Microwave-assisted synthesis and characterization and theoretical calculations of the first example of free and metallophthalocyanines from salen type Schiff base derivative bearing thiophen and triazole heterocyclic rings

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Abstract

Novel metal-free and metallophthalocyanine complexes of Co, Ni, Cu, and Zn have been synthesized by exposure to microwave irradiation and reflux conditions and the products purified by several techniques. The newly prepared compounds have been characterized by elemental analyses, IR, ^{1}H NMR, MS and UV–Vis spectroscopy. Furthermore, theoretical calculations of metallophthalocyanines CuPc, NiPc, ZnPc and CoPc were carried out to comparatively describe the molecular structures, molecular orbital and UV–Vis spectra of metallophthalocyanine complexes by the HF theory. A comparison between the different molecules for the geometry, molecular orbitals was made. The simulated order of the sizes of the central hole was CoPc > NiPc < CuPc < ZnPc, which is in complete accord with the experiment. Moreover, the HOMO–LUMO gaps were varied in order of CoPc > NiPc > ZnPc > CuPc. The calculated structures, electronic absorption spectra of metallophthalocyanine complexes are in good consistency with the experimental results.
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1. Introduction

Phthalocyanines form nowadays an important group of organic compounds that belongs to the most studied subjects of organic functional materials [1]. The most important industrial application of phthalocyanines is the formation of color complexes with metal cations that are used as highly stable pigments and dyes [2]. In addition, they can find commercial applications as: photovoltaic materials in solar cells [3–5], systems for fabrication of light emitting diodes (LED) [6,7], liquid crystalline [8] and nonlinear optical materials [9,10], sensitizers for photodynamic (PDT) cancer therapy [11,12], photoconductors in xerography [13], dyes at recording layers for CD-R and DVD-R optical storage discs [14], as well as diverse catalytic systems [15,16].

Phthalocyanines are usually prepared by the high temperature cyclotetramerization processes of either phthalonitrile (1) or phthalic anhydride (2), in which the template effect afforded by a suitable metal cation is required (Scheme 1). The reactions can be carried out in variety of solvents as well as under solvent-free conditions, but both processes require temperature ca. 200 °C and long reaction times [1]. It is well known that microwave (MW) irradiation can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are supposed to be mostly reduced in the

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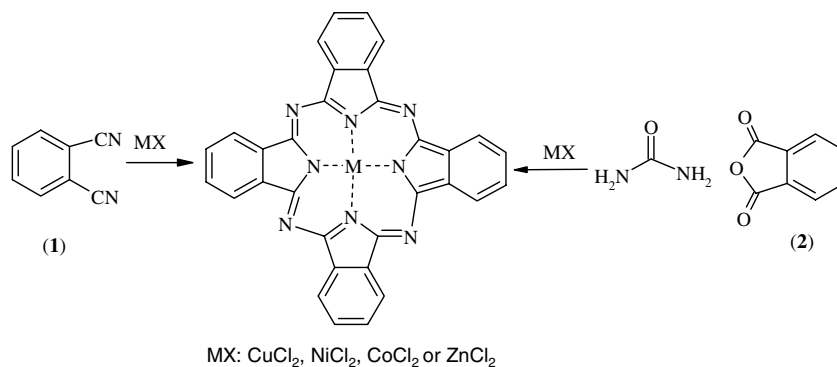
Scheme 1. Synthesis of phthalocyanines from phthalonitrile (1) or phthalic anhydride (2) and urea.

reactions that are run for a long time at high temperatures under conventional conditions [17]. Thus, we have decided to apply microwave irradiation for the synthesis of phthalocyanine in order to check whether such non-classical method of chemical activation might influence yield, selectivity and time of reaction in comparison with a conventional thermal treatment under strictly similar sets of conditions.

In this study, the first example of the phthalocyanines with four salen type Schiff base with triazole and thiophen ring substituents were prepared by conventional and microwave methods. Furthermore, theoretical calculations of metallophthalocyanines CuPc, NiPc, ZnPc and CoPc were carried out to comparatively describe the molecular structures, molecular orbital and UV–Vis spectra of metallophthalocyanine complexes by the HF theory.

2. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [18]. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in DMSO-d_6, and chemical shifts were reported (δ) relative to Me$_4$Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer in KBr pellets. The MS spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer equipped with pyridine–methanol as solvent. All experiments were performed in the positive ion mode. Elemental analyses were performed on a LECO Elemental Analyser (CHNS O932); their values agreed with the calculated ones. UV–Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Beko MD 1500, 2.45 MHz domestic microwave oven, was used in all synthesis of phthalocyanines. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.1. 4-{[(1E)-(2-Hydroxyphenyl)methylene]amino}-5-(2-thienylmethyl)-2,4- dihydro-3H-1,2,4-triazol-3-one (2)

