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Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four 13-membered dithiadiaza macrocycles

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Abstract

Novel, tetrasubstituted metal-free phthalocyanine and metallophtalocyanines bearing four 13-membered dithiadiaza macrocycle peripheral groups were synthesized by cyclotetramerization of the phthalonitrile derivative in a multi-step reaction sequence. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–vis, elemental analysis and MS spectral data.

Keywords: Phthalocyanine; Dithiadiazamacrocycle; Phthalonitrile; Macrocyclization; Tosylation

1. Introduction

Phthalocyanine macrocycles are of considerable interest owing to their fascinating electronic and optical properties. In recent years, a large number of phthalocyanine derivatives have been prepared to facilitate the exploitation of these properties such as gas sensors, electrophotography, fuel cells, solar energy conversion, non-linear optics, catalysis and the photodynamic therapy of cancer [1]. The attractive and challenging characteristics of the phthalocyanines are their great variety, chemical stability, the relative ease with which they can be synthesized and the strong dependence of their properties on peripheral and axial substitution patterns [2]. In this context, substitution on the aromatic groups of phthalocyanine by various groups such as crown ether, thiacrown or mixed donor macrocycle leads to new products having additional functionalities or properties [3]. Among these are supramolecular systems which consist of two identical molecular entities coexisting together without the assistance of covalent binding [4]. The notable feature of these compounds is that they exhibit spectral properties different from those of the individual molecular units.

Phthalocyanines (Pcs) are generally blue-green in color due to the π–π^* bands associated with the planar heteroaromatic π-conjugation system. Phthalocyanines and their metal complexes have been widely used as dyes and pigments. In particular, they have drawn much attention in recent years with their functional properties and potential application to chemical sensors, electrophotography, photovoltaics, optical discs, solar cells, photodynamic therapy, catalysis, etc. [5–11]. Most of the applications of phthalocyanines stem from their characteristic π-conjugation systems.

Macrocyclic ligands containing both nitrogen and sulfur donor atoms are of interest because of their potential for providing molecules capable of mimicking various aspects of macromolecular biological systems. As might be anticipated, the macrocyclic polyamino polythioether ligands exhibit an interesting range of properties intermediate between those of macrocyclic polythioethers and macrocyclic polyamines [12,13].

Microwave processing has attracted potential interest as an alternative to classical thermal processing because of the

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inherent advantages of microwave heating, which is selective, direct, rapid, internal and controllable [14–16]. Microwave-assisted synthesis of phthalocyanines is novel [17–19].

In this paper, we have prepared metal-free and metallophthalocyanines by microwave irradiation and describe the characterization of these compounds, bearing four 13-membered dithiadiaza macrocycles moieties at peripheral positions.

2. Experimental

2,2′-[Propane-1,3-diylbis(thio)]bis[aniline] (**1**) [20] and 4,5-dichlorobenzene-1,2-dinitrile (**4**) [21] were prepared according to the literature while *p*-toluenesulfonylchloride (**2**) was purchased from Merck. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [22]. IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets or NaCl disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, DMSO, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Elemental analyses were determined using an LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected. UV–vis spectra were recorded using a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Domestic microwave oven was used for the synthesis of all phthalocyanines.

2.1. *N,N′-[Propane-1,3-diylbis(thio-2,1-phenylene)]-bis[p-toluenesulfonamide]* (*3*)

