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Microwave-assisted synthesis and characterization of the monomeric phthalocyanines containing naphthalene-amide group moieties and the polymeric phthalocyanines containing oxa-aza bridge

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Abstract

New naphthalene-amide substituted phthalocyanines and oxa-aza bridge polymeric phthalocyanines were prepared by conventional and microwave methods. The chlorides of Cu(I), Ni(II) and Co(II) were employed in order to synthesize the corresponding metal phthalocyanines and $Zn(CH_3COO)_2$ was used for the preparation of the zinc phthalocyanines. For the preparation of the Co-containing phthalocyanines, ammonium molybdate had to be added as catalyst. In the microwave-assisted synthesis, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or DMAE (dimethylaminoethanol) was used as a solvent. The solubility of the phthalocyanines containing naphthalene-amide group (**1a**–**e**, **3a**–**e**) is low in ethanol, ethyl acetate, chloroform, DMF and DMSO. Polymeric phthalocyanines (**2a**–**e**) are not soluble in common organic solvents such as chloroform, DMF and DMSO but are soluble in dilute H_2SO_4.

Keywords: Microwave; Polymeric phthalocyanines; Complexes; Synthesis

1. Introduction

High-speed synthesis with microwave irradiation has attracted a considerable amount of attention in recent years [1]. Microwave irradiation is an electromagnetic irradiation in the frequency range of 0.3–300 GHz. The energy of the microwave photon in this frequency region (0.0016 eV) is too low to break chemical bonds and is also lower than the energy of Brownian motion. It is therefore clear that microwave cannot induce chemical reactions [2–4].

Phthalocyanines have been intensively investigated since their first synthesis in 1907, and intensively used as blue and green dyestuffs due to their unique properties of being very stable against thermal or chemical decomposition and very intense optical absorption in the visible region [5–7].

Our previous contributions describing a series of phthalocyanines with aza, [8–10] oxa-thia [11–14] and triazol-5-on [15] macrocycles reported enhanced solubility of the product with bulky macrocycles on the periphery.

In this study, the monomeric phthalocyanines with four naphthalene-amide substituents and oxa-aza bridge polymeric phthalocyanines were prepared by conventional and microwave methods.

2. Results and discussion

The first step in the synthetic procedure was to obtain phthalonitrile derivatives containing naphthalene-amide group. The general route for the synthesis of the new phthalocyanines is shown in Scheme 1. This was accomplished by a base

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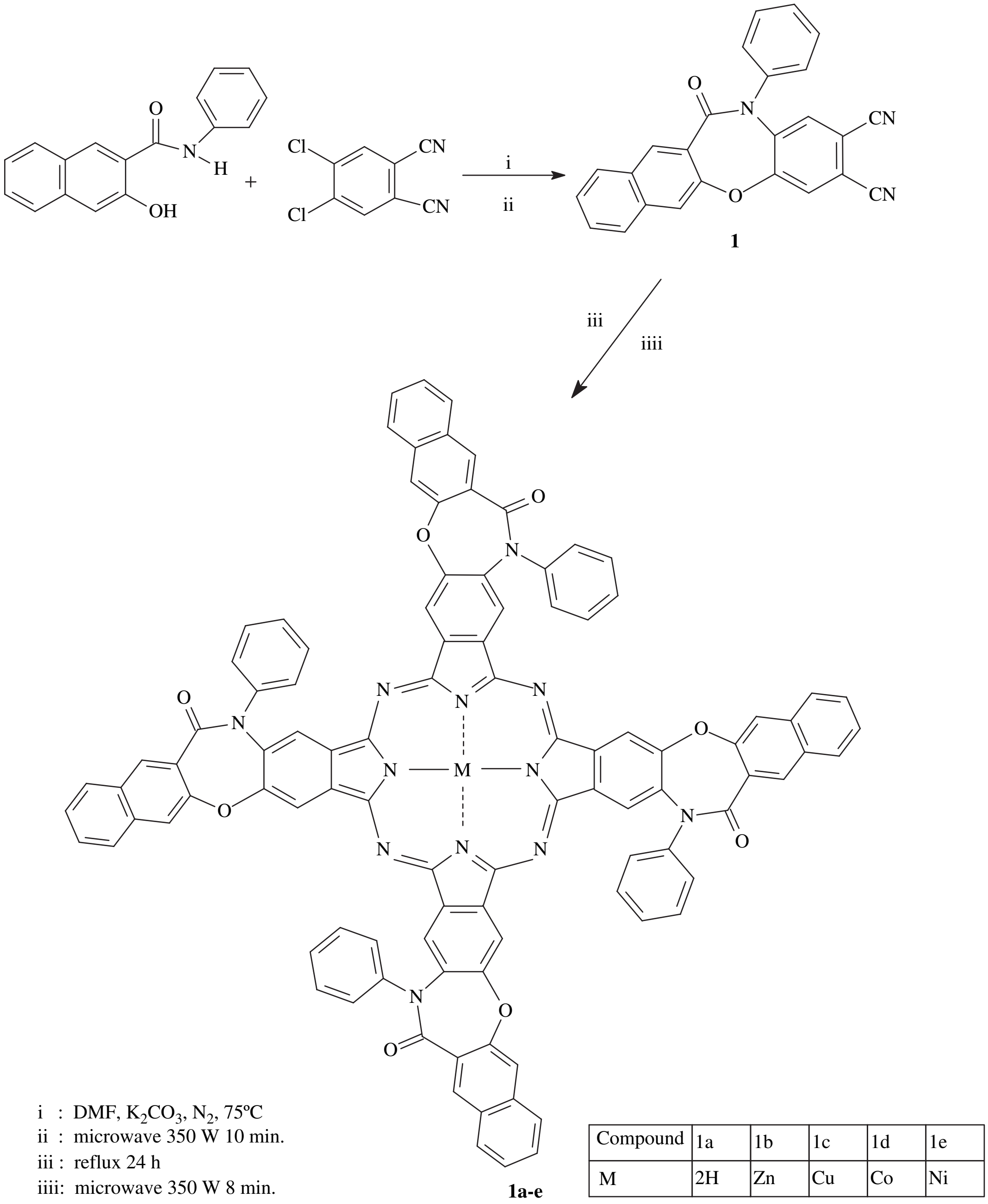