4-Amino-5-(2-thienylmethyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (1) (1.96 g, 10 mmol) and salicylaldehyde (1.05 ml, 10 mmol) was mixed without solvent and carefully heated at 135–140 °C for 2 h under N$_2$. The formed solid products were separated by filtration, purified by crystallization twice from dry ethanol, washed with diethyl ether and dried in a vacuum over P$_2$O$_5$. Yield: 2.40 g, (80%), mp: 190–192 °C. Anal. Calc. for C$_{14}$H$_{12}$N$_4$O$_2$S: C, 55.99; H, 4.03; N, 18.65. Found: C, 55.87; H, 3.86; N, 18.78%. IR (KBr tablet) v_{max}/cm^{-1}: 3166 (–NH), 3045 (Ar-CH), 1711 (C=O), 1618 (CH=N). ^1H NMR. (DMSO-d_6), (δ: ppm): 12.03 (s, 1H, NH), 10.30 (s, 1H, OH), 9.98 (s, 1H, CH=N), 7.88–7.84 (m, 1H, Ar-H$_3$), 7.47–7.31 (m, 2H, Ar-H$_{14,17}$), 7.03–6.89 (m, 4H, Ar-H$_{15,16,1,2}$), 4.28 (s, 2H, CH$_2$). ^{13}C NMR. (DMSO-d_6), (δ: ppm): 158.28 (C=O), 151.86 (CH=N), 151.22, 146.21 (C=N), 138.14, 133.62, 127.59, 127.27, 126.94, 126.01, 120.29, 120.22, 117.10, 26.44 (CH$_2$). MS (ESI), (m/z): 300.52 [M]$^+$.

2.2. 4-[2-((E)-{[5-Oxo-3-(2-thienylmethyl)-1,5-dihydro-4H-1,2,4- triazol-4-yl]imino} methyl) phenoxy] phthalonitrile (3)

Compound (2) (0.50 g, 1.66 mmol), 4-nitrophthalonitrile (2a) (0.29 g, 1.66 mmol), finely ground anhydrous K$_2$CO$_3$ (0.45 g, 3.32 mmol) and dry dimethylformamide (5 ml) were also irradiated in a microwave oven at 360 W for 5 min. At the end of reaction, DMF mixture was added to 250 ml of a cold HCl (5 wt.%) solution to yield a crude product. This precipitate was stirred at room temperature for 24 h. The precipitate was isolated by filtration and was first washed with distilled water, until the filtrate was neutral, and then diethyl ether before drying in vacuo over P$_2$O$_5$. Recrystallization from hot ethanol gave a light brown product. Yield: 0.60 g, (85%), mp: 186 °C. Anal. Calc. for C$_{22}$H$_{14}$N$_6$O$_2$S: C, 61.96; H, 3.31; N, 19.71. Found: C, 62.02; H, 3.32; N, 19.68%. IR (KBr tablet)

v_{max}/cm^{-1}: 3110 (–NH), 3076 (Ar-CH), 2230 (C≡N), 1706 (C=O), 1596 (CH=N). ^{1}H NMR. (DMSO-d_6), (δ: ppm): 12.06 (s, 1H, NH), 9.90 (s, 1H, CH=N), 8.15–8.11 (d, 2H, Ar-H$_{14,24}$), 7.92 (d, 1H, Ar-H$_3$), 7.60 (dd, 2H, Ar-H$_{21,25}$), 7.46–7.38 (m, 2H, Ar-H$_{15,16}$), 7.22 (d, 1H, Ar-H$_{17}$), 7.01–6.94 (m, 2H, Ar-H$_{1,2}$), 4.23 (s, 2H, CH$_2$). ^{13}C NMR. (DMSO-d_6), (δ: ppm): 160.56, 153.17 (C=O), 150.89 (CH=N), 147.09 (C=N), 145.40, 137.13, 136.33, 133.51, 127.10, 126.82, 126.53, 126.23, 125.33, 125.23, 122.92, 122.29, 121.04, 116.74, 115.69 (C≡N), 115.19 (C≡N), 108.77, 25.41 (CH$_2$). MS (ESI), (m/z): 493.4 [M+C$_2$H$_6$O+Na−2]$^+$.

2.3. Metal-free phthalocyanine (4)

A standard Schlenk tube was charged with (0.25 g, 0.59 mmol) of (3), 2 ml of dry *n*-hexanol and (0.09 ml, 0.59 mmol) of 1,8-diazabiscyclo[5.4.0]undec-7-en (DBU) under a nitrogen atmosphere and degassed several times. The temperature was gradually increased up to 90 °C and the flask was degassed again with nitrogen. Then the reaction mixture was stirred at 145–150 °C for 36 h. After the reaction mixture was cooled and evaporated to dryness. The remaining dark green solid was stirred with 25 ml diethyl ether and filtered. Finally, the raw green product was refluxed with dry THF in soxlet equipment for 3 days to give the light green yield. Yield: 0.14 g, (54%), mp: 226–229 °C. Anal. Calc. for C$_{88}$H$_{58}$N$_{24}$O$_8$S$_4$: C, 61.89; H, 3.42; N, 19.68. Found: C, 61.74; H, 3.28; N, 19.86%. IR (KBr tablet) v_{max}/cm^{-1}: 3230–3219 (–NH$_{triazole}$ + –NH$_{pc}$), 3055 (Ar-CH), 2919 (Aliphatic-CH), 1711 (C=O), 1598 (CH=N). ^{1}H NMR. (DMSO-d_6), (δ: ppm): 11.98 (br s, 4H, NH), 9.98 (s, 4H, CH=N), 8.1–7.61 (m, 12H, Ar-H$_{thiophene}$), 7.38–6.53 (m, 28H, Ar-H), 4.24 (s, 8H, CH$_2$), −7.16 (s, 2H, –NH$_{pc}$). ^{13}C NMR. (DMSO-d_6), (δ: ppm): 186.5, 162.33 (C=O), 157.55 (CH=N), 148.02 (C=N), 142.43, 139.11, 137.05, 135.99, 132.27, 129.47, 129.39, 126.83, 126.82, 126.2, 124.39, 124.12, 123.38, 123.11, 122.11, 121.50, 121.44, 115.5, 28.25 (CH$_2$). UV–Vis (pyridine): λ_{max}/nm: [($10^{-5} \varepsilon$ dm^3 mol^{-1} cm^{-1})]: 269 (4.78), 290 (4.76), 305 (5.10), 668 (5.03), 705 (5.06) MS (ESI), (m/z): 1708.50 [M+1]$^+$.