2,2′-[Propane-1,3-diylbis(thio)]bis[aniline] (**1**) (5 g, 17.24 mmol) was dissolved in pyridine (40 ml) under nitrogen and powdered *p*-toluenesulfonylchloride (**2**) (8.21 g, 43.10 mmol) was added portion-wise over 0.5 h to the stirred and ice–salt-cooled solution at −10 °C. Stirring and cooling of the reaction mixture was continued for 1.5 h at −10 °C and the mixture was then stirred at room temperature overnight. The ensuing solution was poured slowly on ice (100 g) and diluted with water (100 ml). The precipitated ditosyl derivative was removed by filtration and washed with cold water and diethyl ether. The product was dried in vacuo and obtained as a grey solid. Yield: 6.29 g (61%), mp: 75–77 °C. Anal. Calcd for $C_{29}H_{30}N_2O_4S_4$: C, 58.16; H, 5.05; N, 4.67%. Found: C, 58.72; H, 5.16; N, 4.81. IR (KBr tablet) ν_{max}/cm^{-1}: 3254 (N–H), 3054 (Ar–H), 2922–2854 (Aliph. C–H), 1587 (N–H bending), 1475, 1335–1161 (SO_2), 1090, 912, 813, 755, 665, 565. ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.61 (s, 2H, N–H), 7.69 (d, 4H, tosyl Ar–H), 7.58 (d, 4H, tosyl Ar–H), 7.28 (d, 2H, Ar–H), 7.25 (t, 2H, Ar–H), 7.21 (t, 2H, Ar–H), 7.17 (d, 2H, Ar–H), 2.53–2.49 (t, 4H, CH_2–S), 2.33 (s, 6H, CH_3), 1.71–1.65 (m, 2H, CH_2–CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 150.01, 144.36, 138.89, 130.23, 129.94, 127.43, 124.88, 119.65, 34.71, 28.61, 21.78. MS (FAB) (*m*/*z*): 599 $[M + 1]^+$.

2.2. *5,19-Di(p-toluenesulfonyl)-5,12,13,19-tetrahydro-11H-tribenzo[b,e,h][1,10,4,7]dithia-diazacyclotridecine-2,3-dicarbonitrile* (*5*)

N,N′-[Propane-1,3-diylbis(thio-2,1-phenylene)]bis[*p*-toluenesulfonamide] (**3**) (5.80 g, 9.68 mmol) was dissolved in dry acetonitrile (250 ml), finely ground anhydrous K_2CO_3 (4.01 g, 29.04 mmol) was added and the mixture was then stirred for 2 h at 50 °C. A solution of 4,5-dichlorobenzene-1,2-dinitrile (**4**) (1.90 g, 9.68 mmol) in dry acetonitrile (75 ml) was added dropwise over 4 h. After stirring for 4 days at 85 °C, the reaction mixture was poured into ice-water and stirred for 2 h. The ensuing mixture was evaporated to a volume of 20 ml under reduced pressure and the residue was extracted with (2 × 120) ml of chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure to give a brown crude product. The crude product was chromatographed on silica gel with chloroform as eluent. Yield: 4.69 g (67%), mp: 156–158 °C. Anal. Calcd for $C_{37}H_{30}N_4O_4S_4$: C, 61.75; H, 4.18; N, 7.75%. Found: C, 61.33; H, 4.36; N, 7.98. IR (KBr tablet) ν_{max}/cm^{-1}: 3084 (Ar–H), 2917–2846 (Aliph. C–H), 2238 (C≡N), 1596 (N–H bending), 1474, 1336–1159 (SO_2), 1090, 914, 813, 755, 664, 565. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.90 (s, 2H, Ar–H), 7.79 (d, 4H, tosyl Ar–H), 7.70 (d, 4H, tosyl Ar–H), 7.66 (t, 2H, Ar–H), 7.63 (d, 2H, Ar–H), 7.58 (d, 2H, Ar–H), 7.22 (t, 2H, Ar–H), 2.53–2.50 (t, 4H, CH_2–S), 2.34 (s, 6H, CH_3), 1.59–1.52 (m, 2H, CH_2–CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 144.16, 139.10, 134.97, 130.03, 129.72, 124.66, 119.41, 115.07, 113.64, 34.52, 30.92, 21.57. MS (FAB) (*m*/*z*): 747 $[M + Na + 1]^+$, 763 $[M + K + 1]$.

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

A mixture of 5,19-di(*p*-toluenesulfonyl)-5,12,13,19-tetrahydro-11*H*-tribenzo[*b*,*e*,*h*][1,10,4,7]dithia-diazacyclotridecine-2,3-dicarbonitrile (**5**) (0.8 g, 1.10 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The green solid product was washed with hot ethanol (45 ml) and dried in vacuo. The solid product was chromatographed on silica gel with chloroform:methanol (9:1) as eluent. This product is soluble in DMF, DMSO and pyridine. Yield: 222 mg (28%), mp > 300 °C. Anal. Calcd for $C_{148}H_{122}N_{16}O_{16}S_{16}$: C, 61.43; H, 4.24; N, 7.74%. Found: C, 61.04; H, 4.76; N, 7.47. IR (KBr tablet) ν_{max}/cm^{-1}: 3280 (N–H), 3076 (Ar–H), 2923–2851 (Aliph. C–H), 1621, 1596, 1421, 1386–1148 (SO_2), 1079, 1012, 936, 889, 745. ^{1}H NMR (DMSO-d_6) (δ: ppm): 8.86–8.20 (s, 8H, Ar–H), 7.47–7.33 (m, 32H, tosyl Ar–H), 7.35–7.24 (d, 16H, Ar–H), 7.31–7.18 (t, 16H, Ar–H), 2.80–2.77 (t, 16H, CH_2–S), 2.39 (s, 24H, CH_3), 1.69–1.63 (m, 8H, CH_2–CH_2): UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 293 (4.87), 315 (4.79), 340 (4.73), 485 (4.59), 695 (4.78), 749 (4.80). MS (FAB) (*m*/*z*): 2893 $[M]^+$.

