

DBU-catalysed synthesis of metal-free phthalocyanines and metallophthalocyanines containing 2(3,4-dimethoxyphenyl)ethanol and 4-hydroxybenzaldehyde groups: characterisation, antimicrobial properties and aggregation behaviour

R. Medyouni^a, B. Hallouma^a, L. Mansour^b, S. Al-Quraishy^b and N. Hamdi^{a,*}

^aResearch Laboratory of Environmental Sciences and Technologies (LR16ES09), Higher Institute of Environmental Sciences and Technology, University of Carthage, Hammam-Lif 2050, Tunisia

^bZoology Department, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Kingdom of Saudi Arabia

^cÁrea de Química Inorgánica-CIESOL, Universidad de Almería, 04120 Almería, Spain

^dChemistry Department, College of Science and Arts, Qassim University, Al-Rass 51921, Kingdom of Saudi Arabia

The synthesis, characterisation, and spectral and antimicrobial properties of novel peripherally tetra-substituted metal-free phthalocyanines and metallophthalocyanines bearing four 2(3,4-dimethoxyphenyl)ethanol or 4-hydroxybenzaldehyde substituents is reported. The aggregation behaviour of these compounds was investigated in different concentrations of DMSO. The compounds exhibited antimicrobial activity against test microorganisms.

Keywords: metallophthalocyanine, phthalonitrile, aggregation, antimicrobial activities

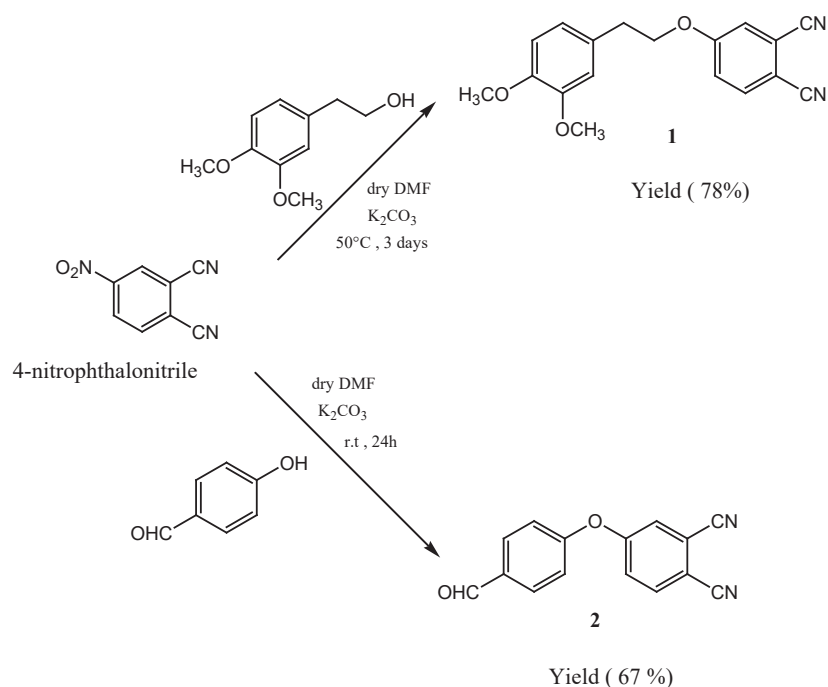
Phthalocyanine (Pc) is a macrocyclic and tetramer molecule, which is a planar conjugated system of 18π electrons exhibiting aromatic behaviour, formed of four isoindoline units. Phthalocyanines are used widely as conventional dyes and pigments and have interesting chemical and physical properties.^{1,2} The optical and electronic properties of phthalocyanine macrocycles make them suitable for a wide range of technological applications, such as photoconductors. These conjugated compounds have attracted much research interest in the fabrication of electronic molecular devices, such as opto-electronic devices, gas sensors,³ static induction transistors,⁴ photoreceptor devices in laser beam printers and photocopiers,^{5–7} liquid crystals,⁸ as Langmuir–Blodgett films,^{9,10} in electrophotographic applications,^{11,12} in optical data storage,¹³ in fuel cells,¹⁴ in electrochemical sensors,^{15,16} and in nonlinear optics.¹⁷

The propensity of phthalocyanines to form aggregates because of the strong interactions between planar macrocycles in solution is well known.¹⁸ Remarkable progress has been made in recent years in the investigations of phthalocyanine derivatives as antioxidants and their antibacterial activities.^{19,20}

In this study, we describe the synthesis and characterisation of phthalocyanines bearing four 2(3,4-dimethoxyphenyl)ethanol or 4-hydroxybenzaldehyde groups on the peripheral positions. We also report the results of an investigation of concentration effects on the aggregation properties of phthalocyanine derivatives in DMSO. Moreover, the antimicrobial activities of the synthesised phthalocyanines are investigated using the disk diffusion method.

Results and discussion

Phthalonitrile derivatives **1** and **2** (Scheme 1) were synthesised via base-catalysed nucleophilic aromatic nitro displacement of



Scheme 1 Syntheses of compounds **1** and **2**.