2.4. Copper(II) phthalocyanine (5)

2.4.1. Method A

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous CuCl$_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was irradiated in a microwave oven at 175 °C, 600 W for 8 min. Then it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether, and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (1:0.1) as eluents to give dark green yield. The yield was more than in Method B. Yield: 0.14 g, (40.9%), mp > 300 °C.

Anal. Calc. for C$_{88}$H$_{56}$N$_{24}$O$_8$S$_4$Cu:C, 59.74; H, 3.19; N, 19.00; Cu, 3.59. Found: C, 59.46; H, 3.34; N, 18.68; Cu, 3.81%. IR (KBr tablet) v_{max}/cm^{-1}: 3393 (–NH$_{triazole}$), 3097 (Ar-H), 2923 (Aliphatic-H), 1717 (C=O), 1600 (CH=N + C=C), 1471 (–CH$_2$), 1450 (CH$_2$–S–C), 1352 (C–N), 1270, 1231, 1097 (C–O–C), 1227 (CH$_2$-S), 946 (–NH), 845 (C–O–C + NH). UV–Vis (pyridine): λ_{max}/nm: [($10^{-4} \varepsilon$ dm^3 mol^{-1} cm^{-1})]: 225 (5.01), 288 (4.90), 323 (4.89), 617 (4.43), 686 (5.06). MS (ESI), (m/z): 1771.30 [M+1]$^+$.

2.4.2. Method B

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous CuCl$_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was heated to 145–150 °C under N$_2$ and held at that temperature for 48 h. After cooling to room temperature, it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, and diethyl ether. Yield: 0.10 g, (29.2%).

2.5. Nickel(II) phthalocyanine (6)

2.5.1. Method A

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous NiCl$_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was irradiated in a microwave oven at 175 °C, 600 W for 8 min. Then it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether, and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (1:0.1) as eluents to give dark green yield. The yield was more than in Method B. Yield: 0.18 g, (52.7%), mp > 300 °C. Anal. Calc. for C$_{88}$H$_{56}$N$_{24}$O$_8$S$_4$Ni: C, 59.90; H, 3.20; N, 19.03; Ni, 3.33. Found: C, 59.61; H, 3.12; N, 18.89; Ni, 3.54%. IR (KBr tablet) v_{max}/cm^{-1}: 3392 (–NH$_{triazole}$), 3093 (Ar-H), 2923 (Aliphatic-H), 1719 (C=O), 1598 (CH=N + C=C), 1473 (–CH$_2$), 1450 (CH$_2$–S–C), 1354 (C–N), 1264, 1235, 1071 (C–O–C), 1223 (CH$_2$–S), 953 (–NH), 842 (C–O–C + NH). ^{1}H NMR. (DMSO-d_6), (δ: ppm): 11.91 (br s, 4H, NH$_{triazole}$), 9.89 (s, 4H, CH=N), 8.41–6.99 (m, 40H, Ar-H$_{thiophene}$ and Ar-H), 3.93 (s, 8H, CH$_2$). UV–Vis (pyridine): λ_{max}/nm: [($10^{-4} \varepsilon$ dm^3 mol^{-1} cm^{-1})]: 231 (4.95), 253 (5.02), 287 (4.93), 315 (5.90), 613 (4.34), 681 (5.12). MS (ESI), (m/z): 597.48 [M+Na+1−C$_{56}$H$_{40}$N$_{16}$O$_8$S$_4$]$^+$.

2.5.2. Method B

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous NiCl$_2$ (0.05 g, 0.387 mmol) and dry DMAE (2 ml) was heated to 145–150 °C under N$_2$ and held at that temperature for 48 h. After cooling to room temperature, it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, and diethyl ether. Yield: 0.13 g, (38.1%).

2.6. Zinc(II) phthalocyanine (7)

2.6.1. Method A

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous $ZnCl_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was irradiated in a microwave oven at 160 °C, 360 W for 4 min. Then it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether, and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (1:0.1) as eluents to give dark green yield. The yield was more than in Method B. Yield: 0.19 g, (55.4%), mp > 300 °C. Anal. Calc. for $C_{88}H_{56}N_{24}O_8S_4Zn$: C, 59.67; H, 3.19; N, 18.98; Zn, 3.69. Found: C, 59.38; H, 3.26; N, 18.71; Zn, 3.98%. IR (KBr tablet) v_{max}/cm^{-1}: 3390 (–NH$_{triazole}$), 3087 (Ar-H), 2925 (Aliphatic-H), 1711 (C=O), 1600 (CH=N + C=C), 1478 (–CH$_2$), 1446 (CH$_2$–S–C), 1316 (C–N), 1241, 1236, 1179 (C–O–C), 1221 (CH$_2$–S), 943 (–NH), 834 (C–O–C + NH). ^{1}H NMR. (DMSO-d_6), (δ: ppm): 11.93 (br s, 4H, NH), 9.66 (s, 4H, CH=N), 8.85–6.68 (m, 40H, Ar-H$_{thiophene}$ and Ar-H), 3.44 (s, 8H, CH$_2$). UV–Vis (pyridine): λ_{max}/nm: [(10^{-4} ε dm^3 mol^{-1} cm^{-1})]: 247 (5.00), 298 (5.07), 345 (4.87), 607 (4.49), 685 (5.13). MS (ESI), (m/z): 1795.78 [M+Na]$^+$.

