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Microwave-assisted synthesis and characterization of a new soluble metal-free and metallophthalocyanines peripherally fused to four 18-membered tetrathiadiaza macrocycles

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ABSTRACT

Preparation of some novel symmetrically tetrasubstituted metal-free phthalocyanine (**6**) and metallophthalocyanines (**7**–**10**) containing four 18-membered tetrathiadiaza macrocycles moieties on peripheral positions has been achieved by cyclotetramerization reaction of phthalonitrile derivative (**5**) in a multi-step reaction sequence. Metal-free phthalocyanine (**6**) was synthesized by microwave irradiation of 13,24-bis[(4-methylphenyl)sulfonyl]-6,7,14,15,23,24-hexahydro-13*H*,22*H*-tribenzo[*b*,*h*,*n*][1,4,10,13,7,16]tetrathiadiazacyclo-octadecine-18,19-dicarbonitrile (**5**) in 2-(dimethylamino)ethanol. The metallophthalocyanines (**7–10**) were prepared by the reaction of the phthalonitrile compound (**5**) with $NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$ salts, respectively, by microwave irradiation in 2-(dimethylamino)ethanol for at 175 °C, 350 W. The new compounds were characterized by IR, ^1H NMR, ^{13}C NMR, UV–Vis, elemental analysis and MS spectra data.

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1. Introduction

Just like many other scientists all over the world, we have closely been dealing with phthalocyanines and their derivatives because of their fascinating and fairly useful chemical features for various scientific areas. The aforementioned word of phthalocyanine, which is derived from the Greek term for naphtha (rock oil) and cyanine (dark blue), was first used by Professor Reginald P. Linstead of the Imperial College of Science and Technology in 1933 to describe a class of organic compounds which consists of metal-free or di hydrogen phthalocyanines or metallophthalocyanines and their derivatives [1].

Phthalocyanines, which are of enormous technological importance for the manufacture of green and blue pigments [2] and are of considerable interest owing to their fascinating electronic and optical properties [3], do not occur in nature [4]. In many fields, phthalocyanines have been remarkably used because of their magnificently versatile properties to illustrate photodynamic reagents for cancer therapy [5,6], and other medical applications [7], for optical read–write discs [8], in chemical sensors, in photocopying machines [9,10], Langmuir–Blodgett films [11], solar cells, electrochromism, high energy batteries [1,12], fibrous assemblies [13], coloring for plastics and metal surfaces and dyestuffs for clothing [8]. Phthalocyanines, on the other hand, can also photocatalytically reduce methyl viologen [1].

Peripherally unsubstituted phthalocyanines and metallophthalocyanines are slightly soluble in common organic solvents. Generally, the low solubility circumstance in various organic solvents or water is a major problem for phthalocyanine and metallophthalocyanine derivatives. However, some groups such as bulky groups [7,14–16], or paraffinic alkyl, polyoxyethylene [13], alkoxy, alkylthio chains [11,17,18], placed into the peripheral and nonperipheral positions, can increase the solubility of phthalocyanines or metallophthalocyanines. Furthermore; amino, sulfo or carboxyl groups provide water-soluble products [15,16,19–21]. In addition, phthalocyanines are soluble in concentrated phosphoric and sulfuric acids, and in chlorosulfonic, anhydrous hydrofluoric, ethylsulfuric and trichloroacetic acids [22]. The solubility of the phthalocyanine increases when substituents are placed on the phthalocyanine ring. At this circumstance, supramolecular organisation may be achieved [4].

Recently, microwave processing techniques have been received a great deal of attention due to its various advantages such as selectivity, rapid, direct, controllable, internal, etc. [23–25].

We have already described the synthesis of metal phthalocyanines tetrathia macrocyclic moieties on the periphery [26]. In this study, we described the microwave-assisted synthesis and characterization of a new soluble metal-free (**6**) and metallophthalocyanines (**7–10**) peripherally fused to four 18-membered

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tetrathiadiaza macrocycles. We have prepared 1,2-di(*o*-aminophenylthio)ethane (**1**) according to the literature [27].

2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using Standard Schlenk techniques. 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene **4** was prepared according to the literature [28]. All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by reported procedure [29]. Acetonitrile was dried by distillation over P_2O_5. And prior to use, K_2CO_3 was dried at 130 °C.