* Correspondent. E-mail: naceur.hamdi@isste.rnu.tn

4-nitrophthalonitrile with 2(3,4-dimethoxyphenyl)ethanol and 4-hydroxybenzaldehyde, respectively, using K_2CO_3 as a base in anhydrous DMF.^{21–24} This reaction was carried out at 50 °C for 72 h and the yield was moderate in the case of the phthalonitrile **1**.

The synthesis of 4-(4-formylphenoxy) phthalonitrile (**2**) was performed by the reaction of 4-nitrophthalonitrile with 4-hydroxybenzaldehyde in dry DMF in the presence of dry K_2CO_3 at room temperature under an N_2 atmosphere for 24 h. The crude products (**1** and **2**) were purified by column chromatography on silica gel with $CHCl_3$ as the eluent.

For compounds **1** and **2**, spectroscopic analyses (IR, 1H NMR, ^{13}C NMR, 2D NMR) and elemental analyses were consistent with the proposed structures. The CN band in the IR spectrum of **1** was observed at 2233 cm^{-1} and the aromatic C–H peaks appeared at 3049 cm^{-1} . In the 1H NMR spectrum of **1**, the aromatic protons appeared as a multiplet between 6.81 and 8.04 ppm. The ^{13}C NMR spectrum of compound **1** showed the presence of nitrile carbon atoms at 121.4 and 121.5 ppm.

In the IR spectrum of **2**, the broad peak for the OH bands for 4-hydroxybenzaldehyde disappeared and the characteristic vibrations of the $C\equiv N$ peak appeared at 2227 cm^{-1} . In the 1H NMR spectrum of **2**, the disappearance of the OH peaks of 4-hydroxybenzaldehyde, as well as the presence of additional aromatic protons indicated that nucleophilic aromatic nitro displacement was achieved. The ^{13}C NMR spectral data of **2** are also in accordance with the expected structure, showing the presence of CN carbon atoms at 117.3 and 116.2 ppm, and the CO carbon atom at 192.7 ppm.

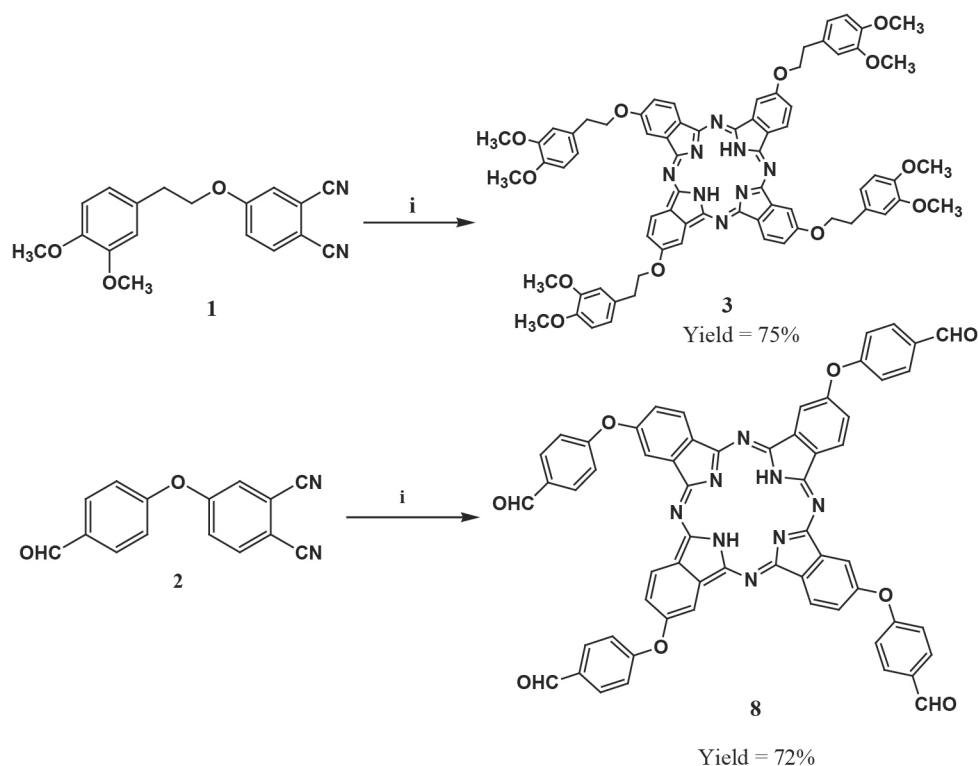
1H NMR spectral assignments were also supported *via* a 1H - ^{13}C HMBC experiment (Fig. 1 in the ESI), which shows that H_2 at 3.00 ppm correlates with methoxylic carbon at 60.6 ppm and C_3 at 135.1 ppm. The resonance H_6 at 8.00 ppm correlates to C_3 at 135.1 ppm. The MS spectra of compounds **1** and **2**,

which show peaks at $m/z = 308.33$ ($[M]^+$) and $m/z = 249.23$ ($[M]^+$), respectively, support the proposed formulae for these compounds.