2.6.2. Method B

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous $ZnCl_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was heated to 145–150 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, and diethyl ether. Yield: 0.15 g, (43.7%).

2.7. Cobalt(II) phthalocyanine (8)

2.7.1. Method A

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous $CoCl_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was irradiated in a microwave oven at 175 °C, 600 W for 15 min. Then it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether, and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (1:0.1) as eluents to give dark green yield. The yield was more than in Method B. Yield: 0.11 g, (32%), mp > 300 °C. Anal. Calc. for $C_{88}H_{56}N_{24}O_8S_4Co$: C, 59.89; H, 3.20; N, 19.05; Co, 3.34. Found: C, 59.81; H, 3.08; N, 18.81; Co, 3.51%. IR (KBr tablet) v_{max}/cm^{-1}: 3394 (–NH$_{triazole}$), 3088 (Ar-H), 2923 (Aliphatic-H), 1720 (C=O), 1600 (CH=N + C=C), 1479 (–CH$_2$), 1450 (CH$_2$–S–C), 1354 (C–N), 1244, 1233, 1152 (C–O–C), 1220 (CH$_2$–S), 952 (–NH), 845 (C–O–C + NH). UV–Vis (pyridine): λ_{max}/nm: [(10^{-4} ε dm^3 mol^{-1} cm^{-1})]: 256 (4.90), 284 (5.07), 307 (4.81), 604 (4.34), 670 (4.99). MS (ESI), (m/z): 1765.01 [M+1]$^+$.

2.7.2. Method B

A mixture of compound (3) (0.33 g, 0.77 mmol), anhydrous $CoCl_2$ (0.05 g, 0.39 mmol) and dry DMAE (2 ml) was heated to 145–150 °C under N_2 and held at that temperature for 60 h. After cooling to room temperature, it was diluted with hot ethanol (ca. 30 ml) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, and diethyl ether. Yield: 0.07 g, (20.5%).

3. Results and discussion

The preparation of Schiff bases (2), (3), the target metal-free (4) and metallophthalocyanines (5, 6, 7) and (8) are shown in Scheme 1. The structures of novel compounds were characterized by a combination of ^{1}H/^{13}C NMR, IR, UV–Vis, elemental analysis and MS spectral data. 4-Amino-5-(2-thienylmethyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (1) was prepared from the reaction of hydrazine hydrate to the N'-(1-ethoxy-2-thiophene-2-yl-ethlydene)-hydrazine carbocyclic acid ethyl ester in 1:1 ratio for 6 h [19] (Scheme 2).

The condensation of (1) with salicylaldehyde at 1:1 ratio was gave the salicylic Schiff base (2) in a high yield-(80.1%) [19]. In the IR spectrum of (2), the intense absorption bands at 3316–3218 cm^{-1}, corresponding to the –NH$_2$ groups, disappear after the conversation to salicylaldehyde and appear a new band at 1645 cm^{-1} corresponding to C=N group, indicating that the combining has occured. The rest of the spectra of (2) resembles closely that of (1) and (1a) including the characteristic vibration of aliphatic, thiophene and phenolic groups. ^{1}H NMR spectra of (2) are almost identical, with only small changes in shifts. The difference between the two spectra of substituted amine (1) and Schiff base (2) is clear from the presence of iminic carbon –CH=N at 9.98 ppm. ^{13}C NMR spectra of (2) clearly indicates the presence of C=O, CH=N and C=N group bands at 158.28, 151.86 and 146.21 ppm, and the others (aliphatic and aromatic carbons), respectively. The MS mass spectrum of (2) shows a molecular ion peak at $m/z = 300.52$ [M]$^+$, supporting the proposed formula for this compound.