2.4. Nickel(II) phthalocyanine (7)

The same procedure as above was followed but using compound **5** (0.8 g, 1.10 mmol) anhydrous $NiCl_2$ (35.66 mg, 0.27 mmol) and 2-(dimethylamino)ethanol (2 ml). The green solid product was chromatographed on silica gel with chloroform:petroleum ether:methanol (7:2:1) as eluent. This product is soluble in DMF, DMSO and pyridine. Yield: 211 mg (26%), mp > 300 °C. Anal. Calcd for $C_{148}H_{120}N_{16}O_{16}S_{16}Ni$: C, 60.25; H, 4.09; N, 7.59; Ni, 1.98%. Found: C, 59.96; H, 4.34; N, 7.26; Ni, 2.13. IR (KBr tablet) ν_{max}/cm^{-1}: 3077 (Ar–H), 2924–2852 (Aliph. C–H), 1618, 1597, 1418, 1390–1135 (SO_2), 1070, 966, 889, 784. ^1H NMR (DMSO-d_6) (δ: ppm): 8.88–8.23 (s, 8H, Ar–H), 7.49–7.36 (m, 32H, tosyl Ar–H), 7.38–7.27 (d, 16H, Ar–H), 7.33–7.20 (t, 16H, Ar–H), 2.85–2.82 (t, 16H, CH_2–S), 2.42 (s, 24H, CH_3), 1.70–1.64 (m, 8H, CH_2–CH_2). UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε $dm^3\,mol^{-1}\,cm^{-1}$)]: 330 (4.82), 358 (4.60), 612 (4.40), 650 (4.24), 681 (4.73). MS (FAB) (*m/z*): 2951 $[M+1]^+$.

2.5. Zinc(II) phthalocyanine (8)

The same procedure as above was adopted but using compound **5** (0.8 g, 1.10 mmol), anhydrous zinc acetate (50.42 mg, 0.27 mmol) and 2-(dimethylamino)ethanol (2 ml). The solid product was chromatographed on silica gel with chloroform:petroleum ether (6:4) as eluent. This product is soluble in DMF, DMSO and pyridine. Yield: 244 mg (30%), mp > 300 °C. Anal. Calcd for $C_{148}H_{120}N_{16}O_{16}S_{16}Zn$: C, 60.11; H, 4.09; N, 7.57; Zn, 2.21%. Found: C, 59.88; H, 4.36; N, 7.21; Zn, 2.41. IR (KBr tablet) ν_{max}/cm^{-1}: 3080 (Ar–H), 2924–2846 (Aliph. C–H), 1623, 1598, 1440, 1371–1159 (SO_2), 1086, 940, 892, 740. ^1H NMR (DMSO-d_6) (δ: ppm): 8.87–8.24 (s, 8H, Ar–H), 7.48–7.37 (m, 32H, tosyl Ar–H), 7.39–7.26 (d, 16H, Ar–H), 7.32–7.21 (t, 16H, Ar–H), 2.86–2.83 (t, 16H, CH_2–S), 2.43 (s, 24H, CH_3), 1.72–1.66 (m, 8H, CH_2–CH_2). UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε $dm^3\,mol^{-1}\,cm^{-1}$)]: 329 (4.54), 379 (4.72), 482 (4.21), 617 (4.40), 686 (4.82). MS (FAB) (*m/z*): 2957 $[M]^+$.