i : DMF, K_2CO_3, N_2, 75°C
ii : microwave 350 W 10 min.
iii : reflux 24 h
iiii: microwave 350 W 8 min.

Compound	1a	1b	1c	1d	1e
M	2H	Zn	Cu	Co	Ni

Scheme 1. Synthesis of ligands and complexes.

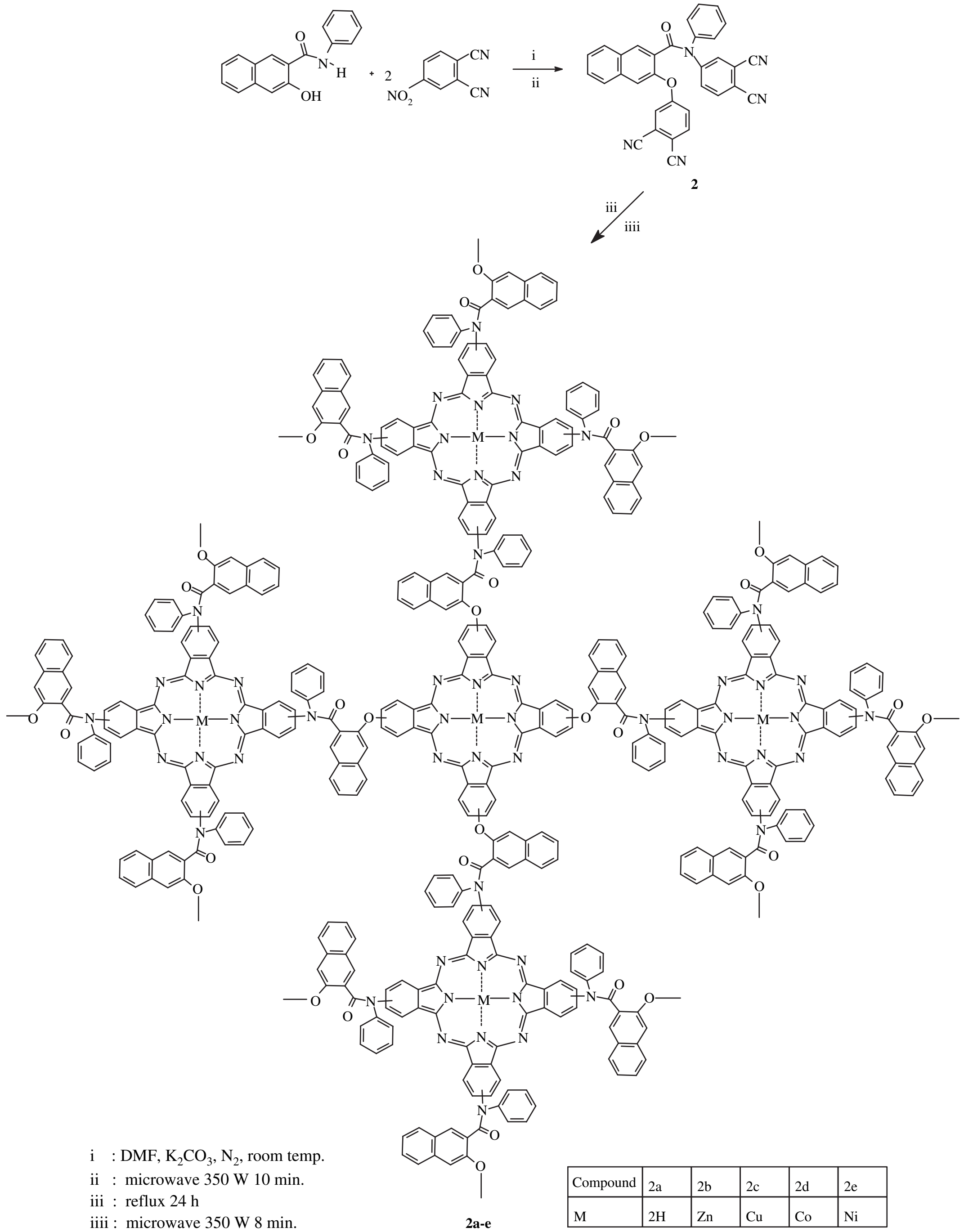
catalyzed nucleophilic aromatic dichloro displacement of 4,5-dichlorophthalonitrile with 3-hydroxy-2-naphthoic acid anilide [16]. This reaction was carried out at 75 °C in DMF with K_2CO_3 as the base and the yield (**1**) was moderate. In addition to this, the reaction was also carried out by using microwave method in DMAE at 350 W for 10 min. In this method the yield was more than the conventional method and also the reaction time was reduced from 48 h to 10 min.