Elemental analyses of the complexes were performed on a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer, respectively. FT-IR spectra were obtained on a Perkin Elmer 1600 FT-IR spectrophotometer with the samples prepared as KBr pellets. UV–Visible spectra were recorded using a Unicam UV–Visible spectrometer operating in the range 200–850 nm with quartz cells. NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (δ) relative to TMS as an internal standard. Mass spectra were recorded on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used for all synthesis of phthalocyanines.

2.1. N,N′-[ethane-1,2-diylbis(thio-2,1-phenylene)]bis(4 methylbenzene sulfonamide) (**3**)

1,2-Di(*o*-aminophenylthio)ethane **1** (1.50 g, 5.43 mmol) was dissolved in pyridine (40 ml) under nitrogen atmosphere. Tosyl chloride **2** (2.58 g, 13.58 mmol), which was dissolved in pyridine (20 ml), was added dropwise to first solution with stirring over 2 h at −5 °C. After complete addition, the reaction mixture was continuously stirred at −5 °C for 3 h and then overnight at the room temperature. At the end of this elapsed period, the orange solution was poured slowly on a mixture which contained HCl (187 ml conc.) and ice (70 g) and diluted with water (100 ml). The reaction mixture was extracted with chloroform (50 ml × 3) and the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, ethanol (30 ml) was added to residue and filtered off. The brown solid product was crystallized from ethanol to give pure product and then dried *in vacuo* (P_2O_5). Yield: 2.32 g (73%), mp: 180–182 °C. *Anal.* Calc. for $C_{28}H_{28}S_4O_4N_2$: C, 57.51; H, 4.83; N, 4.79. Found: C, 57.01; H, 4.61; N, 4.83%. IR (KBr tablet) ν_{max}/cm^{-1}: 3265 (N–H), 3069 (Ar–H), 2922–2854 (Aliph. C–H), 1597 (N–H bending), 1473, 1338–1167 (SO_2), 1089, 909, 803, 760, 668, 561. ^1H NMR ($CDCl_3$) (δ: ppm): 8.63 (s, 2H, N–H), 7.67 (d, 4H, tosyl, Ar–H), 7.63 (d, 2H, Ar–H), 7.61 (t, 2H, Ar–H), 7.31 (d, 2H, Ar–H), 7.28 (d, 4H, tosyl, Ar–H), 7.24 (t, 2H, Ar–H), 2.45 (t, 4H, CH_2–S), 2.36 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) (δ: ppm): 144.29, 138.87, 136.11, 135.39, 130.23, 129.78, 127.22, 124.89, 122.77, 119.81, 35.13, 21.60. MS (FAB), (*m/z*): 585[M+1]$^+$.

2.2. 13,24-Bis[(4-methylphenyl)sulfonyl]-6,7,14,15,23,24-hexahydro-13H,22H-tribenzo [b,h,n][1,4,10,13,7,16]tetrathiadiazacyclo-octadecine-18,19-dicarbonitrile (**5**)

N,N′-[ethane-1,2-diylbis(thio-2,1-phenylene)]bis(4 methylbenzene sulfonamide) **3** (2.0 g, 3.42 mmol) was dissolved in dry acetonitrile (200 ml) under nitrogen atmosphere. Finely ground anhydrous potassium carbonate (1.42 g, 10.26 mmol) was added to the solution. After stirring for 2 h at 50 °C, the reaction temperature was gradually increased up to 85 °C. A solution of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene **4** (1.71 g, 3.42 mmol) in dry acetonitrile (200 ml) was added dropwise over 3 h. The reaction mixture was continuously stirred under nitrogen atmosphere at reflux temperature for 5 days. The reaction mixture was through monitored by thin layer chromatography (TLC) chloroform/methanol (3:1) solvent system. At the end of this period, the reaction mixture was filtered off and the solvent was evaporated under reduced pressure, resulting in a light-brown precipitate. The obtained product was washed with EtOH, diethylether and then dried *in vacuo* (P_2O_5). Yield: 1.53 g (54%), mp: 172–174 °C. *Anal.* Calc. for $C_{40}H_{36}O_4N_4S_6$: C, 57.94; H, 4.38; N, 6.66. Found: C, 57.61; H, 4.83; N, 6.21%. IR (KBr tablet) ν_{max}/cm^{-1}: 3065 (Ar–H), 2924–2853 (Aliph. C–H), 2230 (CN), 1567, 1461, 1347–1159 (SO_2), 1090, 964, 894, 757, 671, 574. ^1H NMR ($CDCl_3$) (δ: ppm): 7.70 (s, 2H, Ar–H), 7.69 (d, 4H, tosyl, Ar–H), 7.65 (d, 2H, Ar–H), 7.59 (t, 2H, Ar–H), 7.37 (d, 2H, Ar–H), 7.34 (d, 4H, tosyl, Ar–H), 7.19 (d, 2H, Ar–H), 3.62 (t, 4H, N–CH_2), 3.55 (s, 4H, CH_2–S), 2.98 (t, 4H, S–CH_2), 2.38 (s, 6H, CH_3–tosyl). ^{13}C NMR ($CDCl_3$) (δ: ppm): 144.32, 143.61, 140.23, 138.07, 136.67, 131.41, 130.27, 128.31, 126.67, 125.92, 123.61, 119.23, 115.12, 114.57, 51.72, 38.62, 31.65, 20.43. MS (FAB), (*m/z*): 830 [M+1]$^+$.

