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The synthesis and characterization of metal-free and metallophthalocyanine polymers by microwave irradiation containing diazadithia macrocyclic moieties

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ABSTRACT

A tetranitrile monomer was synthesized by nucleophilic aromatic substitution of N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) onto 4-nitrophthalonitrile. A metal-free phthalocyanine polymer was prepared by the reaction of the tetranitrile monomer under N_2 in the presence of 2-(dimethylamino)ethanol at 145 °C for 24 h. Zinc(II), copper(II), cobalt(II), nickel(II), lead (II), phthalocyanine polymers were prepared by reaction of the tetranitrile with the chlorides of zinc (II), copper (II), cobalt (II), nickel (II), lead (II), employing microwave irradiation in the presence 2-(dimethylamino)ethanol at 175 °C, 350 W for 10 min. The thermal stabilities of the phthalocyanine compounds were determined by thermogravimetric analysis. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–vis, elemental analysis and MS spectral data.

1. Introduction

Phthalocyanines are an important class of organic materials with a very stable electronic configuration which makes them an important class of functional materials [1]. Metal-free phthalocyanine and its metal complexes have been intensively investigated since the early-1930s. Phthalocyanine chemistry is undergoing a renaissance because phthalocyanines and many of their derivatives exhibit singular and unconventional physical properties which are interesting for applications in materials science [2]. They can be used in jet printing inks [3], catalysts [4], gas sensors [5] and photonic devices [6,7] and because of the flexibility in tailoring the electrical and optical properties, phthalocyanines can be used in many devices like: fuel cells, organic metals, electronic media, photoelectrical detectors, xerographic media, field effect transistors [8], light-emitting diodes [9–11], optical recording, optical memories, information displays [12], hole-burning memories, light-limiters, lasers, non-linear optical elements, etc. [13]. The photoactive semiconducting properties of phthalocyanine monomers and polymers makes possible the production of low cost, flexible [14,15]. In organic photovoltaic devices, dissociation of photo-generated excitons occurs leading to photocurrent in the external circuit [16–18].

Recently, phthalocyanines have been used as photosensitizers in the treatment of cancer [19–21] and intimal hyperplasia [22] for photodynamic therapy (PDT). Due to the intense absorption in the visible region, high efficiency to generate reactive oxygen species (such as singlet oxygen), and low dark toxicity, phthalocyanines have been used in this avenue for the treatment of various cancers and photoinactivation of viruses [23–25]. PDT dyes are recognized as efficient sensitizers of singlet oxygen and the involvement of singlet oxygen in the PDT process is now widely accepted, thus, the relative photooxidation rate by singlet oxygen catalyzed by these dyes has been examined.

In the recent years, it has been recognized that microwave processing has attracted potential as an alternative to classical processing because of the inherent advantages of microwave heating, which is selective, direct, rapid, internal, and controllable [26]. Microwave processing has therefore been applied in such varied fields as pulp drying, food cooking, organic synthesis, ceramic sintering, composite joining, chemical analyses, and waste treatment [27,28].

Being discovered in 1950s, polymeric phthalocyanine remains an enigmatic material and many of its intrinsic properties are known rather insufficiently [29]. Polymeric phthalocyanines were mainly prepared via polycyclotetramerization reactions of bifunctional

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monomers such as various nitriles or tetracarboxylic acid derivatives in the presence of metal salts or metals.

We have previously described the synthesis of novel tetrakis [N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl)) bis(4-methylbenzenesulfonamide)-phthalocyanine] and its metal derivatives [30] and new polymeric phthalocyanines substituted with pyridine through methyleneoxy bridges [31]. In the present paper, we describe the synthesis and characterization of metal-free **4** and metallophthalocyanine polymers **5, 6, 7, 8** and **9** by microwave irradiation.