The metal-free derivative (H_2Pc) (**1a**) was obtained directly by the reaction of phthalonitrile (**1**) with amyl alcohol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

Cyclotetramerization of phthalonitrile in the presence of metal salts by two different methods gave the metal phthalocyanines (**1b**–**e**) .The solvents used for conventional method were quinoline for Zn(II) (**1b**), *N*,*N*-dimethylaminoethanol (DMAE) for Cu(I) (**1c**), ethyleneglycol for Co(II) (**1d**) and quinoline for Ni(II) (**1e**). In these reactions we used different solvents which were more useful for obtaining more yields in shorter times. In the microwave-assisted method, the reactions of **1a**–**e** were accomplished in DMAE at 350 W for 8 min. The solubility of the phthalocyanines was low in common organic solvents such as ethyl acetate, chloroform, DMSO and DMF.

For this reason, the ^{13}C NMR spectra of these phthalocyanines could not be obtained in DMSO-d_6 or $CDCl_3$.

The second step of the synthetic procedure was to obtain the oxa-aza bridge polymeric phthalocyanines (**2a**–**e**) and other



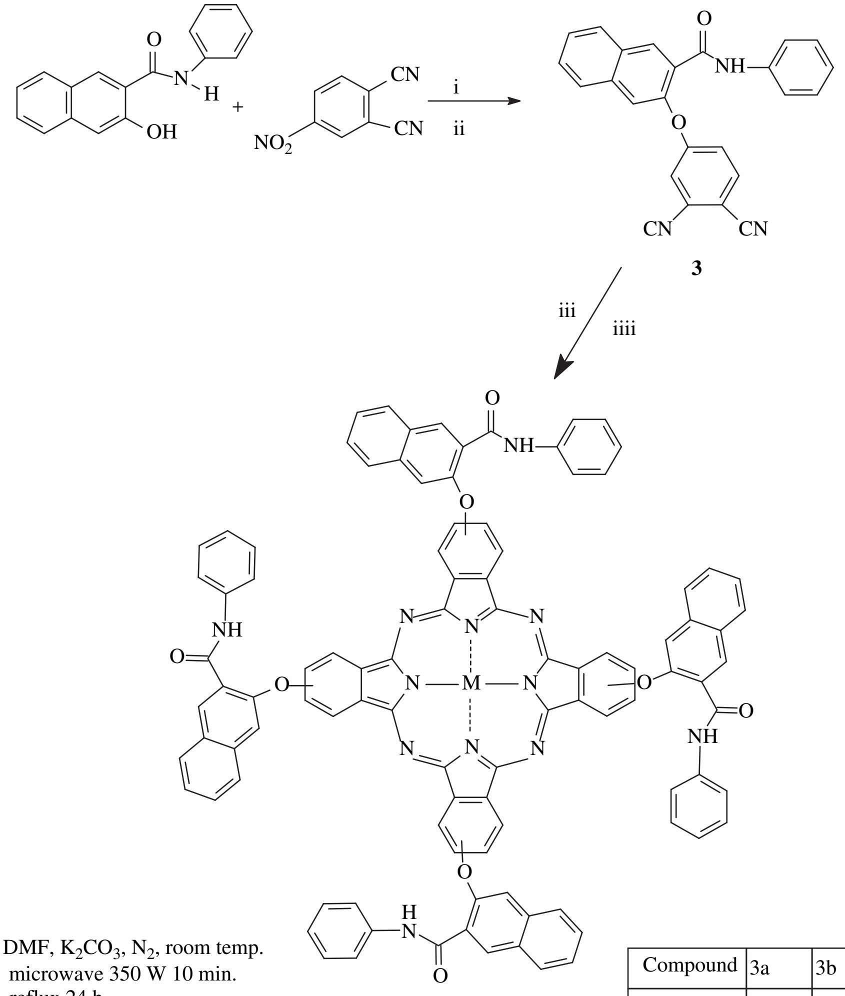
i : DMF, K_2CO_3, N_2, room temp.
ii : microwave 350 W 10 min.
iii : reflux 24 h
iiii : microwave 350 W 8 min.

Compound	2a	2b	2c	2d	2e
M	2H	Zn	Cu	Co	Ni

Scheme 2. Synthesis of ligands and complexes.

phthalocyanines containing naphthalene-amide group (**3a**–**e**). The general route for the synthesis of the new phthalocyanines is shown in Schemes 2 and 3. These were accomplished by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with 3-hydroxy-2-naphthoic acid anilide [17]. This reaction was carried out at room temperature in DMF with K_2CO_3 as the base. Then the obtained product was washed with hot ethanol. Product **2** is insoluble in hot ethanol although product **3** is soluble in hot ethanol. Compound **2** was obtained by the substitution reaction of the H atoms of NH and OH groups of the 3-hydroxy-2-naphthoic acid anilide with 4-nitrophthalonitrile and this product is insoluble in hot ethanol. Compound **3** was obtained by the substitution reaction of the H atom only OH group of the 3-hydroxy-2-naphthoic acid anilide with 4-nitrophthalonitrile. Due to the hydrogen bonding between NH group and ethanol this product is soluble in hot ethanol. The yields of compound **2** and compound **3** were 36.73% and 44.25%, respectively. In addition, this reaction was also carried out by microwave-assisted method in DMF at 350 W for 10 min.