The self-condensation of **1** and **2** in a high-boiling point solvent in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 150 °C under an N_2 atmosphere afforded unmetallated phthalocyanine compounds **3** and **8**, with moderate yields after purification by column chromatography using chloroform:methanol (91:9) as the eluent (Scheme 2).

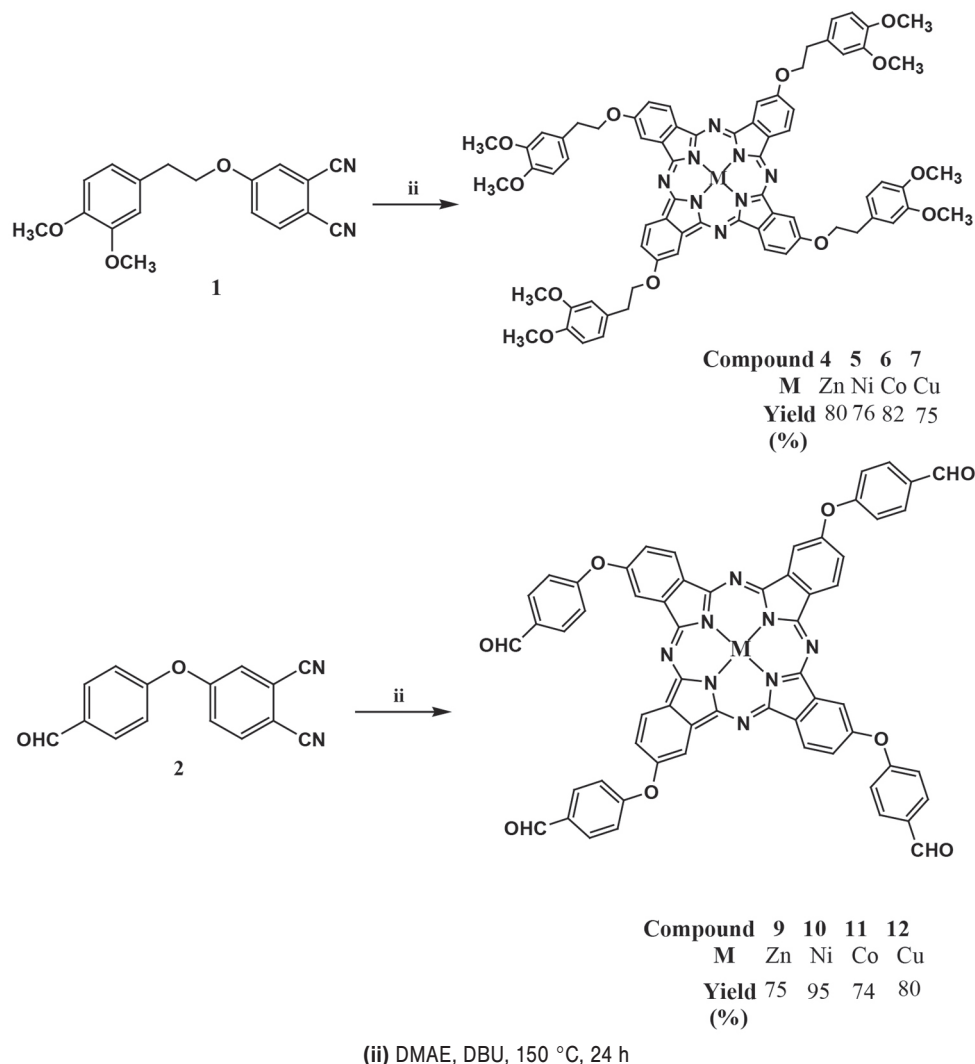
The formulae of metal-free phthalocyanine compounds **3** and **8** were elucidated by elemental analysis and nuclear magnetic resonance, FTIR and UV-Vis spectroscopies (Experimental). The IR spectrum of **3** showed a peak at 3431 cm^{-1} due to NH vibrations. The disappearance of the CN stretching vibration in the IR spectra of **1** indicated the formation of compound **3**. In the 1H NMR spectrum of compound **3**, the typical shielding of inner core protons could not be observed due to the probable strong aggregation of the molecules (especially for our molecules, due to multiplicities of the numbers of aromatic benzenes).²⁵ The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave a significant absorbance characteristic of the proposed structure. The elemental analysis results confirmed the structure of the desired compound **3**. In the NMR spectra of **8**, the aldehydic proton signals appeared at 9.1 ppm as a singlet integrating for 4 protons and the aromatic protons appeared as a multiplet integrating for 16 protons between 7.2 and 8.1 ppm, clearly suggesting compound formation had occurred.

Metal-free **3** and **8** are highly soluble in various organic solvents, including dichloromethane, chloroform, tetrahydrofuran, dimethylformamide and dimethyl sulfoxide, owing to the incorporation of four 2(3,4-dimethoxyphenyl) ethanol and 4-hydroxybenzaldehyde groups into the phthalocyanine rings.