The compound (3) was obtained from the reaction of (2) to 4-nitrophthalonitrile (2a) in dry K_2CO_3/dry DMF under Microwave oven atmosphere at room temperature, 360 W for 5 min. These were accomplished by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with (2) [20,21]. Similarly, Comparison of the IR spectral data clearly indicated the formation of compound (3) by the disappearance of the O–H band of (2) at 3590 zand 1352 cm^{-1} and of NO$_2$ band of (2a) at 1519 and 1333 cm^{-1}, and the appearance of a new absorption at 2230 cm^{-1} (C≡N). ^{1}H NMR spectra of (3) showed a new signal due to iminic carbon (–CH=N) at $\delta = 9.90$ ppm, as expected. While the ^{1}H NMR spectra of (2) and (3) are similar, the proton-decoupled ^{13}C NMR spectrum indicated the presence of nitrile carbon atoms in (3) at $\delta = 115.69$ and 115.19 ppm, respectively. In addition, the MS mass spectrum
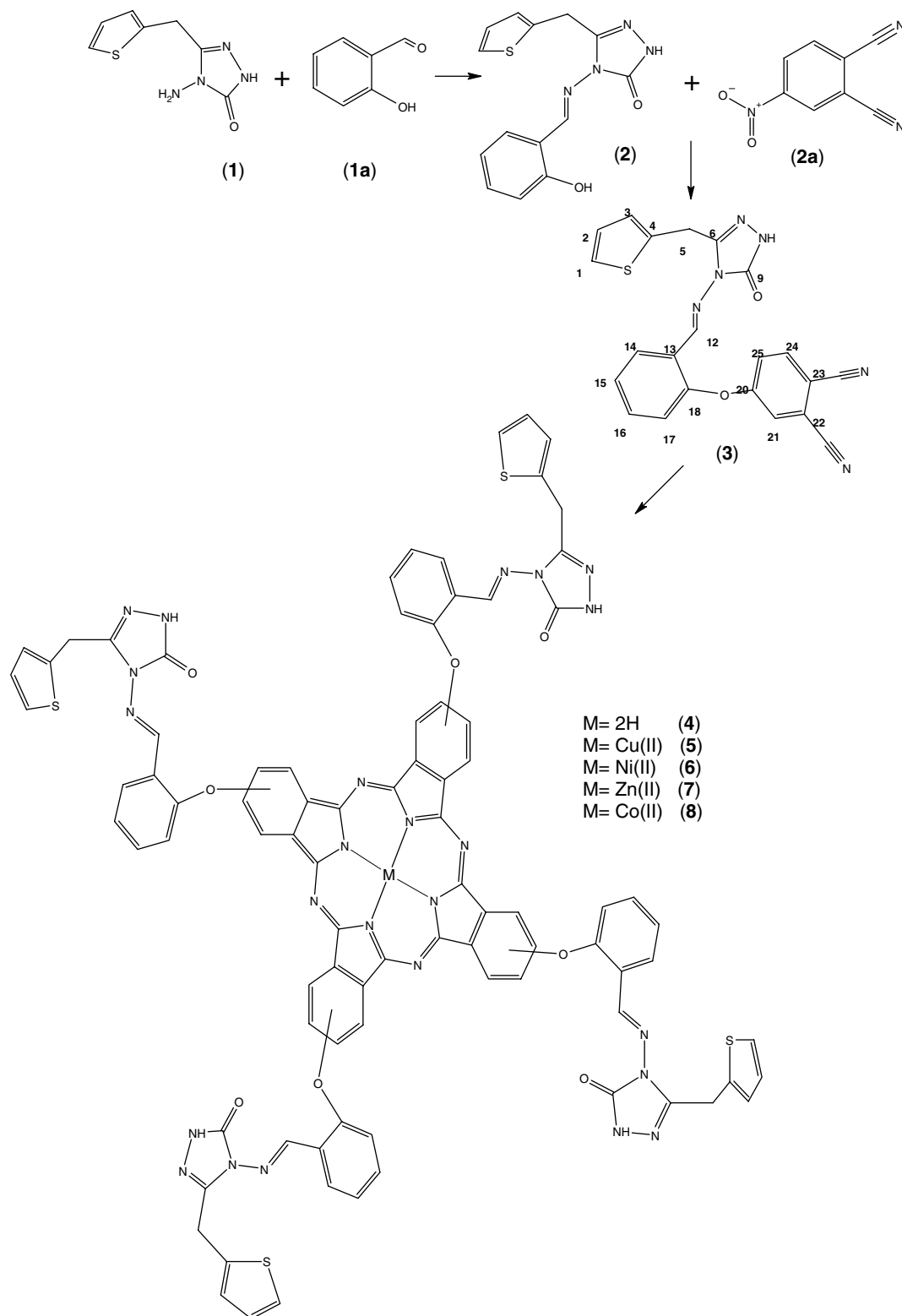
Scheme 2. The synthesis of metal-free and metallophthalocyanines.

of (3) shows a molecular ion peak at $m/z = 493.4$ $[M+C_2H_6O+Na-2]^+$, supporting the proposed formula for this compound.

The metal-free derivative (H$_2$Pc) (4) was obtained directly by the reaction of substituted phthalonitrile (3)

with dry n-hexanol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [22].

Cyclotetramerization of phthalonitrile based on thiophene (3) in the presence of metal salts by two different methods gave the metal phthalocyanines (5, 6, 7) and (8)

[23,24]. The solvent for conventional method was DMAE (*N,N*-dimethylaminoethanol) for all metal salts. In addition, in the microwave-assisted method, the reactions of (**5**, **6**, **7**) and (**8**) were accomplished in DMAE at 600 W for 8 min for Cu(II) and Ni(II), 360 W for 4 min for Zn(II) and 600 W for 15 min for Co(II). The solubility of the phthalocyanines was low in common organic solvents such as ethyl acetate, acetone, tetrahydrofurane, ethanol DMF.

The IR spectrum of metal-free phthalocyanine (**4**) shows two different –NH bands (inner –NH and triazolic –NH) at 3230–3219 cm^{-1}. The rest of spectrum of (**4**) is exactly similar that (**3**) except for C≡N group in (**3**). The inner core –NH protons of metal-free phthalocyanine (**4**) were also identified in the ¹H NMR spectrum. Interestingly, at high concentration strong shielding of the cavity protons in the phthalocyanine core of this compound was indicated by a single sharp resonance at $\delta = -7.16$ ppm, while be expected to a broad resonance [25] which could be attributed to the inner –NH resonance. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave significant absorbance characteristic of the proposed structure. The MS mass spectrum of (**4**) shows a molecular ion peak at $m/z = 1708.50$ [M+1]⁺, supporting the proposed formula for this compound.