The metal-free phthalocyanines (**2a**, **3a**) were synthesized by heating a mixture of the dicyano compounds (**2**, **3**) with amyl alcohol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)



i : DMF, K_2CO_3, N_2, room temp.
ii : microwave 350 W 10 min.
iii : reflux 24 h
iiii : microwave 350 W 8 min.

Compound	3a	3b	3c	3d	3e
M	2H	Zn	Cu	Co	Ni

Scheme 3. Synthesis of ligands and complexes.

in the absence of solvent. The metallophthalocyanines (**2b**–**e**, **3b**–**e**) were prepared from the corresponding dicyano derivatives and the metal salts in high boiling anhydrous solvents such as ethyleneglycol and quinoline. In the microwave-assisted method, the reactions were accomplished in DMAE at 350 W for 8 min. The yields were satisfactory and depended upon the transition metal ion. The decomposition temperatures of the obtained phthalocyanines were higher than 200 °C.

Metal-free phthalocyanines (**1a**, **3a**) and metallophthalocyanines (**1b**–**e**, **3b**–**e**) are less soluble in dimethylformamide, dimethylsulfoxide and sulfuric acid. The most evident feature of metal-free phthalocyanine (**2a**) polymer and metallophthalocyanines (**2b**–**e**) polymers is that they are not soluble in common organic solvents such as chloroform, dichloromethane, ethanol, dimethylformamide and dimethylsulfoxide but are rather soluble in dilute H_2SO_4.

The elemental analytical results of the starting materials and phthalocyanines show good agreement with the calculated values (given in Table 1). Characterization of the products involved a combination of methods including elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and UV/vis spectroscopic techniques.

2.1. UV spectra

UV/vis spectra of the phthalocyanine systems exhibit characteristic Q and B bands. The phthalocyanines (**1a**–**e**, **2a**–**e** and **3a**–**e**) show typical electronic spectra with two strong absorption regions, one of them in the UV at about 270–367 nm (B band) and the other in the visible region at 670–711 nm (Q band) [18].

2.2. IR spectra

Spectral investigations of the newly synthesized intermediates and phthalocyanines are in accordance with the proposed structures. Comparison of the IR spectra of each step gave some information as to the nature of the products. In this context, comparison of the IR spectral data clearly indicated the formation of compound **1** by the disappearance of the NH band at about 3300 cm^{-1}, the OH band at about 3500 cm^{-1} in 3-hydroxy-2-naphthoic acid anilide and the appearance of a new CN band at about 2237 cm^{-1} in 12,13-dihydro-12-oxo-13-phenylbenzo[*b*]naphth[*f*][1,4]-oxazepine-2,3-dicarbonitrile

Table 1
Elemental analyses data for the starting materials and the phthalocyanines

Compound	Formula	Molecular weight	Calculation (%)			Found (%)			Yield (%) method		Mp (°C)
			C	H	N	C	H	N	A	B	
1	$C_{25}H_8 N_3O_2$	382.4	78.53	2.11	10.99	78.52	2.12	10.97	46	49	253
2	$C_{33}H_{17} N_5O_3$	515.53	76.88	3.32	13.59	76.79	3.34	13.51	37	44	213
3	$C_{25}H_{13} N_3O_2$	387.40	77.51	3.38	8.26	77.42	3.31	8.27	44	48	140
1a	$C_{100}H_{54}N_{12}O_8$	1551.6	77.41	3.51	10.83	7.38	3.56	10.78	13	17	(200)[a]
1b	$C_{100}H_{52}N_{12}O_8Zn$	1614.9	74.37	3.25	10.41	74.35	3.26	10.43	20	38	(200)[a]
1c	$C_{100}H_{52}N_{12}O_8Cu$	1613.1	74.46	3.25	10.42	74.48	3.28	10.36	60	64	(200)[a]
1d	$C_{100}H_{52}N_{12}O_8Co$	1608.5	74.67	3.26	10.45	74.64	3.28	10.41	6	11	(200)[a]
1e	$C_{100}H_{52}N_{12}O_8Ni$	1608.3	74.46	3.25	10.42	74.46	3.28	10.43	11	22	(200)[a]
2a	$C_{132}H_{70}N_{20}O_8$	2062.1	76.81	3.42	13.57	76.84	3.41	13.53	27	36	(200)[a]
2b	$C_{132}H_{68}N_{20}O_8Zn$	2127.5	74.52	3.22	13.17	74.50	3.25	13.18	34	44	(200)[a]
2c	$C_{132}H_{68}N_{20}O_8Cu$	2125.7	74.59	3.22	13.18	74.61	73.22	13.15	42	58	(200)[a]
2d	$C_{132}H_{68}N_{20}O_8Co$	2121.1	74.75	3.23	13.21	74.71	3.24	13.19	50	68	(200)[a]
2e	$C_{132}H_{68}N_{20}O_8Ni$	2120.8	74.56	3.23	13.21	74.55	3.21	13.23	24	32	(200)[a]
3a	$C_{100}H_{62}N_{12}O_8$	1559.7	77.01	4.01	10.78	76.98	4.03	10.74	36	46	(200)[a]
3b	$C_{100}H_{60}N_{12}O_8Zn$	1623.1	74.00	3.73	10.36	74.02	3.69	10.32	44	55	(200)[a]
3c	$C_{100}H_{60}N_{12}O_8Cu$	1621.2	74.09	3.73	10.37	74.11	3.70	10.38	51	64	(200)[a]
3d	$C_{100}H_{60}N_{12}O_8Co$	1616.6	74.29	3.74	10.40	74.27	3.75	10.40	43	63	(200)[a]
3e	$C_{100}H_{60}N_{12}O_8Ni$	1616.3	74.31	3.74	10.40	74.28	3.71	10.38	35	61	(200)[a]

[a] Decomposition point, method A: conventional; method B: microwave irradiation.