(i) DMAE, DBU, 150 °C, 24 h

Scheme 2 Synthetic route for unmetallated phthalocyanine compounds **3** and **8**.



Scheme 3 Synthetic scheme for metallated phthalocyanines **4–7** and **9–12**.

The cyclotetramerisation of compounds **1** and **2** in the presence of the corresponding metal salts $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 2-(dimethylamino)ethanol and DBU at 150 °C for 24 h under an N_2 atmosphere was performed (Scheme 3).

The dark green products (**4–7** and **9–12**) are slightly soluble in polar solvents such as THF, DMF and DMSO.

The ^1H NMR spectra of compounds **4**, **5** and **9** were taken in DMSO at room temperature. In the ^1H NMR spectrum of **4**, the aromatic protons appeared at between 6.87 and 7.72 ppm as a multiplet, and methoxylic protons appeared at 3.75 ppm as singlets. The ^1H NMR spectra of **4** and **5** were almost identical. ^1H NMR measurements were precluded for the phthalocyanines **6**, **7**, **11** and **12** due to their paramagnetic cobalt and copper atoms.^{26,27}

The IR spectra of metal-free phthalocyanines **3** and **8** and metallophthalocyanines **3–12** are very similar. The significant difference is the presence of (NH) vibrations of the inner phthalocyanine core protons, which are assigned to a weak band at 3448 cm^{-1} for the metal-free derivative **8**. This band is especially beneficial for characterisation of metal-free phthalocyanine derivatives. The intense absorption vibrations at 2227 cm^{-1} corresponding to the CN groups for phthalonitrile compound **2** disappeared after their conversion into the metallophthalocyanines **9–12**.

UV-Vis absorption spectra

The spectra of metallophthalocyanines complexes consist of an intense absorption band in the visible region traditionally near 670 nm, called the Q-band, and a generally weaker band near 340 nm, called the Soret or B-band, both being $\pi-\pi^*$ transitions.^{28,29} UV-Vis spectral data for phthalocyanines **3–7** in DMSO at a concentration of 10^{-5} M are given in Table 1.

The Q-bands of the metal-free phthalocyanine **8** were observed at 611–684 nm with a shoulder at 615 nm in DMF. In contrast, the Q-bands of metallophthalocyanines **9–12** were observed in the expected range, at 629–683, 615–678, 615–686 and 615–687 respectively. The B-band absorptions of phthalocyanines **9–12**, describing the transition of deeper π -levels to the LUMO, were observed at 351, 339, 345 and 334, respectively, in DMF (Table 2).

The electronic absorption spectra of phthalocyanines **3–7** showed characteristic intense Q-bands at 697 (**3**), 636 (**4**), 675 (**5**), 690 (**6**) and 708 (**7**) nm in DMF. The B-bands were observed around 331–343 nm. The wavelengths of the absorption of the Q-bands of **3–12** followed the order $\text{Ni} > \text{Zn} > \text{Cu} > \text{Co}$, due to the nature of the central metal ion. The order shows that the cobalt phthalocyanine (**7**) has the largest blue shift while the nickel phthalocyanine (**5**) has the largest red shift compared with the other metal complexes, **3**, **4** and **6**.

Table 1 UV-Vis spectral data for phthalocyanines (Pcs) **3–7** in DMSO at a concentration of 10^{-5} M

Solvent	Pc	Q-band, λ_{\max} (nm) (log ϵ)	B-band, λ_{\max} (nm) (log ϵ)
DMSO	3 : Free Pc	615 (4.591), 697 (5.135)	340 (5.033)
	4 : ZnPc	636 (4.632), 697 (5.064)	343 (4.834)
	5 : NiPc	614 (4.436), 675 (4.968)	332 (4.645)
	6 : CoPc	614 (4.320), 690 (4.922)	331 (4.462)
	7 : CuPc	622 (4.462), 708 (5.054)	334 (4.728)

Table 2 UV-Vis spectral data for phthalocyanines (Pcs) **8–12** in DMF at a concentration of 10^{-5} M

Solvent	Pcs	Q-band, λ_{\max} (nm) (log ϵ)	B-band, λ_{\max} (nm) (log ϵ)
DMF	8 : Free Pc	611 (4.641), 684 (5.155)	351 (4.846)
	9 : ZnPc	629 (4.541), 683 (4.986)	339 (4.673)
	10 : NiPc	615 (4.159), 678 (4.943)	345 (4.617)
	11 : CoPc	615 (4.195), 686 (4.861)	334 (4.538)
	12 : CuPc	615 (4.195), 686 (4.861)	310 (4.238)

Aggregation studies

Aggregation is the association of the phthalocyanine molecules to form dimers, trimers and higher oligomers. The aggregation behaviour of complexes **4–7** was examined at different concentrations in DMSO. Figures 2 and 3 in the ESI show the series of spectra for complexes **4–7**. As the concentration was increased, the intensity of the absorption of the Q-band also increased. No new band due to the formation of aggregated species was observed.^{30,31} This means that the phthalocyanine derivatives **4–7** did not show aggregation in DMSO at this range of concentrations.