2.3. Metal-free phthalocyanine (**6**)

A mixture of **5** (0.2 g, 0.24 mol) and 2-(dimethylamino)ethanol (2 ml) was irradiated at 175 °C, 350 W for eight minutes by using microwave. After the mixture being cooled to room temperature, EtOH (25 ml) was added, stirred for over night and filtered off. This product was refluxed by EtOH (40 ml) for 4 h. The dark-green product obtained was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* (P_2O_5). This obtained product was purified by preparative thin layer chromatography (TLC) by means of chloroform/methanol (9:1) solvent system. The dark-green solid product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF, THF and pyridine. Yield: 0.272 g (34%), mp >300 °C. *Anal.* Calc. for $C_{160}H_{146}N_{16}O_{16}S_{24}$: C, 57.91; H, 4.43; N, 6.75. Found: C, 57.59; H, 4.81; N, 6.87%. IR (KBr tablet) ν_{max}/cm^{-1}: 3262 (N–H), 3075 (Ar–H), 2923–2853 (Aliph. C–H), 1727, 1647, 1466, 1324–1158 (SO_2), 1090, 910, 830, 742. ^1H NMR ($CDCl_3$) (δ: ppm): 7.79 (s, 8H, Ar–H), 7.73 (m, 32H, tosyl, Ar–H), 7.61 (d, 8H, Ar–H), 7.57 (m, 8H, Ar–H), 7.34 (d, 8H, Ar–H), 7.27 (d, 8H, Ar–H), 4.13 (t, 16H, N–CH_2), 3.63 (t, 16H, CH_2–S), 2.97 (t, 16H, S–CH_2), 2.35 (s, 24H, CH_3). ^{13}C NMR ($CDCl_3$) (δ: ppm): 144.32, 142.83, 141.44, 138.61, 136.53, 131.15, 130.90, 128.96, 128.03, 125.43, 123.71, 118.17, 115.39, 113.25, 56.64, 37.81, 31.03, 22.29. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 237 (5.26), 259 (5.19), 292 (4.92), 644 (4.56), 671 (4.71), 707 (5.07), 740 (5.11).MS (FAB), (*m/z*): 3357 [M+K]$^+$.

2.4. Nickel(II) phthalocyanine (**7**)

A mixture of **5** (0.2 g, 0.24 mol), $NiCl_2$ (0.0078 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated at 175 °C, 350 W for ten minutes by using microwave. After the mixture being cooled to room temperature, EtOH (25 ml) was added, stirred for over night and filtered off. This product was refluxed by EtOH (40 ml) for 4 h. The dark-green product obtained was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* (P_2O_5). The product obtained was purified by preparative thin layer chromatography (TLC) by means of chloroform/methanol (8:2) solvent system. The dark-green solid product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF and pyridine. Yield: 0.293 g (36%), mp >300 °C. *Anal.* Calc. for $C_{160}H_{144}N_{16}O_{16}S_{24}Ni$: C, 56.94; H, 4.30; N, 6.64; Ni, 1.74. Found: C, 56.71; H, 4.60; N, 6.93; Ni, 1.41%. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2912–2851 (Aliph. C–H), 1632, 1585, 1465, 1344–1157 (SO_2), 1088, 965, 891, 721. ^1H NMR ($CDCl_3$) (δ: ppm):

7.99 (s, 8H, Ar–H), 7.71 (m, 32H, tosyl, Ar–H), 7.67 (d, 8H, Ar–H), 7.47 (m, 8H, Ar–H), 7.29 (d, 8H, Ar–H), 7.26 (d, 8H, Ar–H), 3.71 (t, 16H, N–CH_2), 3.27 (t, 16H, CH_2–S), 3.14 (t, 16H, S–CH_2), 2.44 (s, 24H, CH_3. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 278 (6.22), 322 (5.07), 653 (4.83), 710 (5.18). MS (FAB), (*m/z*): 3392 $[M+H_2O]^+$.

