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The synthesis, using microwave irradiation and characterization of novel, metal-free and metallophthalocyanines

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ABSTRACT

The synthesis of novel metal-free (**4**) and metallophthalocyanines (**5**, **6**, **7** and **8**) were prepared by cyclotetramerization of a novel 4-[2-(1-naphthyloxy)ethoxy]phthalonitrile (**3**). New substitute phthalocyanines showed the enhanced solubility in organic solvents. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–Vis and MS spectral data.

1. Introduction

Phthalocyanines are one of the major types of tetrapyrrole derivatives showing a wide range of applications in various areas such as semiconductors, nonlinear optics, electro-chromic display devices, liquid crystals, optical storage, photocatalysis [1,2]. The importance of phthalocyanines in many fields, including photodynamic reagents for cancer therapy [3], laser dyes, new red-sensitive photocopying applications [4], is increasing rapidly as a result of the synthesis of new compounds [5].

Metal-free and metallophthalocyanines have a decisive disadvantage for very limited solubility in common organic solvents [6,7]. In order to improve the solubility of phthalocyanines, it is important to reduce its stacking propensity. The solubility of phthalocyanines can be enhanced by introducing different kinds of solubility-enhancing substituents at the peripheral or axial positions of the phthalocyanines core [8]. The solubility of phthalocyanines can be improved by introducing different kinds of substituents, such as long alkyl, alkoxy, phenoxy groups, crown ethers at the periphery of the phthalocyanines [9,10].

Microwave assisted synthesis reduces chemical reactions times from hours to minutes, and also, reduces side reactions, increases the yield, and improves reproducibility. So, microwaves have been previously used for the synthesis of phthalocyanines and include a wider range of references on the topic [11–21]. In this paper, we describe the synthesis and characterization of metal-free phthalocyanine **4** was accomplished in DBU and *n*-pentanol in a Schlenk tube under N_2 atmosphere and metallophthalocyanines **5**, **6**, **7** and **8** by microwave irradiation.

2. Experimental

2-(1-Naphthyloxy)ethanol **1** [22], 4-nitrophthalonitrile **2** [23] were prepared according to the literatures. 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 et al. [24]. The 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 were 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. Electronic spectra in the UV–Vis region were recorded with a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature.

2.1. Synthesis of 4-[2-(1-naphthyloxy)ethoxy]phthalonitrile (3)

2-(1-Naphthyloxy)ethanol **1** (2 g, 10.62 mmol) was dissolved in dry DMF (35 ml) under N_2 atmosphere and 4-nitrophthalonitrile **2** (1.83 g, 10.62 mmol) was added to the solution. After stirring 10 min, finely ground anhydrous K_2CO_3 (4.39 g, 31.86 mmol)