We also examined the spectra of **7** monitored at different concentrations ranging from 2.0×10^{-6} to 12×10^{-6} mol dm⁻³ as given in DMSO. As shown in Fig. 3 in the ESI, the intensity of the absorption bands increased with increasing concentration and no new bands were observed, signifying no aggregation behaviour at these concentrations for all phthalocyanines **4–7**.

Antimicrobial activities

Compound **7** exhibited the highest *in vitro* antibacterial activity against *Micrococcus luteus* with a minimum inhibitory concentration (MIC) value of 1.34 mg mL⁻¹, while compound **8** showed a moderate antibacterial activity against *M. luteus*, *Staphylococcus aureus*, *Listeria monocytogenes*, *Salmonella typhimurium* and *Pseudomonas aeruginosa*^{32,33} with MIC values ranging from 4 to 8 mg mL⁻¹. The full data for these studies are in the ESI.

Conclusion

In this study, the syntheses of new substituted metal-free and zinc(II), nickel(II), cobalt(II) and copper(II) phthalocyanines containing 2(3,4-dimethoxyphenyl)ethanol and 4-hydroxybenzaldehyde in the peripheral positions have been described. The aggregation behaviour of the metallophthalocyanines **4–7** at different concentrations in DMSO was also studied. No aggregation was demonstrated in DMSO at concentrations between 6×10^{-6} and 14×10^{-6} mol dm⁻³. Antimicrobial activities were also examined.

Experimental

All reactions were carried out under an N₂ atmosphere using Schlenk techniques. All solvents were desiccated and refined according to Perrin and Armarego's method.³⁴ 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), and 4-nitrophthalonitrile were provided from their commercial suppliers were obtained according to the literature procedure.³⁵ ¹H NMR and ¹³C NMR spectra were recorded on a Varian XL-400

NMR spectrophotometer in DMSO-*d*₆, and chemical shifts (δ) were reported in ppm relative to Me₄Si as an internal standard. IR spectra were recorded on a Perkin Elmer Spectrum FTIR spectrometer using KBr pellets. Melting points were measured on an electrothermal apparatus and are uncorrected. MS were recorded on a LC-MS-MS 8030 Shimadzu spectrometer. Elemental analyses were performed on Perkin-Elmer 2400 elemental analyser. The UV spectra were recorded on a Perkin Elmer Lambda 11 spectrophotometer.

4-[2-(3,4-dimethoxyphenyl)ethoxy]phthalonitrile (**1**)

4-Nitrophthalonitrile (1 g, 5.78 mmol) was dissolved in dry DMF (40 mL) and dimethoxyphenyl (1.80 g, 8.45 mmol) was added. After stirring for 15 min, finely ground anhydrous K₂CO₃ (2.35 g, 17.3 mmol) was added in small portions for 2 h with efficient stirring. The reaction mixture was stirred magnetically at 50 °C for 72 h. After reaction completion (observed by TLC), the mixture was poured into an ice-water mixture (200 mL) and the precipitate was filtered and washed with water until the filtrate was neutral, and dried in a vacuum. Finally, the precipitate was crystallised from ethanol to give compound **1** as: White solid; m.p. 220 °C; yield 1.44 g (78%); FTIR (KBr) (n cm⁻¹): 1568 (C=C), 2233 (C≡N), 3049 (C–H_{arom}); ¹H NMR (400 MHz, DMSO-*d*₆, *t*_{amb}): δ 3.00 (t, ³J = 6.00 Hz, 2H, H_{2e}), 3.72 (s, 3H, OCH_{3(a)}), 3.75 (s, 3H, OCH_{3(b)}), 4.35 (t, ³J = 6.20 Hz, 2H, H_{1e}); 6.81–8.04 (m, 6H, H_{arom}); ¹³C NMR (100 MHz, DMSO-*d*₆, *t*_{amb}): δ 39.2 (C_{2e}), 60.6 (OCH_{3(b)}), 60.7 (OCH_{3(a)}), 74.8 (C_{1e}), 111.1 (C₁), 117.1 (C_{5e}), 118.1 (C_{8e}), 120.9 (C₂), 121.5 (CN), 121.4 (CN), 125.3 (C₃), 125.5 (C₅), 126.1 (C_{4e}), 135.1 (C_{3e}), 140.9 (C₆), 152.7 (C_{6e}), 153.8 (C_{7e}), 167.1 (C₄); ES-SM *m/z*: 308.33 [M]⁺. Anal. calcd for C₁₈H₁₆N₂O₃: C, 70.11; H, 5.23; N, 9.08; found: C, 70.1; H, 5.2; N, 9.1%.