2.5. Zinc(II) phthalocyanine (**8**)

A mixture of **5** (0.2 g, 0.24 mol), $Zn(CH_3COO)_2$ (0.0109 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated at 175 °C, 350 W for nine minutes by using microwave. After the mixture being cooled to room temperature, EtOH (25 ml) was added, stirred for over night and filtered off. The product was refluxed by EtOH (40 ml) for 4 h. The green product obtained was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* (P_2O_5). The product obtained was purified by preparative thin layer chromatography (TLC) by means of chloroform/methanol (9:1) solvent system. The green solid product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF, THF and pyridine. Yield: 0.285 g (35%), mp >300 °C. *Anal.* Calc. for $C_{160}H_{144}N_{16}O_{16}S_{24}Zn$: C, 56.82; H, 4.29; N, 6.63; Zn, 1.93. Found: C, 56.52; H, 4.67; N, 6.97; Zn, 1.58%. IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2961–2840 (Aliph. C–H), 1726, 1588, 1466, 1344–1158 (SO_2), 1086, 888, 718. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.82 (s, 8H, Ar–H), 7.76 (m, 32H, tosyl, Ar–H), 7.68 (d, 8H, Ar–H), 7.60 (m, 8H, Ar–H), 7.38 (d, 8H, Ar–H), 7.25 (d, 8H, Ar–H), 4.11 (t, 16H, N–CH_2), 3.60 (t, 16H, CH_2–S), 3.20 (t, 16H, S–CH_2), 2.50 (s, 24H, CH_3). ^{13}C NMR ($CDCl_3$) (δ: ppm): 147.32, 145.61, 141.23, 139.07, 135.67, 132.42, 130.93, 129.74, 128.82, 126.93, 124.13, 119.21, 115.60, 114.57, 68.17, 38.71, 30.35, 23.74. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 244 (5.14), 366 (5.06), 646 (4.64), 718 (5.19).MS (FAB), (*m/z*): 3399 $[M+1+H_2O]^+$.

2.6. Cobalt(II) phthalocyanine (**9**)

A mixture of **5** (0.2 g, 0.24 mol), $CoCl_2$ (0.0078 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated at 175 °C, 350 W for nine minutes by using microwave. After the mixture being cooled to room temperature, EtOH (25 ml) was added, stirred for over night and filtered off. The product was refluxed by EtOH (40 ml) for 4 h. The dark-green product obtained was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* (P_2O_5). This product obtained was purified by preparative thin layer chromatography (TLC) by means of chloroform/methanol (9:1) solvent system. The dark-green solid product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF, THF and pyridine. Yield: 0.301 g (37%), mp >300 °C. *Anal.* Calc. for $C_{160}H_{144}N_{16}O_{16}S_{24}Co$: C, 56.93; H, 4.30; N, 6.64; Co, 1.75. Found: C, 56.53; H, 4.57; N, 6.82; Co, 1.89%. IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2922–2851 (Aliph. C–H), 1726, 1585, 1466, 1345–1157 (SO_2), 1088, 962, 893, 722. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 250 (5.16), 293 (5.12), 643 (4.73), 712 (5.21).MS (FAB), (*m/z*): 3376 $[M+1]^+$.

2.7. Copper(II) phthalocyanine (**10**)

A mixture of **5** (0.2 g, 0.24 mol), $CuCl_2$ (0.0081 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated at 175 °C, 350 W for twelve minutes by using microwave. After the mixture being cooled to room temperature, EtOH (25 ml) was added, stirred for over night and filtered off. The product was refluxed by EtOH (40 ml) for 4 h. The green product obtained was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* (P_2O_5). This product obtained was purified by preparative thin layer chromatography (TLC) by means of chloroform/methanol (9:1) solvent system. The green solid product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF and pyridine. Yield: 0.269 g (33%), mp >300 °C. *Anal.* Calc. for $C_{160}H_{144}N_{16}O_{16}S_{24}Cu$: C, 56.85; H, 4.29; N, 6.63; Cu, 1.88. Found: C, 56.45; H, 4.67; N, 6.83; Cu, 1.67%. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2923–2851 (Aliph. C–H), 1729, 1594, 1465, 1340–1157 (SO_2), 1088, 892, 721. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 254 (5.23), 289 (5.06), 655 (4.83), 720 (5.25). MS (FAB), (*m/z*): 3402 $[M+Na]^+$.

