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Microwave-assisted synthesis and characterization of novel symmetrical substituted 19-membered tetrathiadiaza metal-free and metallophthalocyanines and investigation of their biological activities

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ABSTRACT

This work reports on a new symmetrically substituted metal-free phthalocyanine and its transition metal complexes which were prepared by a condensation of *N*,*N'*-[*propan-1,3-diilbis*(*tiyoetan-2,1-diil*)]*bis*(4-*methylbenzenesulfonamid*) (**1**) and *1,2-bis* (2-*iodomercaptoethyl*)-4,5-*dicyanobenzene* (**2**) with NiCl₂, ZnCl₂, CoCl₂, CuCl₂, and PbO salts in 2-(dimethylamino)ethanol, respectively. The phthalocyanines bearing thia and aza donor atoms at the peripheral position were characterized by IR, UV–Vis, ¹H NMR, ¹³C NMR, Mass spectra, and elemental analysis data. The thermal behaviors of **4**–**9** were investigated by TG/DTA. Novel phthalocyanines were also investigated for enlightening their possible biological activities by employing antimicrobial (antibacterial and antifungal), antineoplastic and antioxidative assays. Of all tested, four samples exhibited antimicrobial activity against test microorganisms, among which, *Branhamella catarrhalis* was the most sensitive one with a MIC value around 0.312 mg/mL followed by a yeast, *Candida albicans* (MIC. 0.625 mg/mL). Due to their colored nature, the samples were found not to be applicable for antioxidative and antineoplastic assays.

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1. Introduction

Phthalocyanine which is a class of organic compounds was first used by Reginald P. Linstead in 1933 [1]. On account of their technological and scientific significance in various fields, phthalocyanines have attracted considerable attention over many decades. They have been employed in several 'hi-tech' applications such as photo conducting material in laser printers and light absorbing layers in recordable CDs [2], and used in optical limiting devices [3–5], liquid crystals (LCs) [6–8], solar cells [9,10], batteries [11]. Due to the fact that diamagnetic central metal ions (such as Zn or Mg) enhance the photo toxicity of the phthalocyanines, the substituted phthalocyanine derivatives can also be used for photodynamic cancer therapy and other processes driven by visible light [12–15].

Generally, phthalocyanines can be obtained by the template reactions of diverse precursors such as phthalonitrile, cyano-benzamide, phthalic acid and phthalamide with metal salts in highboiling nonaqeous solvents at elevated temperatures [16,17]. Recently, microwave processing techniques have attracted considerable interest as potential alternatives to classical template processing in view of the advantages of microwave heating which is direct, rapid, controllable and selective [18–20].

Up to this point, a great variety of symmetrical phthalocyanines have been fairly numerously synthesized [21–23]. We have also synthesized novel phthalocyanines bearing macrocyclic substituents (e.g. diazaheptathia [24], tetraoxamonoaza [25], and dithiadiazadioxa [26]).

In this study, we report that the preparation and characterization by spectral features of metal-free and metallophthalocyanines bearing four 19-membered tetrathiadiaza moieties at the peripheral positions. Besides, we have carried out the thermogravimetric study of tetrasubstituted metal-free phthalocyanine (**4**) and metallophthalocyanines (**5**–**9**) in order to compare their thermal stabilities. We believe that these novel compounds which have a relatively high thermal stability will be fundamental substances for potential applications in the future. Furthermore, in this work we investigate that the four of these novel phthalocyanines exhibit moderate antimicrobial activity against test microorganisms except for *Branhamella catarrhalis*.