The metallophthalocyanines (**5**, **6**, **7**) and (**8**) were obtained from dicyano derivative (**3**) and corresponding anhydrous metal salts $CuCl_2$, $NiCl_2$, $ZnCl_2$ and $CoCl_2$, respectively, both microwave irradiation in DMAE for 4–15 min and in a sealed tube in DMAE for 24–60 h. In the IR spectra of all metallophthalocyanines, the disappearance of strong C≡N stretching vibration of (**3**) and of inner –NH band at ca. 3219 cm^{-1} is an evidence for the formation of Metal-Pcs (**5**, **6**, **7**) and (**8**). Also, in the ¹H NMR spectrum of metallophthalocyanines (**6**) and (**7**) in DMSO-d_6, the peak at $\delta = 11.98$ ppm for Ni(II) and at $\delta = 11.93$ ppm for Zn(II) pertaining to triazolic –NH was found, confirmed that this observation is accurate. In the mass spectrum of compounds (**5**, **6**, **7**) and (**8**), the molecular ion peaks were observed at $m/z = 1771.30$ [M+1]⁺ for Cu(II), 597.48 [M+Na+1−$C_{56}H_{40}N_{16}O_8S_4$]⁺ for Ni(II), 1795.78 [M+Na]⁺ for Zn(II) and 1765.03 [M+1]⁺ for Co(II), confirmed the proposed structure.

In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at ca. 300–500 nm related to the B band and the other in the visible region at ca. 600–750 nm related to the Q band [26]. The Q band absorptions of (**4**) in pyridine at $\lambda = 705$ and 668 nm and the other absorptions (as known B) at 305, 290 and 269 nm are consistent with the results obtained previously known phthalocyanines [27–29], and which have been ascribed to the deeper $\pi \to \pi^*$ levels of LUMO transitions (Fig. 1). The Q band absorption present in (**4**) can be attributed to the fact that the symmetry of metal-free phthalocyanine is nondegenerate (D_{2h}) and is split in a Q_x and a Q_y peak as shown in the spectrum [30]. Also, an increase in the concentration leads to aggregation which is easily monitored by the position of
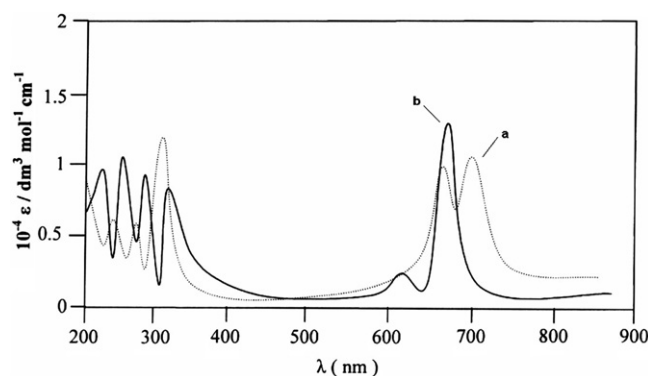

Fig 1. UV–Vis spectra of compounds (**4**) and (**6**) in pyridine; (a) corresponds to H_2Pc and (b) corresponds to NiPc.

the Q band which is shifted to shorter wavelengths, and to a decrease in molar absorption coefficient [31–33].

The UV–Vis absorption spectra of metallophthalocyanines (**5**, **6**, **7**) and (**8**) are given in Figs. 1 and 2. These compounds showed the expected absorptions at the main peaks of the Q and B bands appearing at $\lambda = 686$, 617 nm and 323, 288 and 225 nm for Cu(II), 681, 613 nm and 315, 287, 253 and 231 nm for Ni(II), 685, 607 nm and 345, 298 and 247 nm for Zn(II), and 670, 604 nm and 307, 284 and 256 nm for Co(II), respectively. This result is typical of metal complexes of substituted and unsubstituted Pc with D_{4h} symmetry [2,34].

4. Computational method

In our calculations, for the geometry optimizations, we employed the restricted Hartree–Fock (RHF) method, as coded in HYPERCHEM 7.5 program running on an Intel Pentium D inside cluster. Basis sets used for all calculations were 6-31G(d) for C, S, N and O. The input structures of the complexes were optimized using MM+ method [35]. If the optimized geometry was found to have different conformation, from that in which it coordinates to a metal ion,
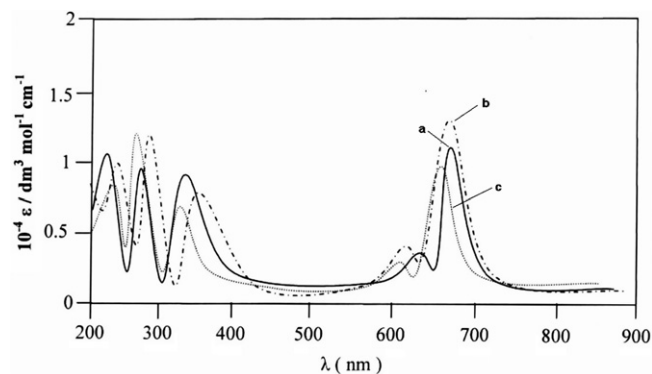

Fig 2. UV–Vis spectra of compounds (**5**), (**7**) and (**8**) in pyridine; (a) corresponds to CuPc, (b) corresponds to ZnPc, and (c) corresponds to CoPc.

some of the torsion angles were appropriately modified to obtain the correct conformation, corresponding to the coordination mode and then the geometry optimizations were made using the ZINDO/S method for MPc [35]. Furthermore, the single point calculations at HF level were carried out on all structures [36,37].