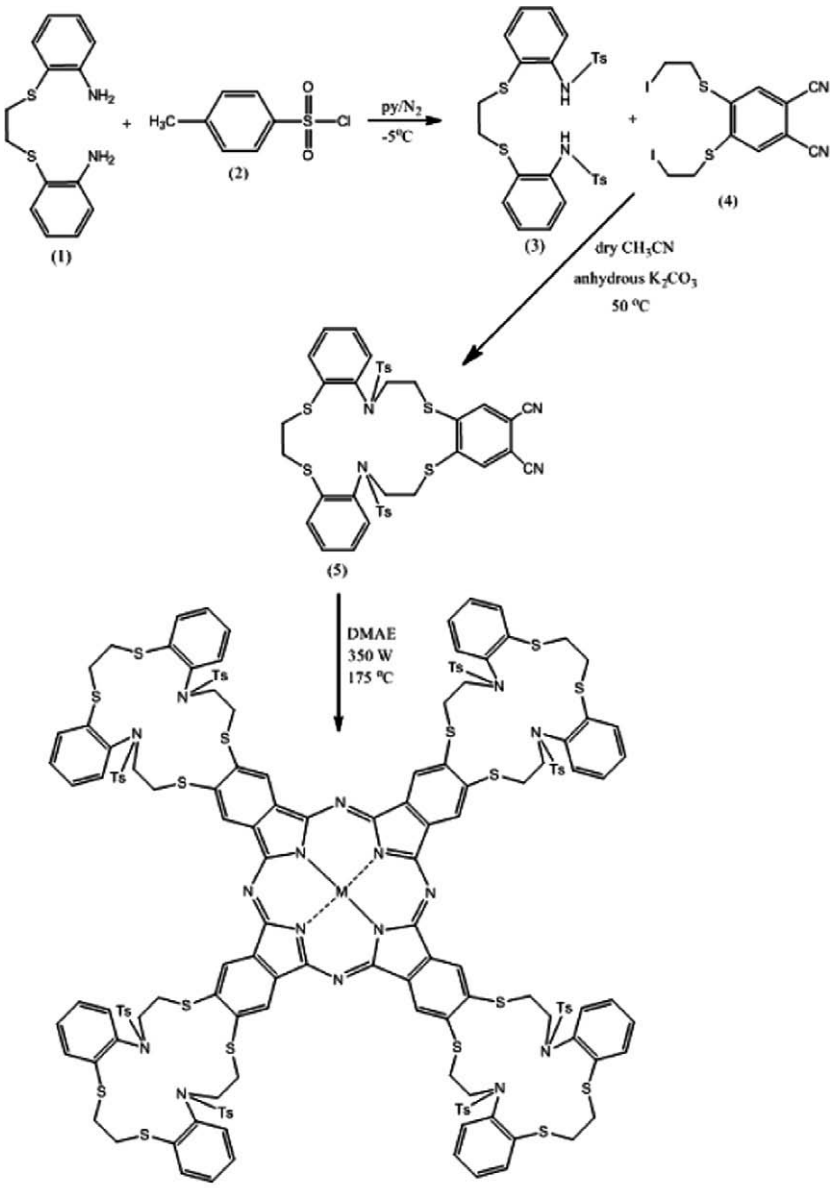
3. Results and discussion

The synthetic procedure, as shown in Scheme 1, started with the synthesis of the 1,2-di(*o*-aminophenylthio)ethane **1** as described according to the reported procedure [27]. The compound **3** was synthesized reaction of 1,2-di(*o*-aminophenylthio)ethane **1** with *p*-toluenesulfonylchloride **2.** The synthesis of the phthalonitrile derivative, namely 13,24-bis[(4-methylphenyl)sulfonyl]-6,7,14,15,23,24-hexahydro-13*H*,22*H*-tribenzo [*b*,*h*,*n*][1,4,10,13,7,16] tetrathiadiazacyclo-octadecine-18,19-dicarbonitrile **5** was obtained 4,5-bis[(2-iodoethyl)sulfanyl]benzene-1,2-dicarbonitrile **4** in dry acetonitrile containing anhydrous potassium carbonate as base [30,31]. This base catalyzed macrocyclization reaction was carried out in dry acetonitrile at 50 °C for 5 days and giving moderate yield (54%). The cyclotetramerization of phthalonitrile derivative **5** in to the metal-free phthalocyanine **6** was accomplished in 2-(dimethylamino)ethanol for 8 min. During the formation of metal-free phthalocyanines, 2-(dimethylamino)ethanol acts as a nucleophilic reagent and it reducts phthalocyanine ring by two electrons, and also acts as donor of protons [32]. The metallophthalocyanines **7–10** were prepared from the corresponding dicyano derivative and the corresponding metal salts (Ni, Zn, Co, Cu) in high boiling solvent (e.g. DMAE) at 175 °C 350 W for 10, 9, 9, 12 min, resulting in moderate yields 36, 35, 37, 33(%), respectively.

All novel compounds were identified through various spectroscopic techniques such as IR, ^{1}H NMR, ^{13}C NMR, UV–Vis, MS spectral data and elemental analysis. The IR spectrum of **3** clearly indicated the presence of the NH group by intense stretching bands at 3265 cm^{-1}. In the ^{1}H NMR spectrum of **3** in deuterated chloroform, the tosylated amino groups were shown by the presence of sulfonamide bands at δ = 8.63 ppm. The aromatic protons belonging to 1,2-di(*o*-aminophenylthio)ethane **1** appear as doublet at δ = 7.63, 7.31 ppm and as triplet at δ = 7.61, 7.28 ppm. The doublet at δ = 7.67, 7.28 ppm belong to aromatic protons of tosyl benzene. The triplet at δ = 2.45 ppm for CH_2–S and singlet at δ = 2.36 ppm for CH_3 protons confirms the proposed structure. ^{13}C NMR spectrum of this compound exhibits characteristic signals at 144.29, 138.87, 136.11, 135.39, 130.23, 129.78, 127.22, 124.89, 122.77, 119.81, 35.13, 21.60. The MS spectrum of **3** shows a peak at *m/z*: 585 $[M+1]^+$ and the elemental analyses support the proposed structure.