2.6. Cobalt(II) phthalocyanine (9)

The same procedure as above was followed but using compound **5** (0.8 g, 1.10 mmol), anhydrous cobalt(II) chloride (35.05 mg, 0.27 mmol) and 2-(dimethylamino)ethanol (2 ml). The solid product was chromatographed on silica gel with chloroform:ethanol (3:2) as eluent. This product is soluble in DMF, DMSO and pyridine. Yield: 284 mg (35%), mp > 300 °C. Anal. Calcd for $C_{148}H_{120}N_{16}O_{16}S_{16}Co$: C, 60.24; H, 4.09; N, 7.59; Co, 1.99%. Found: C, 60.05; H, 4.31; N, 7.31; Co, 2.22. IR (KBr tablet) ν_{max}/cm^{-}: 3083 (Ar–H), 2924–2840 (Aliph. C–H), 1622, 1599, 1417, 1388–1157 (SO_2), 1088, 943, 894, 752. ^1H NMR (DMSO-d_6) (δ: ppm): 8.88–8.25 (s, 8H, Ar–H), 7.49–7.38 (m, 32H, tosyl Ar–H), 7.38–7.27 (d, 16H, Ar–H), 7.31–7.22 (t, 16H, Ar–H), 2.89–2.86 (t, 16H, CH_2–S), 2.45 (s, 24H, CH_3), 1.76–1.70 (m, 8H, CH_2–CH_2). UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε $dm^3\,mol^{-1}\,cm^{-1}$)]: 269 (4.88), 303 (4.77), 374 (4.49), 611 (4.32), 671 (4.90). MS (FAB) (*m/z*): 2950 $[M]^+$.

2.7. Copper(I) phthalocyanine (10)

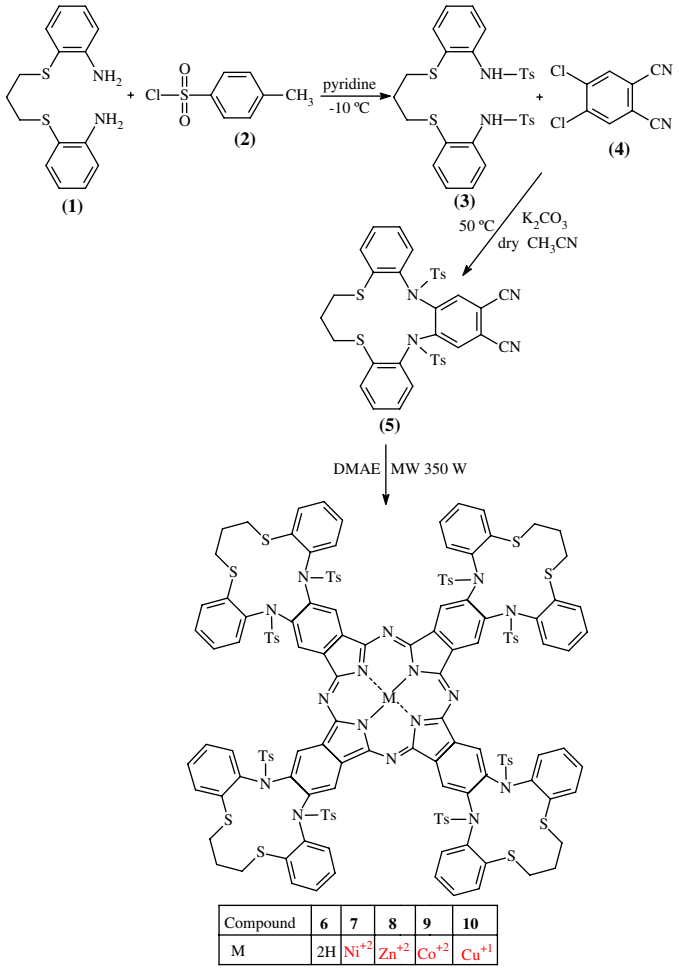
The same procedure as above was adopted but using compound **5** (0.8 g, 1.10 mmol), anhydrous copper(I) chloride (26.73 mg, 0.27 mmol) and 2-(dimethylamino)ethanol (2 ml). The green solid product was chromatographed on silica gel with chloroform:methanol (7:1) as eluent. This product is soluble in DMF, DMSO and pyridine. Yield: 300 mg (37%), mp > 300 °C. Anal. Calcd for $C_{148}H_{120}N_{16}O_{16}S_{16}Cu$: C, 60.15; H, 4.09; N, 7.58; Cu, 2.15%. Found: C, 59.91; H, 4.32; N, 7.26; Cu, 2.38. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2917–2848 (Aliph. C–H), 1620, 1580, 1465, 1358–1133 (SO_2), 1087, 955, 838, 751. UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε $dm^3\,mol^{-1}\,cm^{-1}$)]: 274 (4.81), 305 (4.71), 365 (4.48), 626 (4.30), 692 (4.83). MS (FAB) (*m/z*): 2958 $[M+3]^+$.