(**1**). In the IR spectra of **1** the strong absorption band at 2237 cm^{-1} (CN) corresponding to the CN groups disappears [17] after its conversion to the metal-free phthalocyanine (**1a**) and metallophthalocyanines (**1b–e**).

The only difference is the presence of NH band vibration assigned to a band at 3410 cm^{-1}, in the free phthalocyanine (**1a**). This band was absent in the spectra of the metal complexes. The M–N vibrations were expected to appear at 100–400 cm^{-1} but they were not observed in KBr pellets [19].

The IR spectra of **2** clearly indicated the formation of **2** by the disappearance of the NH band at about 3300 cm^{-1}, the OH band at about 3500 cm^{-1} in 3-hydroxy-2-naphthoic acid anilide and the appearance of a new CN band at about 2230 cm^{-1} in 3-(3,4-dicyanophenoxy)-*N*-phenyl-*N*-(3,4-dicyanophenyl)-2-naphthamide (**2**). The IR spectra of the metal-free (**2a**) and metal polymeric phthalocyanines (**2b–e**) were also very similar. In the IR spectrum of metal-free polymeric phthalocyanine (**2a**), the only difference was the presence of NH band at 3410 cm^{-1}. This band was absent in the spectra of the metal complexes (**2b–e**).

The IR spectra of **3** indicated the formation of **3** by the disappearance of the OH band at about 3500 cm^{-1} in 3-hydroxy-2-naphthoic acid anilide although clearly appearance of the NH band at about 3300 cm^{-1} and the appearance of new CN band at about 2229 cm^{-1} in 3-(3,4-dicyanophenoxy)-*N*-phenyl-2-naphthamide (**3**) are seen. The intense absorption band of **3** at 2229 cm^{-1} corresponding to the CN group disappeared after its conversion into the phthalocyanines (**3a–e**). The band around 3350 cm^{-1} for **3a** can be attributed to the NH stretching frequency of the inner core of the metal-free phthalocyanine.

All the IR spectral data of the newly synthesized intermediates and phthalocyanines were in accordance with the proposed structures.

2.3. NMR spectra

^1H NMR spectra are also consistent with the proposed structures. In the ^1H NMR spectrum of **1**, aromatic protons such as multiplet at 7.37–8.52 ppm was assigned on the basis of the results of previous work on macrocyclic ligands. ^{13}C NMR spectrum of **1** shows signals at 112.24, 112.56, 115.11 (CN), 117.05 (CN), 125.01, 127.12, 129.25, 135.65, 140.49, 140.66, 155.01, 165.01 (C=O) ppm [17].

NMR spectrum of **2** indicated the formation of **2** by the disappearance of OH and NH groups' peaks in 3-hydroxy-2-naphthoic acid anilide, aromatic protons were observed as a multiplet at 7.31–8.31 ppm. ^{13}C NMR spectrum of **2** shows signals for aromatic C=O and CN carbons at 164.12, 122.03, and 122.21 ppm.

In the ^1H NMR spectrum of **3** the singlet at 10.71 ppm clearly indicated the appearance of NH group. Aromatic protons were observed as a multiplet at 7.12–8.53 ppm. The ^{13}C NMR spectrum of **3** shows signals at 118.03 (CN), 128.20–130.32 (Ar) and 160.02 (C=O).

^{13}C NMR data of all phthalocyanines have not been obtained because the solubility of these compounds was very low in deuterated solvents such as $CDCl_3$, C_6D_6 and DMSO-d_6.

3. Experimental

4,5-Dichlorophthalonitrile [20], 4-nitrophthalonitrile [21] and 12,13-dihydro-12-oxo-13-phenylbenzo[*b*]naphth[*f*][1,4]-oxazepine-2,3-dicarbonitrile [17] (**1**) were synthesized according to the reported procedures.

IR spectra were recorded on Jasco FT/IR/430 Fourier Transform Infrared Spectrometer as KBr pellets. UV/vis spectra were recorded on Mattson UNICAM UV/vis spectrometer.

^{1}H NMR and ^{13}C NMR studies were done on Brucker AC-200 FT-200 FT-NMR spectrometer. Elemental analyses were performed by the Instrumental Analyses Laboratory of the TÜBİTAK Gebze Research Center and Atatürk University, Department of Chemistry.

3.1. 12,13-Dihydro-12-oxo-13-phenylbenzo[b]-naphth[f][1,4]-oxazepine-2,3-dicarbonitrile (*1*)

3.1.1. Method A

12,13-Dihydro-12-oxo-13-phenylbenzo[*b*]naphth[*f*][1,4]-oxazepine-2,3-dicarbonitrile (**1**) was synthesized according to the reported procedures [17].