In the IR spectrum of **5**, the presence of intense CN stretching band at 2230 cm^{-1} and the disappearance of the strong NH stretching vibrations at 3265 cm^{-1} confirm the formation of this compound. The ^{1}H NMR spectrum of **5** in deuterated chloroform showed a new signal due to an aromatic proton at δ = 7.70 ppm, as expected. The ^{13}C NMR spectrum of **5** also indicated the presence of nitrile carbon at δ = 114.57 ppm. In the MS spectrum of compound **5**, the presence of characteristic molecular ion peak at *m/z*: 830 $[M+1]^+$ confirmed the proposed structure.

IR spectrum of **6**, the disappearance of CN stretching vibration of **5** is an evidence for the formation of the metal-free phthalocyanine **6**. In addition to this circumstance, the strong NH stretching vibrations and Ar–H vibrations are observed at 3262, 3075 cm^{-1}, respectively. In the ^{1}H NMR spectrum of **6**, the typical shielding of inner core protons could not be observed due to the probable strong aggregation of the molecules [33]. The signals related to aromatic protons and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton were characteristic of the purposed



Compound	6	7	8	9	10
M	2H	Ni^{+2}	Zn^{+2}	Co^{+2}	Cu^{+2}

Scheme 1. The synthesis of the metal-free phthalocyanine **6** and metallophthalocyanines **7**, **8**, **9**, **10**.

structure. In the MS spectrum of **6**, the presence of characteristic molecular ion peak at *m/z*: 3357 $[M+K]^+$ confirmed the proposed structure.

In the IR spectra, the disappearance of strong CN stretching vibration of **5** is also an evidence for the formation metallophthalocyanines **7–10**. The IR spectra of metallophthalocyanines **7–10** are very similar to metal-free phthalocyanine **6**, with the exception of NH stretching vibration appeared at 3262 cm^{-1} due to inner core protons of metal-free phthalocyanine **6**. The ^1H NMR spectra of these compounds in deuterated chloroform were almost identical to those of **6**. In the mass spectra of compounds **7–10**, the presence of molecular ion peaks at *m/z*: 3392 $[M+H_2O]^+$, 3399 $[M+1+H_2O]^+$, 3376 $[M+1]^+$, and 3402 $[M+Na]^+$ confirmed the proposed structures, respectively. In addition to these data, the elemental analysis of these compounds was also determined. Besides, the new phthalocyanines **6–10** were reasonably soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF, pyridine.