4-(4-formylphenoxy)phthalonitrile (**2**)

The synthesis of **2** was similar to **1**, but 4-hydroxybenzaldehyde was employed instead of dimethoxy phenyl ethanol. The reaction mixture was stirred under N₂ at room temperature for 24 h. The other reagents were 4-nitrophthalonitrile (1 g, 5.55 mmol) and anhydrous K₂CO₃ (2 g, 13.88 mmol). Compound **2** was obtained as: White solid; m.p. 350 °C; yield 67%; FTIR (KBr) (n cm⁻¹): 3077 (Ar–CH), 2227 (C≡N), 1601 (C=C), 1263 (C–O–C); ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.49 (d, 1H, H_{2e}), 7.56 (d, 1H, H_{6e}), 7.70 (d, 1H, H_{3e}), 7.74 (d, 1H, H_{5e}), 7.86 (d, 1H, H₅), 7.89 (s, 1H, H₃), 8.15 (d, 1H, H₆), 10.02 (s, 1H, H_{ald}); ¹³C NMR (100 MHz, DMSO-*d*₆, *t*_{amb}): δ 109.3 (C₁), 115.7 (C₂), 116.2 (C_{4e}), 117.3 (CN), 116.2 (CN), 120.8 (C_{2e}), 123.6 (C_{6e}), 126.7 (C_{3e,5e}), 132.0 (C₃), 136.8 (C₅), 138.8 (C₆), 155.1 (C₄), 160.8 (C_{1e}), 192.7 (C_{ald}); ES-SMHR *m/z*: 249.23 [M + H]⁺. Anal. calcd for C₁₅H₈N₂O₂: C, 72.57; H, 3.24; N, 11.28; found: C, 72.4; H, 3.1; N, 11.2%.

Metal-free phthalocyanines (**3** and **8**)

Substituted phthalonitriles (**1** and **2**) (0.196 g, 0.79 mmol for **2**, 0.79 mmol, 0.243g for **1**) were dissolved in dry DMAE (4 mL). After increasing the temperature to 90 °C, DBU (three drops) was added to the media. Thereafter the temperature was raised to 150 °C and stirred for 24 h under N₂. After cooling, the solutions were dropped into ethyl alcohol (40 mL) and the solid raw products were filtered and washed with hot ethanol, methanol, *n*-hexane and diethyl ether. The pure green-coloured products were isolated using a silica gel column with chloroform:methanol (50:0.5) as the solvent system. The spectral data for these products are given below.

Phthalocyanine 3: White solid; m.p. 330 °C; yield 75%; FTIR (KBr) (n cm⁻¹): 3431 (N–H), 3056 (C–H_{arom}), 1232 (C–N)_{arom}, 1613 (C=C); UV-Vis (DMSO, λ_{\max} nm (log ϵ)): 615 (4.591), 697 (5.135), 340 (5.033). Anal calcd for C₇₂H₆₆N₈O₁₂: C, 70.00; H, 5.38; N, 9.07; found: C, 70.1; H, 5.20; N, 9.11%.

Phthalocyanine 8: White solid; m.p. 320 °C; yield 72%; FTIR (KBr) (n cm⁻¹): 3448 (N–H), 3052 (C–H_{arom}), 1296 (C–N)_{arom}, 1638 (C=C); ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.1 (s, 4H, H_{ald}), 7.2–8.1 (m, 16H_{arom}); UV/Vis (DMSO, λ_{\max} nm (log ϵ)): 611 (4.641), 684 (5.155), 351 (4.846). Anal calcd for C₆₀H₃₄N₈O₈: C, 72.42; H, 3.44; N, 11.26; found: C, 72.3; H, 3.30; N, 11.3%.

Synthesis of metallophthalocyanines (4–12); general procedure

A mixture of desired phthalonitriles, compound **1** (0.073 g, 0.24 mmol) or compound **2** (0.06 g, 0.24 mmol), *N,N*-dimethylaminoethanol (DMAE) (4 mL), DBU (1 mL) and the corresponding metal salts (0.06 mmol) were stirred at 150 °C for 24 h under N₂. The progress of the reaction was monitored by TLC. The mixture was left to cool to r.t. then treated with ethylacetate to precipitate the product. The crude product was collected by filtration and washed with water, ethanol and ether, and then dried. The obtained green solid product was purified by column chromatography (silica gel) with chloroform:methanol (100:5) as the solvent system.

Zn(II) phthalocyanine (4): White solid; m.p. 330 °C; yield 80%; FTIR (KBr) (n cm⁻¹): 3024 (C–H_{arom}), 1387 (C–C), 1270 (C–N), 1607 (C=N), 1480 (C=N), 902 (Zn–N); ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.75 (s, 4H, H_{ald}), 6.87–7.72 (m, 16H_{arom}), 3.1 (t, ³J = 6.00 Hz, 8H, H_{2e}), 4.32 (t, ³J = 6.20 Hz, 8H, H_{1e}); UV-Vis (DMF, λ_{max} nm (log ε)): 636 (4.632), 697 (5.064), 343 (4.834). Anal calcd for C₇₂H₆₄N₈O₁₂Zn: C, 66.58; H, 4.96; N, 8.62; found: C, 66.7; H, 5.2; N, 8.7%.