3.1.2. Method B

3-Hydroxy-2-naphthoic acid anilide (12.4 g, 47.1 mmol), 4,5-dichlorophthalonitrile (8 g, 40.6 mmol), finely ground anhydrous K_2CO_3 (13 g, 94.2 mmol) and dry dimethylformamide (20 mL) were also irradiated in a microwave oven at 350 W for 10 min. Above purification method was also applied to this material. The yield was more than in Section 3.1.1. Yield: 8.90 g, 48.77%.

3.2. Metal-free phthalocyanine (*1a*)

3.2.1. Method A

A mixture of compound **1** (1 g, 2.61 mmol), amyl alcohol (25 mL) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (1 mL) was gently heated to 200 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL). This compound is less soluble in $CHCl_3$, DMF and DMSO. Yield: 0.13 g, 12.98%. λ_{max} (DMSO)/nm: 356, 671 (shoulder), 689. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 7.25–8.02 (53H, m, Ar). FTIR ν_{max}/cm^{-1}: 3410 (NH), 3058 (Ar–CH), 1664 (C=O), 1292 (C–O–C).

3.2.2. Method B (microwave-assisted synthesis method for metal-free phthalocyanine)

A mixture of compound **1** (1 g, 2.61 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. Then it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL) and dried. The yield was more than in Section 3.2.1. Yield: 0.17 g, 16.98%.

3.3. Zinc(II) phthalocyanine (*1b*)

3.3.1. Method A

A mixture of compound **1** (1 g, 2.61 mmol), anhydrous $Zn(CH_3COO)_2$ (0.20 g, 1.09 mmol) and dry quinoline (25 mL) was heated to 180 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL). This compound is less soluble in $CHCl_3$, DMF and DMSO. Yield: 0.21 g, 19.87%. λ_{max} (DMSO)/nm: 367, 688. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 7.10–8.12 ppm (52H, m, Ar). FTIR ν_{max}/cm^{-1}: 3056 (Ar–CH), 1657 (C=O), 1296 (C–O–C).

3.3.2. Method B

A mixture of compound **1** (1 g, 2.61 mmol), anhydrous $Zn(CH_3COO)_2$ (0.20 g, 1.09 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. Then it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL) and dried. The yield was more than in Section 3.3.1. Yield: 0.41 g, 38.46%.

3.4. Copper(I) phthalocyanine (*1c*)

3.4.1. Method A

A mixture of compound **1** (0.75 g, 1.96 mmol), anhydrous CuCl (0.25 g, 2.52 mmol) and *N*,*N*-dimethylaminoethanol (25 mL) was heated to 180 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL). This compound is less soluble in $CHCl_3$, DMF and DMSO. Yield: 0.48 g, 60.00%. λ_{max} (DMSO)/nm: 284, 707. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 7.34–8.42 (52H, m, Ar). FTIR ν_{max}/cm^{-1}: 3052 (Ar–CH), 1592 (C=O), 1295 (C–O–C).

3.4.2. Method B

A mixture of compound **1** (0.75 g, 1.96 mmol), CuCl (0.25 g, 2.52 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. Then it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL) and dried. The yield was more than in Section 3.4.1. Yield:0.51 g, 63.75%.

3.5. Cobalt(II) phthalocyanine (*1d*)

3.5.1. Method A

A mixture of compound **1** (0.80 g, 2.09 mmol), anhydrous $CoCl_2$ (0.30 g, 2.31 mmol), ammonium molybdate (0.05 g) and ethyleneglycol (25 mL) was heated to 180 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3×50 mL) and hot water (100 mL). This compound is less soluble in $CHCl_3$, DMF and DMSO. Yield: 0.05 g, 5.60%. λ_{max} (DMSO)/nm: 270, 675. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 7.07–8.49 (52H, m, Ar). FTIR ν_{max}/cm^{-1}: 3058 (Ar–CH), 1658 (C=O), 1295 (C–O–C).

3.5.2. Method B

A mixture of compound **1** (0.80 g, 2.09 mmol), anhydrous $CoCl_2$ (0.30 g, 2.31 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for

8 min. Then it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3 × 50 mL) and hot water (100 mL) and dried. The yield was more than in Section 3.5.1. Yield: 0.097 g, 10.84%.

3.6. Nickel(II) phthalocyanine (*1e*)

3.6.1. Method A

A mixture of compound **1** (1 g, 2.61 mmol), anhydrous $NiCl_2$ (0.30 g, 2.31 mmol), and dry quinoline (25 mL) was heated to 180 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3 × 50 mL) and hot water (100 mL). This compound is less soluble in $CHCl_3$, DMF and DMSO. Yield: 0.12 g, 11.43%. λ_{max} (DMSO)/nm: 301, 683. ^1H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 7.23–8.22 (52H, m, Ar). FTIR ν_{max}/cm^{-1}: 3056 (Ar–CH), 1662 (C=O), 1292 (C–O–C).

3.6.2. Method B

A mixture of compound **1** (1 g, 2.61 mmol), anhydrous $NiCl_2$ (0.30 g, 2.31 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. Then it was diluted with hot ethanol and the product filtered and then refluxed with ethanol (3 × 50 mL) and hot water (100 mL) and dried. The yield was more than in Section 3.6.1. Yield: 0.23 g, 22.12%.