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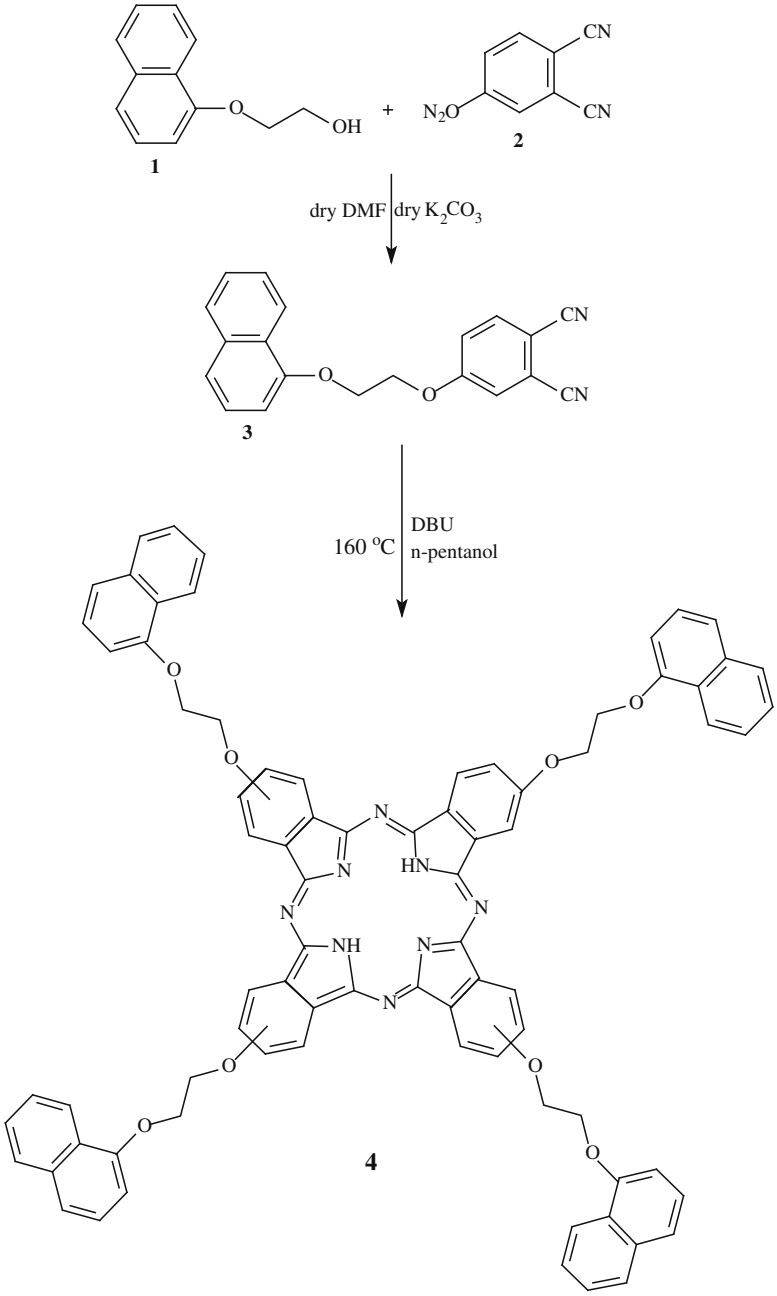
was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50 °C for 72 h. Then the solution was poured into ice-water (100 ml) and was stirred 1 day. Solid product was filtered, washed water and dried in vacuo over P_2O_5. This product was crystallized from ethanol. Yield: 2.23 g (67%), mp: 188–189 °C. IR (NaCl disk), ν_{max}/cm^{-1}: 3071 (Ar–H), 2956–2890 (Aliph. C–H), 2231 (C≡N), 1595, 1577, 1561, 1490, 1397, 1309, 1270, 1253, 1241, 1110, 1039, 883, 791, 780, 522. ^{1}H NMR. ($CDCl_3$), (δ: ppm): 8.26 (d, 1H, Ar–H), 7.84–7.68 (m, 2H, Ar–H), 7.54–7.35 (m, 6H, Ar–H), 6.83 (d, 1H, Ar–H), 4.29 (t, 2H, CH_2–O), 4.12 (t, 2H, CH_2–O). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 156.28, 136.88, 136.50, 130.21, 129.65, 129.54, 128.65, 128.48, 127.81, 127.54, 127.51, 127.30, 123.74, 123.68, 122.74, 121.68, 114.48, 107.07, 71.57, 63.62. MS (ES^+), (m/z): 314 $[M]^+$.

2.2. Metal-free phthalocyanine (**4**)

4-[2-(1-Naphthyloxy)ethoxy]phthalonitrile **3** (300 mg, 0.95 mmol), 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) (5 drop) and dry *n*-pentanol (4 ml) was added in a Schlenk tube and then was heated and stirred at 160 °C for 24 h under N_2. After the reaction mixture was cooled at 30 °C and precipitated by adding ethanol. Solid product was filtered and washed with ethanol, water and diethyl ether. The green solid product was chromatographed on silica gel with chloroform as eluents. Yield: 114 mg (38%). IR (KBr tablet) ν_{max}/cm^{-1}: 3274 (N–H), 3038 (Ar–H), 2921–2851 (Aliph. C–H), 1637, 1595, 1574, 1519, 1461, 1262, 1226, 1091, 1004, 941, 769. ^{1}H NMR ($CDCl_3$), (δ: ppm): 8.19 (m, 4H, Ar–H), 7.64 (m, 8H, Ar–H), 7.43–7.38 (m, 24H, Ar–H), 6.79 (m, 4H, Ar–H), 4.48 (m, 8H, CH_2–O), 4.13 (m, 8H, CH_2–O). ^{13}C NMR. ($CDCl_3$), (δ:



Scheme 1. The synthesis of the metal-free phthalocyanine **4**.

ppm): 155.95, 135.70, 134.43, 132.42, 130.97, 129.85, 128.80, 128.64, 128.31, 127.44, 127.31, 127.18, 126.46, 126.27, 125.77, 121.97, 120.98, 105.01, 68.14, 66.71. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 285 (5.16), 323 (4.97), 621 (4.78), 649 (4.85), 671 (5.10), 707 (5.11). MS (ES^+), (m/z): 1299 $[M+K+H]^+$.

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

A mixture of 4-[2-(1-naphthyloxy)ethoxy]phthalonitrile **3** (300 mg, 0.95 mmol), anhydrous metal salts [$NiCl_2$ (31 mg), $Zn(CH_3COO)_2$ (44 mg), $CoCl_2$ (31 mg), $CuCl_2$ (32 mg)] and 2-(dimethylamino)ethanol (3 ml) was irradiated in a microwave oven at 175 °C, 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 dried in vacuo over P_2O_5. The obtained green solid product was purified from the column chromatography on silica gel with chloroform as eluents.

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

Yield: 195 mg (62%). IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2917–2873 (Aliph. C–H), 1594, 1577, 1463, 1396, 1319, 1267, 1236, 1094, 1064, 960, 770. ^1H NMR ($CDCl_3$), (δ: ppm): 8.18 (d, 4H, Ar–H), 7.78–7.73 (m, 12H, Ar–H), 7.51–7.33 (m, 20H, Ar–H), 6.88 (d, 4H, Ar–H), 4.57 (m, 8H, CH_2–O), 4.23 (m, 8H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ: ppm): 158.01, 135.30, 134.54, 132.42, 130.94, 128.82, 128.76, 128.68, 127.60, 127.42, 126.70, 125.66, 125.52, 121.70, 121.26, 119.73, 119.67, 105.00, 68.17, 66.30. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 284 (5.14), 623 (4.71), 680 (5.08). MS (ES^+), (m/z): 1373 $[M+K+H_2O]^+$.

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

Yield: 219 mg (69%). IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2924–2851 (Aliph. C–H), 1597, 1577, 1459, 1378, 1269, 1121, 1072, 954, 771. ^1H NMR ($CDCl_3$), (δ: ppm): 8.14 (d, 4H, Ar–H), 7.83–7.70 (m, 12H, Ar–H), 7.516–7.31 (m, 20H, Ar–H), 6.88 (d, 4H, Ar–H), 4.57 (m, 8H, CH_2–O), 4.21 (m, 8H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ: ppm): 158.03, 135.31, 134.47, 132.45, 130.95, 129.65, 128.84, 128.74, 127.62, 126.70, 125.66, 125.54, 121.72, 121.30, 119.75, 119.69, 117.90, 105.05, 68.19, 66.33. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 295 (5.11), 351 (4.93), 623 (4.62), 685 (5.10). MS (ES^+), (m/z): 1321 $[M-H]^+$.