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2. Experimental

N,N'-[propan-1,3-diilbis(tiyoetan-2,1-diil)]bis(4-methylbenzenesulfonamid) (1) and 1,2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene (2) were prepared according to the reported procedures [27,28]. All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. All reactions were carried under a dry nitrogen atmosphere using Standard Schlenk techniques. All reagents and solvents were dried and purified before use as described by reported procedure [29]. FT-IR spectra were obtained on a Perkin Elmer 1600 FTIR Spectrophotometer with the samples prepared as KBr pellets.NMR spectra were recorded on a Varian Mercury 200 MHz Spectrometer in CDCl₃, and chemical shifts were reported (δ) relative to Me₄Si as an internal standard. Mass spectra were recorded on a Micromass Quatro LC/ULTIMA LC-MS/MS Spectrometer. Elemental analyses and metal contents of these compounds were performed on a Costech ECS 4010 Spectrophotometer. Melting points were measured on an electrothermal apparatus. UV-Visible spectra were recorded using a Unicam UV2-100 Spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Domestic microwave oven was used for carrying out all synthesis of phthalocyanines. A Seiko II Exstar 6000 thermal analyzer was used to record the DTA curves under a nitrogen atmosphere with a heating rate of 20 °C min⁻¹ in the temperature range of 30–900 °C using platinum crucibles.

2.1. Synthesis

2.1.1. Synthesis of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10,13,14,15,16-dekahydro-2H,8H,12H-1,17,7,11,4,14benzotetrathiadiazacyclononadecin-19,20- dicarbonitrile (**3**)

N,*N*'-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1 diyl)) bis(4-methylbenzene sulfonamide) (1) (0.95 g, 1.9 mmol) was dissolved in dry DMF (20 mL) under a nitrogen atmosphere and finely ground anhydrous K₂CO₃ (0.79 g, 5.7 mmol) was added and the mixture stirred at 50 °C for 2 h. A solution of 1, 2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene (2) (0.95 g, 1.9 mmol) in dry DMF (90 mL) was added dropwise over 3 h. After stirring at 50 °C for 6 days, the reaction mixture was poured into ice (100 g) and stirred for 2 h. The residue was extracted with chloroform $(2 \times 100 \text{ mL})$. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure to give a yellow crude product. The product was precipitated from ethanol. The solid product was chromatographed on silica gel with hexane/ethyl acetate (6:4) as eluents. Yield: 0.75 g (53%) m.p: 127–130 °C. Anal. Calcd. for (C₃₃H₃₈N₄O₄S₆) (%): C, 53.05; H, 5.13; N, 7.50; S, 25.75. Found: C, 53.24; H, 5.26; N, 7.62; S, 25.88%. IR (KBr pellet) v_{max}/cm⁻¹: 3077 (Ar–H), 2922–2851 (Aliph. C–H), 2231 (C≡N), 1588, 1564, 1462, 1345, 1259, 1156, 1120, 970, 904, 833. ¹H NMR(CDCl₃), (δ: ppm): 7.77 (d, 4H, Ar–H),7.55 (d, 4H, Ar–H), 7.26 (s, 2H, Ar-H), 5.86 (t, 4H, S-CH₂), 3.36 (t, 4H, N-CH₂), 3.12 (t, 4H, N-CH₂), 2.63 (t, 4H, S-CH₂), 2.49 (t, 4H, S-CH₂), 2.42 (s, 6H, CH₃), 1.24 (m, 2H, CH₂). ¹³C NMR (CDCl₃), (δ: ppm): 149.72, 145.12, 142.63, 134.12, 126.04, 125.77, 115.17, 114.83, 47.15, 44.69, 41.54, 40.04, 35.23, 32.00, 30.48, 29.74, 25.07. MS (FAB), (*m*/*z*): 743 [M - 3]⁺.