4.1. Molecular structures

The single point energy-minimized structures calculated at HF/6-31(d) level is D_{4h} symmetry for MPc. It is worth pointing out that no imaginary vibration is predicted in the following frequency calculations, indicating that the energy-minimized structures are true energy minima.

As listed in Table 1, the X-ray crystal parameters for CuPc [38], NiPc [39], ZnPc [40] and CoPc [41] are almost in agreement with the calculated data.

Analysis of the calculated structural parameters for CuPc, NiPc, ZnPc and CoPc shows that the sizes of the central holes (N–N distance) are, 3.88920 3.79519, 3.96765 and 3.83584 Å, respectively. That is to say, the order of the sizes of the central hole is CoPc > NiPc < CuPc < ZnPc. It is noteworthy that this pattern is in complete accord with the variation of octahedral M^{2+} ions radii suggested by Shannon [42] and discussed by Hargittai [43] in her paper on the bond lengths of transition metal halides, and studied by Liu on first transition metal phthalocyanines [36]. And the order also agrees well with the experiment. The lengths of the C_α–N_m bonds and the degrees of the $<C_\alpha N_m C_\alpha$ and $<C_\alpha N_c C_\alpha$ also agree with the order, whereas the lengths of C_α–N_c are contrary to the order, CoPc < NiPc > CuPc > ZnPc.

4.2. Electronic structures and molecular orbitals

The energies of the molecular orbitals from HOMO − 5 to LUMO + 3 of the four derivatives are shown in Table 2, and also the pictures of HOMO–LUMO orbitals of all metallophthalocyanines are shown in Figs. 3a and 3b. The calculated energies of the molecular orbitals are exhibited to five numbers after decimal point at the most with the output file; however, four numbers after decimal point reserved are enough to be compared one after another. This is the reason why the energies of the molecular orbitals are kept four numbers after decimal points.

On the basis of our calculation, the energy of the HOMO and the LUMO are both negative for the four compounds. For the four compounds, the maximum of the HOMO corresponds to CoPc, while minimum of the LUMO corresponds to CuPc and are −5.7152 for Co(II) and 3.1709 eV for Cu(II). Hence, CuPc has the minimum of the HOMO–LUMO gaps, 1.9444 eV, which indicates that the Q bands of CuPc should shift to the longest wavelength side. This is because that the position of the Q band has the relation with the HOMO–LUMO gap. The bigger the value of the HOMO–LUMO gap is, the shorter the wavelength of the Q band shifts to. The other HOMO–LUMO gaps for NiPc, ZnPc and CoPc are 2.1056, 1.9692 and 2.1122 eV, respectively. These exhibit that the HOMO–LUMO gaps vary in order of CuPc < ZnPc < NiPc < CoPc, hence the variation of the Q bands ought to follow the trend, CuPc > ZnPc > NiPc > CoPc. The experimental results reveal that the position of Q-band in the electronic spectra about accords with the theoretical ones [36]. Additionally, for all metallophthalocyanines, the Q bands at

Table 1
Bond length (Å) and bond angle (°) of experiment and calculation for CuPc, NiPc, ZnPc and CoPc

Parameter	CuPc		NiPc		ZnPc		CoPc	
	Exp[a]	HF	Exp[b]	HF	Exp[c]	HF	Exp[d]	HF
M–N_c	1.935	1.9321	1.83	1.8441	1.98	1.9799	1.907	1.8979
C_α–N_m	1.328	1.3226	1.375	1.3693	1.331	1.3229	1.317	1.3226
C_α–N_c	1.366	1.3599	1.385	1.3990	1.369	1.3521	1.375	1.3813
C_α–C_β	1.453	1.4405	1.46	1.4256	1.455	1.4571	1.45	1.4501
C_β–C_β	1.4	1.3819	1.38	1.3721	1.4	1.3933	1.384	1.3834
C_β–N_γ	1.388	1.3786	1.39	1.3871	1.393	1.3872	1.384	1.3796
N_γ–N_δ	1.377	1.3674	–	1.3840	1.391	1.3843	1.38	1.3806
N_δ–N_δ	1.413	1.4087	–	1.3890	1.396	1.3851	1.385	1.3823
M–N_c–C_α	126.4	126.37	130.5	131.96	125.4	124.83	126.6	126.84
N_c–C_α–N_m	127.6	128.44	126	128.11	127.8	127.11	127.6	127.83
C_α–N_c–C_α	107.3	106.49	99	107.49	109.1	108.44	106.7	106.44
N_c–C_α–C_β	110.4	110.17	115.5	114.52	108.8	108.69	110.1	110.49
C_α–C_β–C_β	106	105.96	105	104.85	106.6	106.28	106.5	106.81
C_β–C_β–N_γ	121.1	120.84	120	121.03	121.3	121.29	121.4	121.47
C_β–N_γ–N_δ	117.9	117.63	–	117.40	117.3	117.49	117.1	117.20
N_γ–N_δ–N_δ	121	121.41	–	122.33	121.5	120.82	121.5	121.51
C_α–N_m–C_α	121.19	121.77	117	116.83	123.5	122.95	121.5	122.01

[a] Cited from Ref. [38].
[b] Cited from Ref. [39].
[c] Cited from Ref. [40].
[d] Cited from Ref. [41].