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

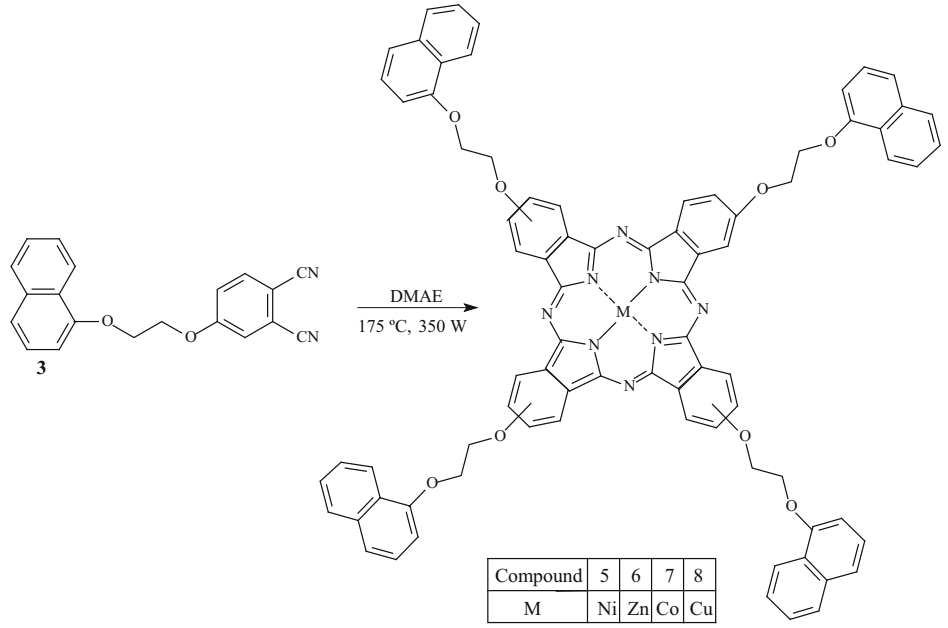
Yield: 205 mg (65%). IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2922–2862 (Aliph. C–H), 1595, 1577, 1462, 1378, 1268, 1237, 1103, 1072, 961, 771. ^1H NMR ($CDCl_3$), (δ: ppm): 8.17 (bs, 4H, Ar–H), 7.85 (m, 12H, Ar–H), 7.66–7.40 (m, 20H, Ar–H), 6.96 (bs, 4H, Ar–H), 4.70 (m, 8H, CH_2–O), 4.38 (m, 8H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ: ppm): 167.79, 135.27, 134.45, 132.40, 130.90, 128.78, 128.68, 128.40, 127.58, 127.38, 126.66, 125.74, 125.50, 121.68, 121.24, 119.70, 119.63, 104.97, 68.13, 66.27. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 290 (5.09), 323 (4.85), 627 (4.63), 681 (5.07). MS (ES^+), (m/z): 1316 $[M]^+$.

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

Yield: 168 mg (57%). IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2950–2884 (Aliph. C–H), 1595, 1577, 1489, 1465, 1397, 1264, 1240, 1109, 790, 774. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 295 (5.04), 321 (4.81), 623 (4.61), 685 (5.08). MS (ES^+), (m/z): 1344 $[M+Na+H]^+$.

3. Results and discussion

Starting from 2-(1-naphthyloxy)ethanol **1** and 4-nitrophthalonitrile **2**, the general synthetic route for the synthesis of new metal-free and metallophthalocyanines are given in Schemes 1 and 2. The synthesis of 4-[2-(1-naphthyloxy)ethoxy]phthalonitrile **3** is based on the reaction of 2-(1-naphthyloxy)ethanol with 4-nitrophthalonitrile (in dry DMF and in the presence of dry K_2CO_3 as base, at 50 °C in 72 h). 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 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at 160 °C in sealed tube. The metallophthalocyanines **5**–**8** were obtained by the anhydrous metal salts [$NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$] in 2-(dimethylamino)ethanol by microwave irradiation. The structures of novel compounds were characterized by IR, ^1H NMR, ^{13}C NMR,



Compound	5	6	7	8
M	Ni	Zn	Co	Cu

Scheme 2. The synthesis of the metallophthalocyanines **5**–**8**.

Table 1
The solubility of phthalocyanines in different solvents.

Compound	Solubility in mg/ml			
	$CHCl_3$	THF	DMF	DMSO
(**4**)	4.6	7.4	8.7	6.4
(**5**)	4.4	7.4	8.6	6.2
(**6**)	4.6	7.5	8.8	6.5
(**7**)	4.5	7.3	8.7	6.3
(**8**)	4.3	7.3	8.5	6.3

UV–Vis and MS spectral data. The solubility of phthalocyanines are summarized in Table 1.