Ni(II) phthalocyanine (5): Elution solvent system: chloroform:methanol (100:3); m.p. 330 °C; yield 76%; FTIR (KBr) (n cm⁻¹): 3020 (C–H_{arom}), 1390 (C–C), 1272 (C–N), 1602 (C=C), 1482 (C=N), 903 (Ni–N); ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.73 (s, 4H, H_{ald}), 6.85–7.71 (m, 16H_{arom}); 3.2 (t, ³J = 6.00 Hz, 8H, H_{2e}); 4.31 (t, ³J = 6.20 Hz, 8H, H_{1e}); UV-Vis (DMSO, λ_{max} nm (log ε)): 614 (4.436), 675 (4.968), 332 (4.645). Anal calcd for C₇₂H₆₄N₈O₁₂Ni: C, 66.93; H, 4.99; N, 8.67; found: C, 66.7; H, 5.1; N, 8.8%.

Co(II) phthalocyanine (6): m.p. 325 °C; yield 82%; FTIR (KBr) (n cm⁻¹): 3020 (C–H_{arom}), 1385 (C–C), 1269 (C–N), 1606 (C=C), 1479 (C=N), 902 (Co–N); UV-Vis (DMSO, λ_{max} nm (log ε)): 614 (4.320), 690 (4.922), 331 (4.462). Anal calcd for C₇₂H₆₄N₈O₁₂Co: C, 66.91; H, 4.99; N, 8.67; found: C, 66.8; H, 5.1; N, 8.7%.

Cu(II) phthalocyanine (7): m.p. 330 °C; yield 75%; FTIR (KBr) (n cm⁻¹): 3016 (C–H_{arom}), 1382 (C–C), 1270 (C–N), 1604 (C=C), 1480 (C=N), 900 (Cu–N); UV-Vis (DMSO, λ_{max} nm (log ε)): 622 (4.462), 708 (5.054), 334 (4.728). Anal calcd for C₇₂H₆₄N₈O₁₂Cu: C, 66.68; H, 4.97; N, 8.64; found: C, 66.7; H, 5.1; N, 8.7%.

Zn(II) phthalocyanine (9): m.p. 315 °C; yield 75%; FTIR (KBr) (n cm⁻¹): 3015 (C–H_{arom}), 1388 (C–C), 1228 (C–N), 1610 (C=C), 1476 (C=N), 905 (Zn–N); ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.1 (s, 4H, H_{ald}), 6.81–7.82 (m, 28H_{arom}); UV-Vis (DMSO, λ_{max} nm (log ε)): 629 (4.541), 683 (4.986), 339 (4.673). Anal calcd for C₆₀H₃₂N₈O₈Zn: C, 68.09; H, 3.04; N, 10.58; found: C, 68.2; H, 3.1; N, 10.4%.

Ni(II) phthalocyanine (10): m.p. 320 °C; yield 95%; FTIR (KBr) (n cm⁻¹): 3016 (C–H_{arom}), 1393 (C–C), 1234 (C–N), 1609 (C=C), 1480 (C=N), 910 (Ni–N); ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.2 (s, 4H, H_{ald}), 6.85–7.85 (m, 28H_{arom}); UV-Vis (DMSO, λ_{max} nm (log ε)): 615 (4.159), 678 (4.943), 345 (4.617). Anal calcd for C₆₀H₃₂N₈O₈Ni: C, 68.52; H, 3.06; N, 10.65; found: C, 68.7; H, 3.1; N, 10.7%.

Co(II) phthalocyanine (11): m.p. 330 °C; yield 74%; FTIR (KBr) (n cm⁻¹): 3015 (C–H_{arom}), 1390 (C–C), 1236 (C–N), 1614 (C=C), 1475 (C=N), 900 (Co–N); UV-Vis (DMSO, λ_{max} nm (log ε)): 615 (4.195), 686 (4.861), 334 (4.538). Anal calcd for C₆₀H₃₂N₈O₈Co: C, 68.51; H, 3.06; N, 10.65; found: C, 68.6; H, 3.1; N, 10.7%.

Cu(II) phthalocyanine (12): m.p. 315 °C; yield 80%; FTIR (KBr) (n cm⁻¹): 3017 (C–H_{arom}), 1391 (C–C), 1231 (C–N), 1612 (C=C), 1478 (C=N), 910 (Cu–N); UV-Vis (DMSO, λ_{max} nm (log ε)): 615 (4.195), 686 (4.861), 310 (4.238). Anal calcd for C₆₀H₃₂N₈O₈Cu: C, 68.21; H, 3.05; N, 10.60; found: C, 68.5; H, 3.2; N, 10.7%.

Acknowledgements

The authors would like to thank the Deanship of Scientific Research at King Saud University for funding the work through the research group project, no. PRG-1436-02.