Table 2
Energy levels (in eV) of some occupied and unoccupied molecular orbital for CuPc, NiPc, ZnPc and CoPc

	CuPc		NiPc		ZnPc		CoPc	
E_{LUMO+3}	−1.5383	B1U	−1.7659	B1U	−1.2833	B1U	−1.8561	B1U
E_{LUMO+2}	−1.7062	EG	−2.2792	EG	−1.5261	EG	−1.9211	EG
E_{LUMO+1}	−3.1709	EG	−3.3359	EG	−3.3577	EG	−3.6030	EG
E_{LUMO}	−3.1709	A1G	−3.3359	A1G	−3.3577	A1G	−3.6030	A1G
ΔE	1.9444		2.1056		1.9692		2.1122	
E_{HOMO}	−5.1153	A1U	−5.4415	A1U	−5.3269	A1U	−5.7152	A1U
E_{HOMO-1}	−7.0957	EG	−7.4117	EG	−7.3257	EG	−7.6599	EG
E_{HOMO-2}	−7.4317	EG	−7.6163	EG	−7.5804	EG	−7.9027	EG
E_{HOMO-3}	−7.5691	B2G	−7.6807	B2G	−7.6596	B2G	−8.0249	B2G
E_{HOMO-4}	−7.5926	B2U	−7.6955	B2U	−7.6975	B2U	−8.0762	B2U
E_{HOMO-5}	−7.6514	A2U	−7.8644	A2U	−7.8514	A2U	−8.1630	A2U

a. Cu-Homo   **b. Ni-Homo**   **c. Zn-Homo**   **d. Co-Homo**
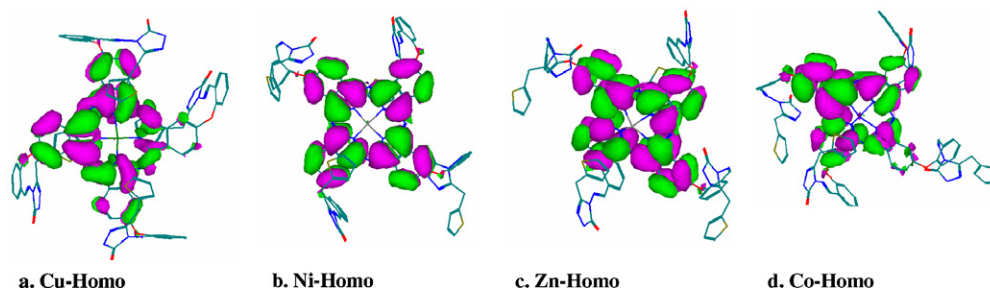
Fig 3a. The molecular orbital map for the HOMO of (a) CuPc, (b) NiPc, (c) ZnPc and (d) CoPc.

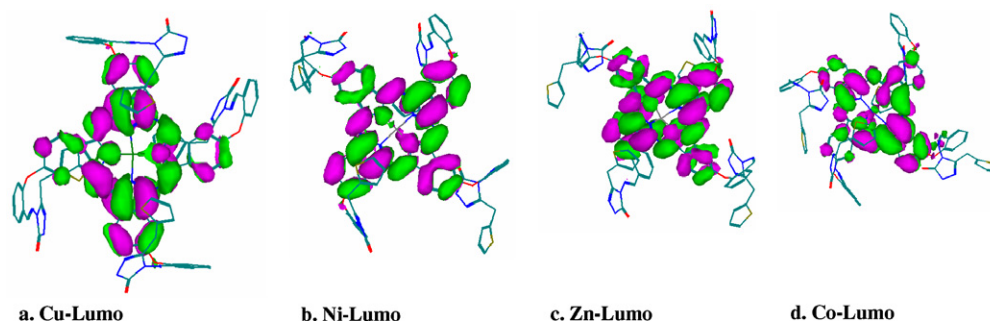**a. Cu-Lumo**   **b. Ni-Lumo**   **c. Zn-Lumo**   **d. Co-Lumo**

Fig 3b. The molecular orbital map for the LUMO of (a) CuPc, (b) NiPc, (c) ZnPc and (d) CoPc.

ca. 686 (experimentally) for Cu(II), 685 for Zn(II), 681 for Ni(II) and 670 nm for Co(II) correspond to HOMO → LUMO + 1 transitions, while the Soret bands at ca. 307–345 nm correspond to HOMO + 2 → LUMO + 1, ca. 284–298 nm fit to HOMO + 5 → LUMO + 1, and ca. 225–256 nm correspond to HOMO → LUMO + 6 transitions, respectively, [37].

5. Conclusions

The cyclotetramerization reaction of the phthalonitrile derivative in a multi-step reaction sequence resulted in the formation of novel tetrasubstituted, metal-free phthalocyanine and metallophtalocyanines bearing four thiophen and triazole heterocyclic peripheral groups. The new compounds were characterized by a combination of IR, ^1H NMR, ^{13}C NMR, UV–Vis, elemental analysis and MS spectral data. Furthermore, theoretical calculations were carried out to comparatively describe the molecular structures, molecular orbital and UV–Vis spectra of metallophthalocyanine complexes and so the geometries of metal cations, Cu^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+}, with six ring clusters of metallophthalocyanine structure were calculated at the HF/6-31G(d) level of theory. All of metal cations localized in the fourfold nitrogen coordination within chosen bulky-type structures. The average distances between the metal cations and four coordinated nitrogen atoms in MPcs, estimated by the HF/6-31G(d) calculations, were in the range of 1.84–1.97 Å, which are close to experimental results. The natures of the main transitions in electronic absorption spectra of the four compounds were also assigned.

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