3.1. IR spectra

In the IR spectra, the formation of dinitrile derivative **3** was clearly confirmed by the disappearance of the OH and NO_2 band at 3448 and 1538–1355 cm^{-1} and appearance of the C≡N band at 2231 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 which are assigned to a weak vibration at 3274 cm^{-1} in the metal-free compound. After conversion of the dinitrile derivative **3** into the metal-free **4** and metallophthalocyanines **5–8**, the sharp peak for the C≡N vibration around 2231 cm^{-1} disappeared.

3.2. NMR spectra

In the ^1H NMR spectrum of **3**, the signal corresponding to the O–H proton in the precursor compound **1** disappeared as expected. Also, ^1H NMR spectrum of **3** exhibited signals at $\delta = 8.26$ (d, 1H, Ar–H), 7.84–7.68 (m, 2H, Ar–H), 7.54–7.35 (m, 6H, Ar–H), 6.83 (d, 1H, Ar–H) belonging to aromatic proton. The ^{13}C NMR data are accord with the expected structure. In the ^{13}C NMR spectrum of **3**

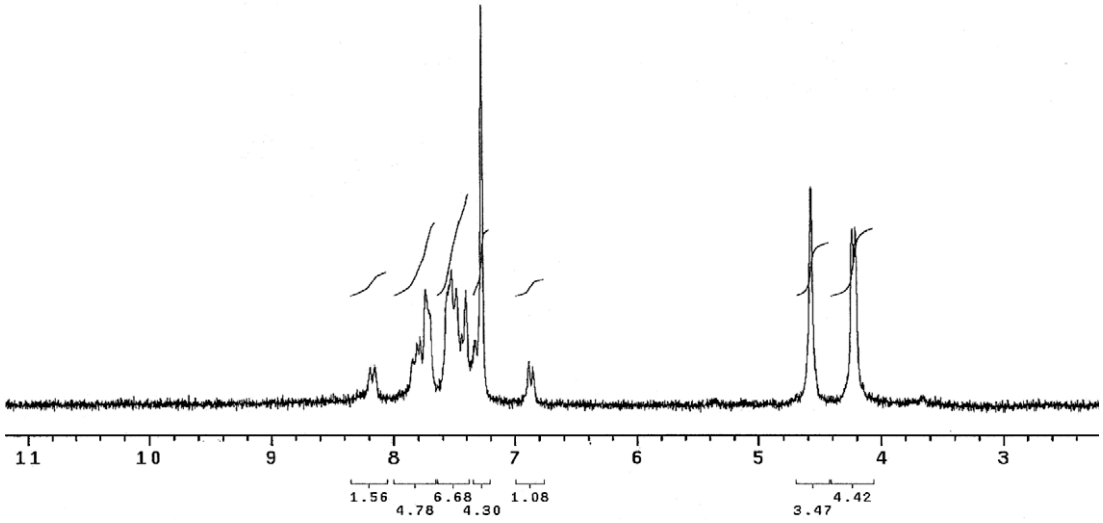


Fig. 1. ^1H NMR spectra of complex **5** in $CDCl_3$.