Electronic Supplementary Information

The ESI is available through:

stl.publisher.intgentaconnect.com/content/stl/jcr/supp-data

Received 11 February 2017; accepted 31 March 2017

Paper 1704596

<https://doi.org/10.3184/174751917X14931195075571>

Published online: 4 May 2017

References

- G. Waltera, B. Rudineb and C.J. Wamsler, *Porphy. Phthalocyanines*, 2010, **14**, 759.
- W. Wu, W. Wu, S. Ji, H. Guo, X. Wang and J. Zhao, *Dyes Pigments*, 2011, **89**, 199.
- I. Muzikante, V. Parra and R. Dobulans, *Sensors*, 2007, **7**, 2984.
- M. Kraus, S. Richler, A. Opitz and W. Brütting, *J. Appl. Phys.*, 2010, **107**, 94503.
- B. Kahveci, S. Şazmaz and M. Özil, *Turk. J. Chem.*, 2006, **30**, 681.
- H. Schultz, H. Lehman, M. Rein and M. Hanack, *Structure and bonding*, SpringerVerlag, Heidelberg, 1992, p 41.
- U. Drechsler, M. Hanack, J.L. Atwood, J.E.D. Davies, D.D. McNicolm and F. Vögtle (eds), *Comprehensive supramolecular chemistry*, Pergamon, Oxford, 1996, Vol. 9, p 283.
- M.K. Engel, P. Bassoul, L. Ossio, H. Lehmann, M. Hanack and M.J. Simon, *Liq. Cryst.*, 1993, **15**, 709.
- M. Burghard, M. Schmelzer, S. Roth, P. Haisch and M. Hanack, *Langmuir*, 1994, **10**, 4265.
- M.J. Cook, *J. Mater. Chem.*, 1996, **6**, 677.
- S. Zhou, X. Jin, W. Hu, Y. Liu and S. Liu, *Solid State Commun.*, 1999, **112**, 269.
- D.M. Pai and B.E. Springett, *Rev. Mod. Phys.*, 1993, **65**, 163.
- R. Ao, L. Kümmert and D. Haarer, *Adv. Mater.*, 1995, **7**, 495.
- A.B.P. Lever, M.R. Hempstead, C.C. Leznoff, W. Liu, M. Melnik, W.A. Nevin and P. Seymour, *Pure Appl. Chem.*, 1986, **58**, 1467.
- B. Simic-Glavaski, *Phthalocyanines: properties and applications*, eds A.B.P. Lever and C.C. Leznoff, VCH, New York, 1993, Vol. 3.
- W. Aijian, L. Lingliang and C. Zhang, *J. Incl. Phenom. Macrocycl. Chem.*, 2011, **71**, 1.
- D. Dini and M. Hanack, *The porphyrin handbook: physical properties of phthalocyanine-based materials*, eds K.M. Kadish, K.M. Smith and R. Guilard, Academic Press, San Diego, CA, 2003, Vol. 17, p 22.
- W. Aijian, L. Lingliang and C. Zhang, *Tetrahedron*, 2012, **68**, 2433.
- L. Guanghui, W. Aijian, S. Jingbao and Z. Qiang, *Inorg. Chem. Commun.*, 2015, **57**, 47.
- A.S. Al-Ayed, *Mediterr. J. Chem.*, 2016, **5**, 632.
- Z. Shen, Y. Masanori, G.D. Andrew, H. Briggs and P. Kyriakos, *J. Am. Chem. Soc.*, 2016, **138**, 1313.
- V. Alexander, E.B. Babkin, B.A. Zodinov, A. Bulgakov, V. Kepman and V. Avdeev, *Eur. Polym. J.*, 2015, **66**, 452.
- R.K. Ali and K. Azam, *Tetrahedron Lett.*, 2012, **53**, 5223.
- T. Hulya, O. Ahmet and H. Tuncer, *Acta Crystallogr. E*, 2012, **68**, o565.
- V. Nostrum, S.J. Picken, A.J. Schouten and R.J.M. Nolte, *J. Am. Chem. Soc.*, 1995, **117**, 9957.
- W. Wu, S. Ji, H. Guo, X. Wang and J. Zhao, *Dyes Pigments*, 2011, **89**, 199.
- A. Selcuk, A. Ahmet and B. Mustafa, *Polyhedron*, 2013, **49**, 41.
- Y. Gök, H. Kantekin, M. B. Kılıç and H. Aslan, *Dyes Pigments*, 2007, **74**, 692.
- H.A. Dinc, A. Gül and M.B. Koc, *J. Porphy. Phthalocya.*, 2004, **8**, 1204.
- D.D. Dominguez, A.W. Snow, J.S. Shirk and P.S. Pong, *J. Porphy. Phthalocya.*, 2001, **5**, 582.
- M.N. Yaras, M. Kandaz, B.F. Senkal, A. Koca and B. Salih, *Polyhedron*, 2007, **26**, 5235.
- K. Güven, E. Yücel and F.Çetintaş, *Pharm. Biol*, 2006, **44**, 79.
- P.A. Wayne, National committee for clinical laboratory standards. Proposed standard M38-P, 1998.
- D.D. Perrin and W.L.F. Armarego, *Purification of laboratory chemicals*, Pergamon, Oxford, 1989.
- G.J. Young and W.J. Onyebuagu, *Org. Chem.*, 1990, **55**, 2155.