2.1.2. Metal-free phthalocyanine (4)

A mixture of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10,13, 14,15,16-dekahydro-2H,8H,12H-1,17,7,11,4,14-benzotetrathiadiazacyclononadecin-19,20-dicarbonitrile (**3**) (0.10 g, 0.13 mmol), 2-(dimethylamino)ethanol (2 mL) and DBU (2 drops) were irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to the room temperature, this reaction mixture was refluxed with ethanol. The dark green product was filtered off, washed with hot ethanol and methanol, and then dried *in vacuo* over P_2O_5 . This product obtained was purified by column chromatography with silica gel, using chloroform: methanol (4:6) as the solvent system. Yield: 0.035 g (35%), m.p: 206–270 °C. Anal. Calcd. for $(C_{132}H_{154}N_{16}O_{16}S_{24})$ (%): C, 53.02; H, 5.19; N, 7.49; S, 25.74. Found: C, 52.83; H, 5.37; N, 7.61; S, 25.62%. IR (KBr pellet) ν_{max}/cm^{-1} : 3065 (Ar–H), 2921–2851 (Aliph. C–H), 1585, 1506, 1454, 1377, 1322, 1250, 1152, 1124, 1073, 962, 746. ¹H NMR (CDCl₃): (δ : ppm): 7.69 (m, 16H, Ar–H), 7.30 (s, 8H, Ar–H), 5.07 (t, 16H, S–CH₂), 3.34 (t, 16H, N–CH₂), 3.25 (t, 16H, N–CH₂), 2.78 (t, 16H, S–CH₂), 2.36 (t, 16H, S–CH₂), 2.17 (s, 24H, CH₃), 1.5 (m, 24H, CH₂). ¹³C NMR (CDCl₃). (δ : ppm): 153.77, 146.23, 140.93, 135.23, 132.95, 122.03, 115.55, 114.61, 48.36, 45.23, 40.81, 38.84, 36.31, 34.46, 31.94, 29.16, 25.13. UV–Vis [(pyridine) [(10⁻⁵ ε dm³ mol⁻¹cm⁻¹)]: 707 (5.08), 665 (5.04), 338 (5.23). MS (FAB), (*m*/*z*): 2987 [M + 1]⁺.

2.1.3. Nickel (II) phthalocyanine (5)

A mixture of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10,13,14, 15,16-dekahydro-2H,8H,12H-1,17,7,11,4,14-benzotetrathiadiazacyclononadecin-19,20-dicarbonitrile (3) (0.10 g, 0.13 mmol), anhydrous NiCl₂ (0.0043 g, 0.033 mmol), and 2-(dimethylamino)ethanol (2 mL) were irradiated in a microwave oven at 175 °C, 350 W for 7 min. After cooling to the room temperature, this reaction mixture was refluxed with ethanol. The dark green product was filtered off, washed with hot ethanol and methanol, and then dried in vacuo over P₂O₅. This product obtained was purified by column chromatography with silica gel, using chloroform: ethanol (4:6) as the solvent system. Yield: 0.045 g (44%), m.p: 226–257 °C. Anal. Calcd. for (C₁₃₂H₁₅₂N₁₆NiO₁₆S₂₄) (%): C, 52.03; H, 5.03; N, 7.36; S, 25.26. Found: C, 52.20; H, 5.21; N, 7.47; S, 25.34%. IR (KBr pellet) v_{max}/cm⁻¹: 3069 (Ar–H), 2922–2846 (Aliph. C–H), 1586, 1414, 1344, 1157, 1122, 960, 880, 812. ¹H NMR (CDCl₃): (δ: ppm): 7.62 (m, 16H, Ar-H), 7.48 (s, 8H, Ar-H), 5.70 (t, 16H, S-CH₂), 3.33 (t, 16H, N-CH₂), 3.21 (t, 16H, N-CH₂), 2.78 (t, 16H, S-CH₂), 2.46 (t, 16H, S–CH₂), 2.15 (s, 24H, CH₃), 1.27 (m, 24H, CH₂). ¹³C NMR (CDCl₃), (δ: ppm): 150.31, 144.67, 140.14, 130.76, 125.49, 123.52, 115.24, 115.02, 46.05, 44.78, 41.50, 38.66, 32.95, 32.07, 30.18, 29.72, 25.95. UV-Vis [(pyridine) [$(10^{-5} \varepsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$]: 716 (5.18), 647 (4.80), 368 (5.11). MS (FAB), (m/z): 3043 $[M + 1]^+$.