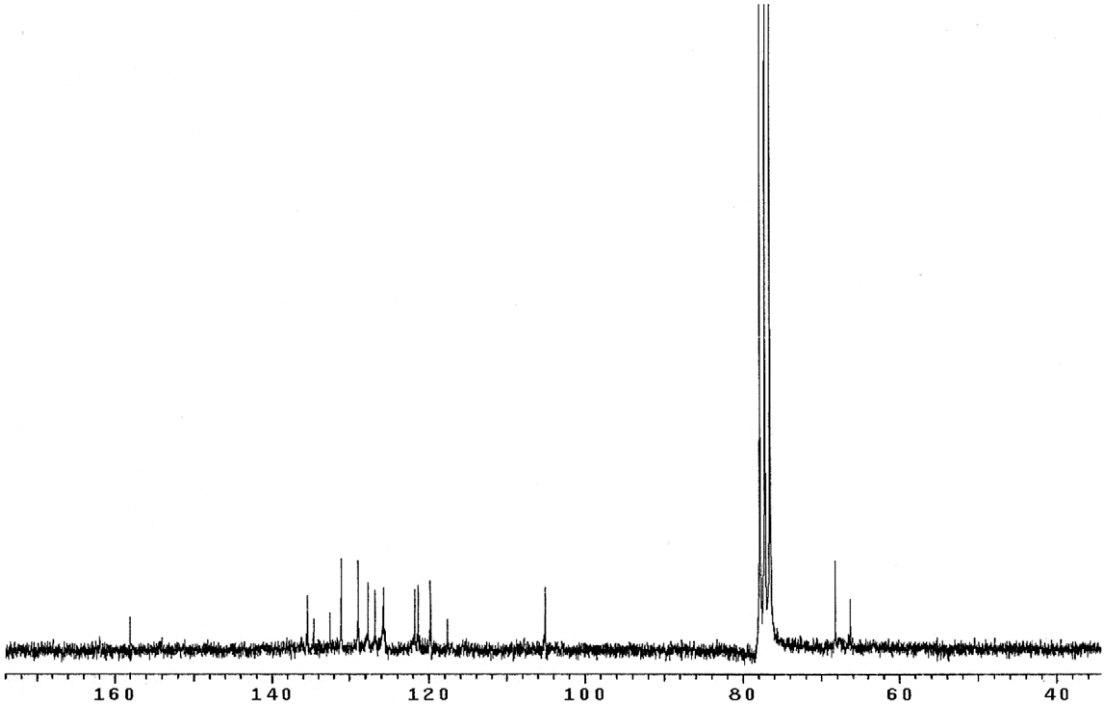


Fig. 2. ^{13}C NMR spectra of complex **5** in $CDCl_3$.

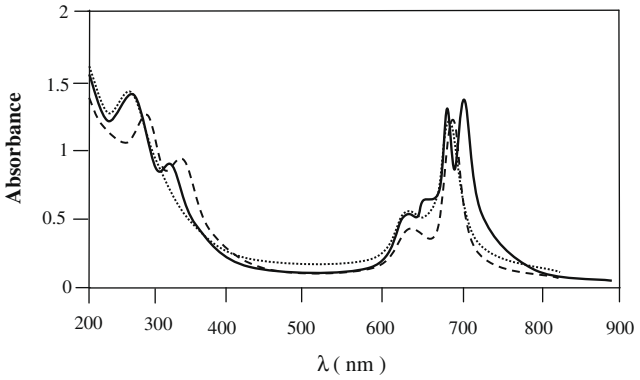


Fig. 3. UV–Vis spectra of compounds **4** (–), **5** (····) and **6** (- - -) in chloroform.

indicated the presence of nitrile carbon atom in **3** at δ = 114.48 ppm. The ^{1}H NMR investigation of compound **4** provided the characteristic chemical shifts for the expected structure except for the inner core N–H protons because of the probable strong aggregation of the molecules [25]. In the ^{13}C NMR spectrum of this compound, all the signals are identical to those of the precursor compound **3** except for the dicyano carbon atoms. In the ^{1}H NMR spectrum of **5** exhibited signals at δ = 8.18 (d, 4H, Ar–H), 7.78–7.73 (m, 12H, Ar–H), 7.51–7.33 (m, 20H, Ar–H), 6.88 (d, 4H, Ar–H), 4.57 (m, 8H, CH_2–O), 4.23 (m, 8H, CH_2–O) belonging to aromatic and aliphatic protons (Fig. 1). In the ^{13}C NMR spectrum of **5** indicated carbon atoms at δ = 158.01, 135.30, 134.54, 132.42, 130.94, 128.82, 128.76, 128.68, 127.60, 127.42, 126.70, 125.66, 125.52, 121.70, 121.26, 119.73, 119.67, 105.00, 68.17, 66.30 (Fig. 2). In addition, ^{1}H NMR and ^{13}C NMR spectra of **6** and **7** were almost identical with that of the compound **4**. ^{1}H NMR measurement of the copper(II) phthalocyanine **8** was precluded owing to its paramagnetic nature.