3. Results and discussion

The mode of preparation of the metal-free **6** and metallophthalocyanines **7**, **8**, **9** and **10** is shown in Scheme 1. The structures of the novel compounds were characterized by a combination of ^1H NMR, ^{13}C NMR, IR, UV–vis, elemental analysis and MS spectral data. 2,2′-[Propane-1,3-diylbis(thio)]-bis[aniline] (**1**) [20] and 4,5-dichlorobenzene-1,2-dinitrile (**4**) [21] were prepared according to the literature.

The aromatic amine groups of **1** were tosylated in pyridine at −10 °C with *p*-toluenesulfonylchloride (**2**) to protect the amino groups and to make use of the high reactivity of tosylamides in further cyclization reactions. ^1H NMR, ^{13}C NMR, IR, elemental analysis and MS spectra verified the structure of **3**. In the IR spectrum of **1**, the intense absorption bands at 3449–3355 cm^{-1} for **1**, corresponding to the–NH_2 groups, disappeared after conversion to the tosylamino derivative. The remainder of the spectra of **1** resembled closely that of **3** including the characteristic vibration of aliphatic and other groups. The IR spectrum of **3** clearly indicated the presence of the N–H group by the intense stretching bands at 3254 cm^{-1}; the ^1H NMR spectrum of **3** was almost identical, with only small changes in shifts. The difference between the spectra of the tosylated amino and free amino groups, **1** and **3**, is shown by the presence of sulfonamide bands in **3** at 8.61 ppm. The ^{13}C NMR spectrum of **3** clearly indicates the presence of a tosyl Ar–H group by the intense bands in **3** at 150.01, 138.89, 130.23 and 129.94 ppm. The MS mass spectrum of **3**, which shows a peak at $m/z = 599$ $[M+1]^+$, supports the proposed structure of this compound.

Compound **5** was prepared from *N*,*N*′-[propane-1,3-diylbis(thio-2,1-phenylene)]bis[*p*-toluenesulfonamide] (**3**) with 4,5-dichlorobenzene-1,2-dinitrile (**4**) in dry acetonitrile containing potassium carbonate as base [23,24]. The reaction was carried out in dry acetonitrile at 85 °C and gave moderate yields (67%). Comparison of the IR spectra clearly indicated the formation of compound **5** by the disappearance of the



Scheme 1. The synthesis of the metal-free phthalocyanine and metallophthalocyanines (Ts = *p*-toluenesulphonyl).

C–Cl band of 4,5-dichlorobenzene-1,2-dinitrile at 684 cm^{-1} and of the NH band of compound **3** at 3254 cm^{-1}, as well as the appearance of a new absorption at 2238 cm^{-1} (C≡N). The spectrum of **5** also indicates the presence of alkyl, CN, and SO_2 groups as given by the intense stretching bands at 2917–2846 (C–H), 2238 (C≡N) and 1336–1159 cm^{-1} ($-SO_2$). The ^1H NMR spectra of **5** showed a new signal due to an aromatic proton at $\delta = 7.90$ ppm, as expected. While the ^1H NMR spectra of **3** and **5** were similar, the proton-decoupled ^{13}C NMR spectrum indicated the presence of nitrile carbon (C≡N) atoms in **5** at $\delta = 113.64$ ppm. The MS mass spectrum of compound **5**, which shows a peak at $m/z = 747$ $[M + Na + 1]^+$, 763 $[M + K + 1]^+$ supports the proposed structure for this compound.

The metal-free phthalocyanine **6** was synthesized by microwave irradiation [25] of the corresponding dicyano compound **5** 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. Also, 2-(dimethylamino)ethanol acts donor of protons [26] The IR spectrum of **6** showed 3280 (NH) and 3076 (Ar–H) vibrations. In the ^1H NMR spectrum of **6**, shielding of the inner core protons was not observed due to the probable strong aggregation of the molecules [27]. The signals related to aromatic protons and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton were characteristic of the proposed structure. The disappearance of the C≡N stretching vibration in the IR spectra of **5** suggested the formation of compound **6**. The mass spectrum of compound **6**, which shows a peak at $m/z = 2893$ $[M]^+$ supports the proposed structure of this compound.