2.1.4. Zinc (II) phthalocyanine (6)

A mixture of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10, 13,14,15,16-dekahydro- 2H,8H,12H-1,17,7,11,4,14-benzotetrathiadiazacyclononadecin-19,20-dicarbonitrile (3) (0.10 g, 0.13 mmol), anhydrous ZnCl₂ (0.0045 g, 0.033 mmol), and 2-(dimethylamino)ethanol (2 mL) were irradiated in a microwave oven at 175 °C, 350 W for 9 min. After cooling to the room temperature, this reaction mixture was refluxed with ethanol. The dark green product was filtered off, washed with hot ethanol and methanol, and then dried in vacuo over P2O5. This product obtained was purified by column chromatography with silica gel, using chloroform: ethanol (4:6) as the solvent system. Yield: 0.028 g (36%), m.p: 202–240 °C. Anal. Calcd. for (C₁₃₂H₁₅₂N₁₆ZnO₁₆S₂₄) (%): C, 51.92; H, 5.02; N, 7.34; S, 25.20. Found: C, 51.80; H, 5.24; N, 7.42; S, 25.38%. IR (KBr pellet) ν_{max}/cm^{-1} : 3069 (Ar-H), 2922-2846 (Aliph. C-H), 1586, 1404, 1333, 1158, 1088, 959, 888, 742. ¹H NMR (CDCl₃): (δ: ppm): 7.90 (m, 16H, Ar–H), 7.53 (s, 8H, Ar-H), 5.67 (t, 16H, S-CH₂), 3.81 (t, 16H, N-CH₂), 3.62 (t, 16H, N-CH₂), 2.69 (t, 16H, S-CH₂), 2.42 (t, 16H, S-CH₂), 2.22 (s, 24H, CH₃), 1.25 (m, 24H, CH₂). ¹³C NMR (CDCl₃), (δ: ppm): 150.13, 146.74, 143.29, 135.60, 127.12, 120.43, 115.92, 115.34, 50.32, 45.44, 42.83, 40.28, 39.27, 33.47, 30.75, 29.64, 24.78. UV–Vis [(pyridine) $[(10^{-5} \varepsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$: 713 (5.25), 644 (4.75), 365 (5.08). MS (FAB), (*m/z*): 3049 [M]⁺.

2.1.5. Cobalt (II) phthalocyanine (7)

A mixture of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10,13,14, 15,16-dekahydro-2H,8H,12H-1,17,7,11,4,14-benzotetrathiadiazacyclononadecin-19,20-dicarbonitrile (**3**) (0.10 g, 0.13 mmol), anhydrous CoCl₂ (0.0043 g, 0.033 mmol), and 2-(dimethylamino)ethanol (2 mL) were irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to the room temperature, this reaction mixture was refluxed with ethanol. The dark green product was filtered off, washed with hot ethanol and methanol, and then dried *in vacuo* over P₂O₅. This product obtained was purified by column chromatography with silica gel, using chloroform: ethanol (4:6) as the solvent system. Yield: 0.045 g (44%), m.p: 208–245 °C. Anal. Calcd. for ($C_{132}H_{152}N_{16}CoO_{16}S_{24}$) (%): C, 52.03; H, 5.03; N, 7.35; S, 25.25. Found: C, 52.18; H, 5.18; N, 7.49; S, 25.41%. IR (KBr pellet) $\nu_{max}/$ cm⁻¹: 3074 (Ar–H), 2912–2851 (Aliph. C–H), 1585, 1411, 1377, 1157, 1119, 963, 891. UV–Vis [(pyridine) [(10⁻⁵ ε dm³ mol⁻¹ cm⁻¹)]: 692 (5.28), 617 (4.82), 479 (4.65). MS (FAB), (*m*/*z*): 3069 [M + Na + 3]⁺.

2.1.6. Copper (II) phthalocyanine (8)

A mixture of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10,13,14, 15,16-dekahydro-2H,8H,12H-1,17,7,11,4,14-benzotetrathiadiazacyclononadecin-19,20-dicarbonitrile (3) (0.10 g, 0.13 mmol), anhydrous CuCl₂ (0.0044 g, 0.033 mmol), and 2-(dimethylamino)ethanol (2 mL) were irradiated in a microwave oven at 175 °C, 350 W for 7 min. After cooling to the room temperature, this reaction mixture was refluxed with ethanol. The dark green product was filtered off, washed with hot ethanol and methanol, and then dried in vacuo over P₂O₅. This product obtained was purified by column chromatography with silica gel, using chloroform: methanol (8:2) as the solvent system.. Yield: 0.038 g (37%), m.p: 221-263 °C. Anal. Calcd. for (C132H152N16CuO16S24) (%):C, 51.95; H, 5.02; N, 7.34; S, 25.22. Found: C, 52.03; H, 5.07; N, 7.39; S, 25.31%. IR (KBr pellet) v_{max}/ cm⁻¹: 3070 (Ar–H), 2923–2857 (Aliph. C–H), 1722, 1596, 1410, 1326–1157 (SO₂), 1092, 954, 814, 661. UV–Vis (chloroform): $\lambda_{max}/\lambda_{max}$ nm: $[(10^{-5} \varepsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$: 710 (5.21), 662 (5.11), 377 (5.20). MS (FAB), (m/z): 3046 $[M - 1]^+$.

