-NMR spectrum of **3** exhibited signals at $\delta = 8.14$ (d, 2H, Ar–H), 7.81 (d, 2H, Ar–H), 7.55 (s, 2H, Ar–H), 7.49–7.35 (m, 8H, Ar–H), 6.80 (d, 2H, Ar–H) belonging to aromatic protons. The ^{1}H-NMR investigation of **4** provided characteristic chemical shifts for the expected structure except for the inner core N–H protons because of the strong aggregation of



Compound	5	6	7	8
M	Ni	Zn	Co	Cu

Scheme 2. The synthesis of the metallophthalocyanines **5**–**8**. Reagents and conditions: (iii) $NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$, DMAE, 175°C, 350 W.

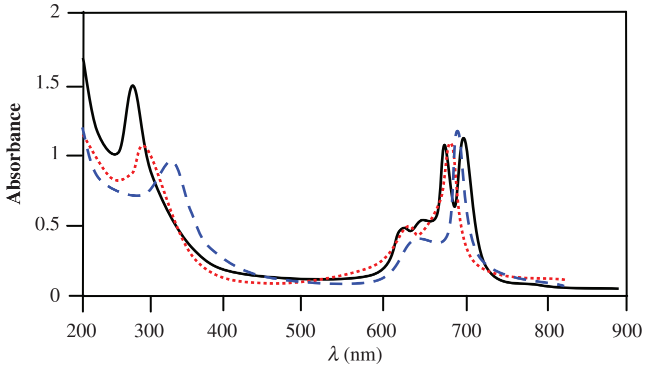


Figure 1. UV-Vis spectra of **4** (—), **5** (···), and **6** (- - -) in chloroform.

the molecules [25]. The ^{1}H-NMR spectrum of **5** exhibited signals at $\delta = 8.26$ (d, 8H, Ar–H), 7.72 (m, 8H, Ar–H), 7.43–7.30 (m, 40H, Ar–H), 6.72 (d, 8H, Ar–H), 4.28 (m, 32H, CH_2–O), 4.05 (m, 32H, CH_2–O) belonging to aromatic and aliphatic protons. In addition, the ^{1}H-NMR spectra of **6** were almost identical with that of **4**. The ^{1}H-NMR measurement of the cobalt(II) and copper(II) phthalocyanines (**7**,**8**) were precluded owing to their paramagnetism.

The best indications for phthalocyanine systems are given by the UV-Vis spectra of **4**–**6** in the solution (figure 1). The UV-Vis spectra of phthalocyanines exhibit characteristic Q and B bands, one in the UV region at 300–350 nm (B band) and the other in the visible part of the spectrum around 600–700 nm (Q band). In the UV-Vis spectrum of metal-free phthalocyanine **4** in chloroform, the characteristic split Q band was observed at 705 and 669 nm. These intense bands indicate monomeric species with D_{2h} symmetry (two intense absorptions around 700 nm) [26]. The lower absorption than the typical split Q bands at 637 and 619 nm are due to the dimeric association for higher aggregates [27]. 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 18π electron system. The UV-Vis absorption spectra of metallophthalocyanines **5**–**8** in chloroform showed the expected absorptions of the Q and B bands appearing (673), (683), (675), (677) and 301, 345, 321, 305 nm for the corresponding compounds **5**, **6**, **7**, and **8**, respectively.

4. Conclusion

In this work, we describe the synthetic procedure and characterization of new metal-free and metallophthalocyanines substituted with octakis(4,5-bis{2-[2-(1-naphthyloxy)-ethoxy]ethoxy}) groups. The target symmetrical phthalocyanines were separated by column chromatograph and characterized by a combination of IR, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, and MS spectral data. When we compared this study with previous study containing 4-(4-phenoxy-phenoxy) groups in peripheral positions, we have shown that the long ethoxy group extends the solubility of phthalocyanines [28] as compared with previous study containing 4-(4-phenoxy-phenoxy) groups [29] in peripheral positions. The solubility of phthalocyanines can be improved by the introduction of substituents such as long ethoxy groups of the molecule [17].

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