The metallophthalocyanines, **7**, **8**, **9** and **10** were synthesized in moderate yields of 26, 30, 35, and 37%, respectively, and were obtained from the dicyano derivative **5** and corresponding anhydrous metal salts $NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$ and CuCl, respectively, by microwave irradiation in 2-(dimethylamino)ethanol for 8 min. In the IR spectra of **7**, **8**, **9** and **10**, the disappearance of the strong C≡N stretching vibration of **5** is evidence for the formation of the metallophthalocyanines **7**, **8**, **9** and **10**. The remainder of the IR spectra of metallophthalocyanines was very similar to those of the metal-free phthalocyanine **6**; the ^1H NMR spectra of these compounds were almost identical to those of **6**. Also, it should be mentioned that the other differences in the ^1H NMR spectra of the metal-free phthalocyanine and the metallophthalocyanines were the broad signals encountered in the cases of **7**, **8**, **9** and **10**, owing to aggregation of the planar phthalocyanine molecules at the very high concentration used for NMR measurements. These were in agreement with the structural information. In the mass spectrum of compounds **7**, **8**, **9** and **10**, the presence of molecular ion peaks at $m/z = 2951$ $[M + 1]^+$, 2957 $[M]^+$, 2950 $[M]^+$ and 2958 $[M + 3]^+$, respectively, confirmed the proposed structures. We used a domestic microwave oven for the synthesis of **6**, **7**, **8**, **9**, and **10** at 300 W and 175 °C.

In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at about 300–500 nm related to the B band and the other in the visible region at 600–700 nm related to the Q band [28]. The split Q bands in **6**, which are characteristic of metal-free phthalocyanines were observed at $\lambda_{max} = 749$ and 695 nm. These Q band absorptions show the monomeric species with D_{2h} symmetry due to the phthalocyanine ring being related to the fully conjugated 18 π electron system [29–31]. The presence of strong absorption bands in **6** in the near UV region at $\lambda_{max} = 485$, 340, 315 and 293 nm also shows Soret region B bands which can be ascribed to the deeper π–π* levels of LUMO transitions.

The UV–vis absorption spectra of the metallophthalocyanines **7**, **8**, **9** and **10** in pyridine showed intense Q absorption at $\lambda_{max} = 681$, 686, 671 and 692 nm, with weaker absorptions at 650, 617, 611 and 626 nm, respectively (Fig. 1). The single Q bands in the metallo derivatives **7**, **8**, **9** and **10** were characteristic of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [32]. B band absorptions of compounds **7**, **8**, **9** and **10** were observed at $\lambda_{max} =$ (358 and 330), (482, 379 and 329), (374, 303 and 269), (365, 305 and 274) nm as expected, respectively.

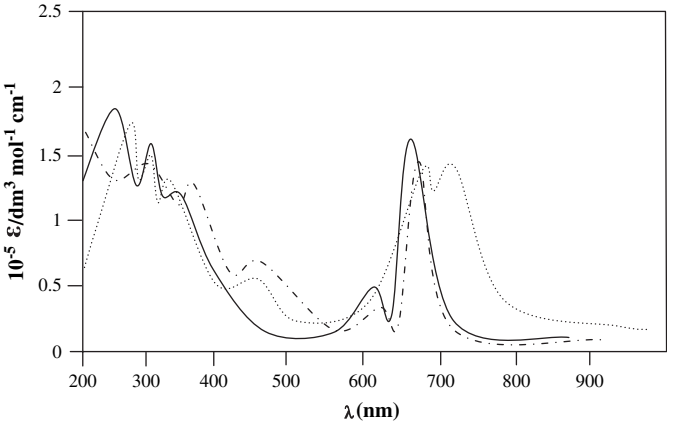


Fig. 1. UV–vis spectra of compounds **6** (···), **8** (–·–·–) and **9** (—) in pyridine.

4. 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 13-membered dithiadiaza macrocycle peripheral groups. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–vis, elemental analysis and MS spectral data.

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