2.1.7. Lead (II) phthalocyanine (9)

A mixture of 4,14-bis[(4-methylphenyl)sulfonyl]-3,4,5,6,9,10,13,14, 15,16-dekahydro-2H,8H,12H-1,17,7,11,4,14-benzotetrathiadiazacvclononadecin-19,20-dicarbonitrile (3) (0.10 g, 0.13 mmol), anhydrous PbO (0.0074 g, 0.033 mmol), and 2-(dimethylamino)ethanol (2 mL) were irradiated in a microwave oven at 175 °C, 350 W for 6 min. After cooling to the room temperature, this reaction mixture was refluxed with ethanol. The dark green product was filtered off, washed with hot ethanol and methanol, and then dried in vacuo over P2O5. This product obtained was purified by column chromatography with silica gel, using chloroform: methanol (9:1) as the solvent system. Yield: 0.064 g (59%) m.p: 225-260 °C. Anal. Calcd. for (C₁₃₂H₁₅₂N₁₆PbO₁₆S₂₄) (%):C, 49.61; H, 4.79; N, 7.01; S, 24.08. Found: C, 49.65; H, 4.80; N, 7.05; S, 24.24%. IR (KBr pellet) v_{max}/ cm⁻¹: 3042 (Ar-H), 2928-2844 (Aliph. C-H), 1709, 1584, 1477, 1364–1155 (SO₂), 1064, 940, 883, 767. ¹H NMR (CDCl₃), (δ: ppm): 7.73 (m, 16H, Ar-H), 7.56 (m, 16H, Ar-H), 7.20 (s, 8H, Ar-H), 4.86 (t, 32H, CH₂-N), 4.10 (t, 16H, CH₂-S), 3.48 (t, 32H, CH₂-S), 2.02 $(m, 8H, CH_2-), 1.25 (s, 24H, CH_3).$ ¹³C NMR (CDCl₃), (δ : ppm): 158.24, 154.52, 153.26, 147.39, 140.68, 138.36, 136.80, 130.44, 122.10, 105.00, 50.54, 44.15, 43.47, 41.25, 38.17, 33.32, 26.94. UV-Vis (chloroform): λ_{max}/nm : [(10⁻⁵ ε dm³ mol⁻¹ cm⁻¹)]: 751 (5.29), 677 (4.82), 425 (5.00). MS (FAB), (m/z): 3189 $[M - 2]^+$.

3. Biological activity assays

3.1. Antibacterial and antifungal assays

The samples were individually tested against a panel of seven microorganisms including five bacteria; *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923, *Bacillus subtilis* ATCC 6633, *B. catarrhalis* ATCC 25238, *Pseudomonas aeruginosa* and two yeasts; *Candida albicans* ATCC 60193 and Candida glabrata ATCC

Table 1

Antimicrobial activity of the sample	s against selected microorganisms. ^a
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Compound	E. coli	St. aureus	B. subtilis	B. catarrhalis	C. albicans
5	1.25 (10) ^b	2.5 (8)	1.25 (9)	0.312 (14)	0.625 (11)
6	1.25 (8)	2.5 (7)	1.25 (10)	0.156 (15)	0.625 (10)
7	1.25 (8)	2.5 (8)	1.25 (9)	0.156 (14)	0.625 (11)
8	1.25 (8)	2.5 (8)	1.25 (9)	0.312 (14)	0.625 (10)
Ampicillin ^c	1.562 (21)	0.781 (23)	1.562 (20)	0.781 (23)	N.A.
Amp B ^d	N.A.	N.A.	N.A.	N.A.	31.25 (21)

^a Only the samples exhibiting positive activity were given in the Table.

 b Inhibition zone in diameter (mm) around the discs impregnated with 300 $\mu g/$ disc of individual sample dissolved in DMSO. All inhibition zones are given in parenthesis.