3.3. UV–Vis spectra

The best indications for phthalocyanine systems are given by their UV–Vis spectra in solution (Fig. 3). UV–Vis spectra of phthalocyanines exhibit characteristic Q and B bands, one of them in the UV region at about 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 with absorptions at 707 and 671 nm which can be attributed $a_{1u} \rightarrow e_g$ transition [26]. A typical spectrum of the metal-free phthalocyanine **4** in chloroform showed a B band region at 323 and 285 nm. The UV–Vis absorption spectra of metallophthalocyanines **5–8** in chloroform showed the expected absorptions at the main peaks of the Q and B bands appearing 680, 685, 681, 685 and 284, (295, 351), (290, 323), (295, 321) nm for the corresponding compounds **5**, **6**, **7** and **8**, respectively.

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References

[1] A. Bilgin, B. Ertem, Y. Gök, Polyhedron 24 (2005) 1117.
[2] J. Simon, T. Toupance, in: D.N. Reinhoudt (Ed.), Comprehensive Supramolecular Chemistry, vol. 10, Pergamon Press, Exeter, 1996.
[3] I. Rosental, Photochem. Photobiol. 53 (1991) 859.
[4] C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines, Properties and Applications, vol. 4, VCH, New York, 1996.
[5] T. Komatsu, K. Ohta, T. Fujimoto, I. Yamamoto, J. Mater. Chem. 4 (1994) 533.
[6] A. Bilgin, B. Ertem, Y. Gök, Supramol. Chem. 18 (2006) 361.
[7] Ö. Bekaroğlu, Appl. Organomet. Chem. 10 (1996) 605.
[8] S. Wie, D. Huang, L. Li, Q. Meng, Dye Pigm. 56 (2003) 1.
[9] Z. Bıyıklıoğlu, H. Kantekin, İ. Acar, Inorg. Chem. Commun. 11 (2008) 1448.
[10] Z. Bıyıklıoğlu, H. Kantekin, Dye Pigm. 80 (2009) 17.
[11] Z. Bıyıklıoğlu, H. Kantekin, M. Özil, J. Organomet. Chem. 692 (2007) 2436.
[12] Z. Bıyıklıoğlu, H. Kantekin, Transition Met. Chem. 32 (2007) 851.
[13] H. Kantekin, Z. Bıyıklıoğlu, Dye Pigm. 77 (2008) 98.
[14] H. Kantekin, Z. Bıyıklıoğlu, Dye Pigm. 77 (2008) 432.
[15] Z. Bıyıklıoğlu, H. Kantekin, J. Organomet. Chem. 693 (2008) 505.
[16] H. Kantekin, G. Dilber, Z. Bıyıklıoğlu, J. Organomet. Chem. 693 (2008) 1038.
[17] Z. Bıyıklıoğlu, H. Kantekin, Polyhedron 27 (2008) 1650.
[18] Z. Bıyıklıoğlu, E.T. Güner, S. Topçu, H. Kantekin, Polyhedron 27 (2008) 1707.
[19] Z. Bıyıklıoğlu, İ. Acar, H. Kantekin, Inorg. Chem. Commun. 11 (2008) 630.
[20] H. Kantekin, Z. Bıyıklıoğlu, E. Çelenk, Inorg. Chem. Commun. 11 (2008) 633.
[21] O. Bekircan, Z. Bıyıklıoğlu, İ. Acar, H. Bektaş, H. Kantekin, J. Organomet. Chem. 693 (2008) 3425.
[22] C. Bolchi, P. Catalano, L. Fumagalli, M. Gobbi, M. Pallavicini, A. Pedretti, A. Villa, G. Vistoli, E. Valoti, Bioorg. Med. Chem. 12 (2004) 4937.
[23] G.J. Young, W. Onyebuagu, J. Org. Chem. 55 (1990) 2155.
[24] D.D. Perin, W.L.F. Armarego, D.R. Perin, Purification of Laboratory Chemicals, 2nd ed., Pergamon Press, New York, 1985.
[25] C.F. van Nostrum, S.J. Picken, A.J. Schouten, R.J.M. Nolte, J. Am. Chem. Soc. 117 (1995) 9957.
[26] K.R.V. Reddy, J. Keshavayya, Dye Pigm. 53 (2002) 187.