3.7. 3-(3,4-Dicyanophenoxy)-N-phenyl-N-(3,4-dicyanophenyl)-2-naphthamide (*2*) and 3-(3,4-dicyanophenoxy)-N-phenyl-2-naphthamide (*3*)

3.7.1. Method A

3-Hydroxy-2-naphthoic acid anilide (5.7 g, 21.67 mmol) was dissolved in DMF (150 mL) under N_2 and 4-nitrophthalonitrile (7.5 g, 43.35 mmol) was added. After stirring for 10 min, finely ground anhydrous K_2CO_3 (5 g, 36.23 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at room temperature for 48 h. Water was then added and the product filtered and washed with water until the filtrate was neutral. Then the reaction mixture was poured into ice water (500 mL). The product was filtered off and washed with 10% NaOH solution for removing unreacted 3-hydroxy-2-naphthoic acid anilide and water until filtrate became neutral. The product was washed with hot ethanol and filtered off. Compound **2** was insoluble in ethanol (yield: 2.03 g, 36.73%); Mp: 213 °C, although compound **3** was soluble in ethanol (yield: 1.88 g, 44.25%); Mp: 140 °C. These compounds are soluble in chloroform, DMF and DMSO. For compound **2**, ^1H NMR (200 MHz, d_6-DMSO, Me_4Si): δ_H 7.31–8.31(17H, m, ArH). ^{13}C NMR (200 MHz, DMSO-d_6, Me_4Si): δ_C 127.4–135.5 (Ar), 122.03 (CN), 122.21 (CN), 164.12 (C=O). FTIR ν_{max}/cm^{-1}: 3078 (Ar–CH), 2230 (CN), 1686 (C=O), 1309 (C–O–C). For compound **3**, ^1H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 7.12–8.53(m, Ar H), 10.71 (s, NH). ^{13}C NMR (200 MHz, d_6-DMSO, Me_4Si): δ_C 128.20–130.32 (Ar), 118.03 (CN), 160.02 (C=O). FTIR ν_{max}/cm^{-1}: 3430 (NH), 3071 (Ar–CH), 2229 (CN), 1686 (C=O), 1309 (C–O–C).

3.7.2. Method B

3-Hydroxy-2-naphthoic acid anilide (5.7 g, 21.67 mmol), 4-nitrophthalonitrile (7.5 g, 43.35 mmol), finely ground anhydrous K_2CO_3 (5 g, 36.23 mmol) and dry dimethylformamide (20 mL) were irradiated also in a microwave oven at 350 W for 10 min. Above purification method was also applied to this material. The yields were more than in Section 3.7.1. For compound **2**, yield: 2.41 g, 43.61%. For compound **3**, yield: 2.02 g, 47.55%.

3.8. Metal-free phthalocyanine (*2a*)

3.8.1. Method A

The reaction was carried out by the compound **1a** procedure using compound **2** (0.365 g, 0.71 mmol). This compound is soluble in dilute H_2SO_4. Yield: 0.10 g, 27.40%. λ_{max} (dilute H_2SO_4)/nm: 271, 670 (shoulder), 685. FTIR ν_{max}/cm^{-1}: 3410 (NH), 3054 (Ar–CH), 1654 (C=O), 1242 (C–O–C).

3.8.2. Method B (microwave-assisted synthesis method for metal-free phthalocyanine)

The reaction was carried out by the compound **1a** procedure using compound **2** (0.4 g, 0.78 mmol). The yield was more than in Section 3.8.1. Yield: 0.13 g, 35.62%.

3.9. Zinc(II) phthalocyanine (*2b*)

3.9.1. Method A

The reaction was carried out by the compound **1b** procedure using compound **2** (0.5 g, 0.97 mmol) and anhydrous $Zn(CH_3COO)_2$ (0.20 g, 1.09 mmol). This compound is soluble in dilute H_2SO_4. Yield: 0.17 g, 34.00%. λ_{max} (dilute H_2SO_4)/nm: 326, 705. FTIR ν_{max}/cm^{-1}: 3055 (Ar–CH), 1654 (C=O), 1241 (C–O–C).

3.9.2. Method B

The reaction was carried out by the compound **1b** procedure using compound **2** (0.5 g, 0.97 mmol). The yield was more than in Section 3.9.1. Yield: 0.22 g, 44.00%.

3.10. Copper(I) phthalocyanine (*2c*)

3.10.1. Method A

The reaction was carried out by the compound **1c** procedure using compound **2** (0.3 g, 0.58 mmol) and anhydrous CuCl (0.08 g, 0.80 mmol). This compound is soluble in dilute H_2SO_4. Yield: 0.13 g, 41.89%. λ_{max} (dilute H_2SO_4)/nm: 293, 694. FTIR ν_{max}/cm^{-1}: 3055 (Ar–CH), 1648 (C=O), 1242 (C–O–C).

3.10.2. Method B

The reaction was carried out by the compound **1c** procedure using compound **2** (0.3 g, 0.58 mmol). The yield was more than in Section 3.10.1. Yield: 0.18 g, 58.01%.

3.11. Cobalt(II) phthalocyanine (**2d**)

3.11.1. Method A

The reaction was carried out by the compound **1d** procedure using compound **2** (0.4 g, 0.78 mmol) and anhydrous $CoCl_2$ (0.045 g, 0.35 mmol). This compound is soluble in dilute H_2SO_4. Yield: 0.19 g, 49.90%. λ_{max} (dilute H_2SO_4)/nm: 293, 692. FTIR ν_{max}/cm^{-1}: 3057 (Ar–CH), 1663 (C=O), 1244 (C–O–C).