 $^{\rm c}$ Ampicillin (µg/mL) was used as reference antibiotic in micro-well dilution assay (Sigma) for antibacterial activity assay.

^d AmpB = Amphotericin B (μ g/mL) was used as reference antibiotic in micro-well dilution assay (Sigma) for antifungal activity assay. N.A. Not applicable.

66032. Disc-diffusion, micro-well dilution, and MIC agar dilution assays were performed following the methodology given in the previous study [30]. For these, all samples were dissolved in dimethylsulfoxide (DMSO) and prepared as 10 mg/mL concentration prior to the respective assays. Standard antibiotics employed as controls are also given in Table 1.

3.2. Antioxidant activity assays

The antioxidative capacity of the samples was evaluated by using DPPH and β -carotene/linoleic acid assays [31,32]. In both assays, butylated hydroxytoluene (BHT) was used as positive control.

4. Results and discussion

The preparation of the target metal-free (**4**) and Ni (II) (**5**), Zn (II) (6), Co (II) (7), Cu (II) (8), Pb (II) (9) phthalocyanines was shown in Scheme 1. Compound **3** was synthesized by the reaction of N,N'-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1diyl))bis (4-methylbenzenesulfonamide) (1) [27] with 1,2-bis (2-iodomercaptoethyl)-4,5-dicyanobenzene (2) [28] in dry DMF containing finely ground anhydrous K₂CO₃ as a template agent at 50 °C under a nitrogen atmosphere. Compound 3 was obtained with a percent yield of 53%. (Scheme 1). The characteristic vibration changes which were observed in the IR spectrum were clearly evident for the formation of the compound 3. The absence of N–H and the presence of C \equiv N stretching vibration at 2231 cm⁻¹ in the IR spectrum confirmed the formation of **3** (Table 2). In the ¹H NMR spectrum of this compound, the chemical shifts of NH protons in precursor compound 1 disappeared after the macrocyclization reaction. ¹³C NMR spectrum of this compound clearly indicated the presence of nitrile carbon atoms with peak at δ = 115.17 and 114.83 ppm. This compound displayed the expected molecular ion peak at (m/z) = 743 indicating formation of $[M - 3]^+$. The elemental analysis results of compound **3** were in accordance with its calculated results.

Metal-free phthalocyanine (**4**) was synthesized by microwave irradiation of the corresponding dicyano compound **3** in 2-(dimethyl-amino) ethanol in the presence a few drops of DBU for 10 min. The disappearance of the $C \equiv N$ stretching vibration in the IR spectrum of compound **3** supported the formation of compound **4** (Table 2). In the ¹H NMR spectrum of this compound, the chemical shifts which belong to the inner core protons of compound **4** could not be observed due to the strong aggregation of this molecule [33]. In the mass spectrum of this compound, the molecular ion peak which was appeared at $(m/z) = 2987 [M + 1]^+$ supported the



Scheme 1. The synthesis of the metal-free phthalocyanine 4 and metallophthalocyanines 5-9.

proposed formula for this structure. The elemental analysis results were confirmed the desired structure of the compound **4**.

Metallophthalocyanines (**5**–**9**) were obtained with a percent yield of 44, 36, 44, 37, 59% respectively. Metallophthalocyanines (**5**–**9**) were obtained from dicyano derivative (**3**) and the corresponding anhydrous metal salts NiCl₂, ZnCl₂, CoCl₂, CuCl₂, and PbO respectively, by microwave irradiation in 2-(dimethylamino)ethanol in the range of 6 to 10 min. In the IR spectra of metallophthalocyanines (**5**–**9**), the disappearance of strong $C \equiv N$ stretching vibration of **3** was a clearly evidence for the formation of metallophthalocyanines (**5**–**9**) (Table 2). The ¹H NMR spectrum of metallophthalocyanines and metalfree phthalocyanine were almost identical as expected. In the MS (FAB) spectra of **5**–**9**, we observed the molecular ion peaks at (*m*/*z*): 3043 [M + 1]⁺, (*m*/*z*): 3049 [M]⁺, (*m*/*z*): 3069 [M + Na + 3]⁺, (*m*/*z*):

Table 2	
The spectral IR data of new compounds.	