Electronic spectra are especially useful to identify the structure of the phthalocyanines. Generally, UV–Vis spectra of phthalocyanines show typical electronic spectra with two strong absorbtion bands known as Q and B-bands. The Q-band in the visible region at *ca.* 600–750 nm (Q-band) is attributed to the π–π^* transition from HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc (−2) ring and the B-band in the UV region at *ca.* 300–400 nm (B-band) arises from the deeper π–π^* transitions [34].

The electronic spectra are given for compound **6**, **7**, **8** (Fig. 1) and **9**, **10** (Fig. 2). In the UV–Vis spectrum of metal-free phthalocyanine **6** in chloroform, the characteristic split Q-band was observed with absorptions at λ_{max}: 707 and 740 nm. The UV–Vis absorption

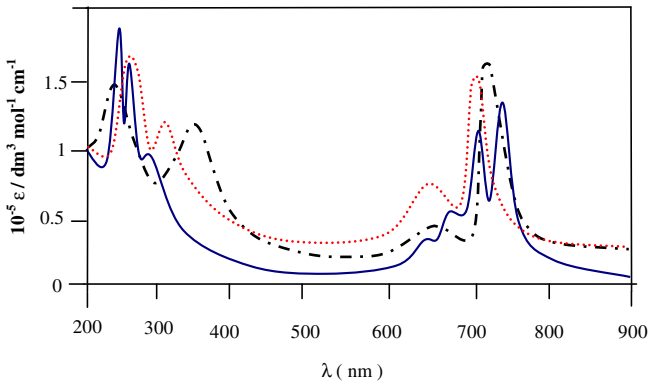


Fig. 1. UV–Vis spectra of compounds **6** (—), **7** (····) and **8** (– · – ·) in chloroform.

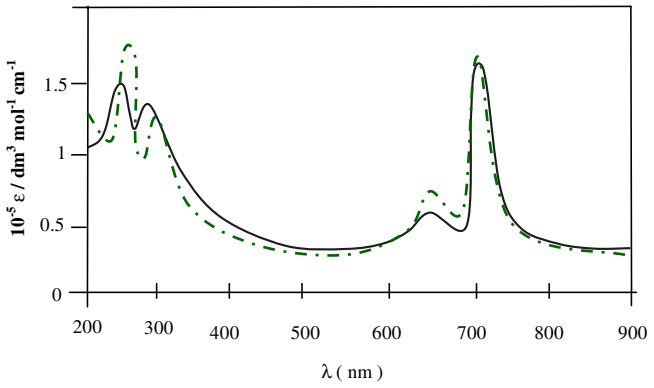


Fig. 2. UV–Vis spectra of compounds **9** (—) and **10** (– · – ·) in chloroform.

spectra of metallophthalocyanines **7**, **8**, **9** and **10** in chloroform were observed the intense Q absorbtion at λ_{max}: 710, 718, 712 and 720 nm with weaker absorptions at 653, 646, 643 and 655 nm, respectively (Figs. 1 and 2.). In addition, the UV–Vis spectra of **7**, **8**, **9** and **10** in chloroform were observed the intense B absorbtion at λ_{max}: (278 and 322), (244 and 366), (250 and 293) and (254 and 289) nm as expected.

4. Conclusion

We have presented the synthesis of a new soluble phthalocyanine **6** and four metallophthalocyanines (**7–10**) from the new macrocyclic ligand **5** by microwave irradiation in 2-(dimethylamino)ethanol for at 175 °C, 350 W. It is seen that structural characterization shows the similarity of the coordination environment around the ligand (**5**) for the pcs. All phthalocyanines show a similar absorbtion band in chloroform at the room temperature. In the UV spectra, the peaks in which B- and Q-bands support the formation of complexes. Generally, the low solubility in various organic solvents or water is a great problem for phthalocyanine and metallophthalocyanine complexes. But, our investigations show that the obtained metal-free phthalocyanine and its transition metal complexes can dissolve various solvents such as $CHCl_3$, CH_2Cl_2, DMSO, DMF, THF and pyridine.

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