3.11.2. Method B

The reaction was carried out by the compound **1d** procedure using compound **2** (0.4 g, 0.78 mmol). The yield was more than in Section 3.11.1. Yield: 0.26 g, 68.29%.

3.12. Nickel(II) phthalocyanine (**2e**)

3.12.1. Method A

The reaction was carried out by the compound **1e** procedure using compound **2** (0.5 g, 0.97 mmol) and anhydrous $NiCl_2$ (0.06 g, 0.46 mmol). This compound is soluble in dilute H_2SO_4. Yield: 0.12 g, 24.00%. λ_{max} (dilute H_2SO_4)/nm: 294, 685. FTIR ν_{max}/cm^{-1}: 3050 (Ar–CH), 1646 (C=O), 1240 (C–O–C).

3.12.2. Method B

The reaction was carried out by the compound **1e** procedure using compound **2** (0.5 g, 0.97 mmol). The yield was more than in Section 3.12.1. Yield: 0.16 g, 32.00%.

3.13. Metal-free phthalocyanine (**3a**)

3.13.1. Method A

The reaction was carried out by the compound **1a** procedure using compound **3** (0.365 g, 0.71 mmol). This compound is less soluble in DMSO and DMF. Yield: 0.13 g, 35.62%. λ_{max} (DMSO)/nm: 354, 680 (shoulder), 698. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 10.02 (s, NH), 7.13–8.43 (57H, m, Ar). FTIR ν_{max}/cm^{-1}: 3423 (NH), 3350 (NH, inner core), 3061 (Ar–CH), 1657 (C=O), 1244 (C–O–C).

3.13.2. Method B (microwave-assisted synthesis method for metal-free phthalocyanine)

The reaction was carried out by the compound **1a** procedure using compound **3** (0.4 g, 0.78 mmol). The yield was more than in Section 3.13.1. Yield: 0.17 g, 46.32%.

3.14. Zinc(II) phthalocyanine (**3b**)

3.14.1. Method A

The reaction was carried out by the compound **1b** procedure using compound **3** (0.3 g, 0.77 mmol) and anhydrous $Zn(CH_3COO)_2$ (0.05 g, 0.27 mmol). This compound is less soluble in DMSO and DMF. Yield: 0.14 g, 44.00%. λ_{max} (DMSO)/nm: 293, 687. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 10.21 (s, NH), 6.98–8.32 (56H, m, Ar). FTIR ν_{max}/cm^{-1}: 3435 (NH), 3066 (Ar–CH), 1652 (C=O), 1249 (C–O–C).

3.14.2. Method B

The reaction was carried out by the compound **1b** procedure using compound **3** (0. 3 g, 0.77 mmol). The yield was more than in Section 3.14.1. Yield: 0.17 g, 54.49%.

3.15. Copper(I) phthalocyanine (**3c**)

3.15.1. Method A

The reaction was carried out by the compound **1c** procedure using compound **3** (0.3 g, 0.77 mmol) and anhydrous CuCl (0.05 g, 0.50 mmol). This compound is less soluble in DMSO and DMF. Yield: 0.16 g, 51.28%. λ_{max} (DMSO)/nm: 324, 711. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 10.01 (s, NH), 7.13–8.41 (56H, m, Ar). FTIR ν_{max}/cm^{-1}: 3412 (NH), 3059 (Ar–CH), 1647 (C=O), 1244 (C–O–C).

3.15.2. Method B

The reaction was carried out by the compound **1c** procedure using compound **3** (0.3 g, 0.77 mmol). The yield was more than in Section 3.15.1. Yield: 0.20 g, 64.10%.

3.16. Cobalt(II) phthalocyanine (**3d**)

3.16.1. Method A

The reaction was carried out by the compound **1d** procedure using compound **3** (0.4 g, 1.03 mmol) and anhydrous $CoCl_2$ (0.045 g, 0.35 mmol). This compound is less soluble in DMSO and DMF. Yield: 0.18 g, 43.36%. λ_{max} (DMSO)/nm: 310, 670. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 10.32 (s, NH), 7.01–8.13 (56H, m, Ar). FTIR ν_{max}/cm^{-1}: 3423 (NH), 3058 (Ar–CH), 1666 (C=O), 1246 (C–O–C).

3.16.2. Method B

The reaction was carried out by the compound **1d** procedure using compound **3** (0.4 g, 1.03 mmol). The yield was more than in Section 3.16.1. Yield: 0.26 g, 62.65%.

3.17. Nickel(II) phthalocyanine (**3e**)

3.17.1. Method A

The reaction was carried out by the compound **1e** procedure using compound **3** (0.3 g, 0.77 mmol) and anhydrous $NiCl_2$ (0.05 g, 0.38 mmol). This compound is less soluble in DMSO and DMF. Yield: 0.11 g, 35.48%. λ_{max} (DMSO)/nm: 294, 682. ^{1}H NMR (200 MHz, DMSO-d_6, Me_4Si): δ_H 10.13 (s, NH), 7.11–8.67 (56H, m, Ar). FTIR ν_{max}/cm^{-1}: 3399 (NH), 3044 (Ar–CH), 1624 (C=O), 1218 (C–O–C).

3.17.2. Method B

The reaction was carried out by the compound **1e** procedure using compound **3** (0.3 g, 0.77 mmol). The yield was more than in Section 3.17.1. Yield: 0.19 g, 61.29%.

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