Compound	γ (Ar–H)	γ (Aliph. C–H)	γ (C \equiv N)
3	3077	2922-2851	2231
4	3065	2921-2851	_
5	3069	2922-2846	_
6	3069	2922-2846	_
7	3074	2912-2851	_
8	3070	2923-2857	_
9	3042	2928-2844	-

3046 $[M - 1]^+$, (m/z): 3189 $[M - 2]^+$ respectively, which confirmed the proposed structure.

The spectra of phthalocyanine 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 [34]. The metal-free phthalocyanine (**4**) displayed a typical electronic spectrum with two significant absorption bands [35], were of them in the visible region at λ_{max} =707 nm and 665 nm corresponding to the Q



Fig. 1. UV-Vis spectra of compounds 4 (----), 5 (...) and 6 (---) in pyridine.



Fig. 2. UV–Vis spectra of compounds $7\ (---)$ in pyridine, $8\ (---)$ and $9\ (...)$ in chloroform.

Table 3

Thermal properties of the new phthalocyanines.

Compound	М	Initial decomposition temperature in °C	Main decomposition temperature in °C
4	2H	206.7	270.7
5	Ni	226.0	257.1
6	Zn	202.4	240.2
7	Со	208.1	245.4
8	Cu	221.2	263.8
9	Pb	225.4	260.4

band and the other one in the visible region at 338 nm corresponding to the B band (Fig. 1). This result indicated that the symmetry of the metal-free phthalocyanine is D_{2h} .

The UV–Vis spectra of metallophthalocyanines **5–7** in pyridine **8** and **9** in chloroform showed intense Q absorption at λ_{max} = 716, 713, 692, 710 and 751 nm with a weaker absorption at 647, 644, 617, 662 and 677 nm, respectively (Fig. 1), (Fig. 2). The single Q bands in metallo derivatives **5–9** are characteristic. Metallation which maintains the planarity of the molecule increases the symmetry to D_{4h} [36]. B band absorptions of compounds **5–9** were observed at λ_{max} = 368, 365, 479, 377, 425 nm as expected, respectively.

The thermal behaviors of the metallophthalocyanines were investigated by TG/DTA. Although the potential thermal stabilities of phthalocyanines are well known, the obtained novel phthalocyanines (**4**–**9**) were observed not to be stable above 202 °C. The initial and main decomposition temperatures were given in Table 3. The initial decomposition temperatures decreased in the order of **5** > **9** > **8** > **7** > **4** > **6**.

The metallophthalocyanines were also investigated for their possible biological activities by employing antimicrobial (antibacterial and antifungal), antineoplastic and antioxidative assays. Of all tested, only four samples exhibited moderate antimicrobial activity against test microorganisms except for *B. catarrhalis* (Table 1). After all, stronger activity was observed by exhibiting MIC values around 312 mg/mL followed by a yeast, *C. albicans* (MIC. 0.625 mg/mL). Due to their colored nature, the samples were found not to be applicable for antioxidative and antineoplastic assays where spectrophotometrical applications are required.

5. Conclusion

We have synthesized and characterized new symmetrically substituted metal-free(**4**) and metallophthalocyanines (**5**–**9**) which were prepared by a condensation of *N*,*N'*-[*propan*-1,3-*diilbis*(*tiyoe*-*tan*-2,1-*diil*)]*bis*(4-*methylbenzenesulfonamid*) (**1**) and 1,2-*bis* (2-*iodomercaptoethyl*)-4,5-*dicyanobenzene* (**2**) with Ni (II), Zn (II), Co

(II), Cu (II), and Pb (II) salts in DMAE, respectively. The novel phthalocyanines were characterized by IR, UV–Vis, ¹H NMR, ¹³C NMR, Mass spectra, and elemental analysis data. The thermal behaviors of the metal-free phthalocyanine (**4**) and metal-lophthalocyanines (**5**–**9**) were investigated by TG/DTA and it was seen that our novel compounds were not stable above 202 °C. Their possible biological activities were also investigated and four samples exhibited antimicrobial activity against test microorganisms. However, due to their colored nature, the samples were found not to be applicable for antioxidative and antineoplastic assays.

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