2. Experimental

All reactions were carried out under a nitrogen atmosphere using Standard Schlenk techniques. The IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer, using potassium bromide pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in DMSO-d$_6$ or $CDCl_3$, and chemical shifts (d) are reported relative to Me_4Si as internal standard. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. Elemental analysis were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. UV–vis absorption spectra were measured by a Unicam UV–visible spectrometer. A Seiko II Exstar 6000 thermal analyzer was used to record DTA curves under nitrogen atmosphere with a heating rate of 20 °C min^{-1} in the temperature range 30–900 °C using platinum crucibles. Melting points were measured on an electrothermal apparatus. A domestic microwave oven (Arçelik MD 823) was used for all the syntheses of phthalocyanines.

*2.1. N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(N-(3,4-dicyanophenyl)-4-methylbenzenesulfonamide)(**3**)*

N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1diyl))bis(4-methylbenzenesulfonamide) **1** [30] (1 g, 1.99 mmol) was dissolved in dry DMF (20 mL) under N_2 and 4-nitrophthalonitrile **2** (0.688 g., 3.98 mmol) was added to the solution. After stirring for 10 min, finely ground anhydrous K_2CO_3 (0.823 g, 5.97 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50 °C for 5 days. Then the solution was poured into ice-water (100 g). The precipitate formed was dried in vacuo over P_2O_5. The crude product was crystallized from ethanol. Yield: % 82, 1.230 g, mp: 197–199 °C. Anal. Calcd. For ($C_{37}H_{34}N_6O_4S_4$) (%): C, 58.86; H, 4.54; N, 11.13; S, 16.99. Found: C, 58.54; H, 4.24; N, 11.46; S, 16.46. IR (KBr pellets) ν_{max}/cm^{-1}: 3070 (Ar–H), 2925–2856 (Aliph. C–H), 2234 (C≡N), 1668 (C=C), 1489–1387 (S=O), 1445–1408–1254–706 (CH$_2$–S–C), 1353 (C–N). ^1H NMR ($CDCl_3$), (δ:ppm): 8.01 (d, 2H, Ar–H4), 7.74 (s, 2H, Ar–H1), 7.71 (d, 2H, Ar–H5), 7.48 (dd, 8H, Ar–Ts–H,), 2.95 (t, 4H, N–CH$_2$), 2.87 (s, 6H, CH$_3$), 2.60 (m, 4H, CH$_2$–S–CH$_2$), 2.43 (m, 4H, CH$_2$–S–CH$_2$), 1.24 (m, 2H, CH$_2$). ^{13}C NMR ($CDCl_3$): δ = 144.14 (Ar–C14), 134.45(Ar–C4), 132.47 (Ar–C13), 130.16 (Ar–C5), 127.33 (Ar–C12–Ts), 123.90 (Ar–C2), 114.70 (C≡N), 49.77 (N–CH$_2$), 30.55 (S–C9), 29.72 (S–C8), 21.68 (CH$_2$), 21.59 (CH$_3$). MS; m/z = 754 [M]$^+$.

*2.2. Metal-free phthalocyanine (**4**)*

Compound **3** (0.2 g, 0.265 mmol) and 2-(dimethylamino) ethanol (2 mL) was placed in a Schlenk tube under nitrogen in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.232 g, 1.5 mmol), gently heated, and subsequently heated at 145 °C for 24 h. After cooling to room temperature the reaction mixture refluxed with ethanol (30 mL) to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. Yield: 0.057 g. (37%), mp: >300 °C. Anal. Calcd. (for CN end groups) ($C_{148}H_{138}N_{24}O_{16}S_{16}$)$_n$ (%): C, 58.82; H, 4.60; N, 11.12; S, 16.98. Found: C, 57.73; H, 4.76; N, 11.82; S, 17.17. IR (KBr pellets): 3436 (N–H), 3058 (Ar–H), 2921–2851 (Aliph. C–H), 2214 (C≡N), 1722, 1640 (C=C), 1593, 1465–1158 (S=O), 1401 (CH$_2$–S–C), 1245 cm^{-1} (Ar–N–C), 1090, 814. ^1H NMR (DMSO): δ = 7.74 (m, 12H, Ar–H), 7.71 (m, 16H, Ar–Ts), 7.49 (m, 16H, Ar–Ts), 7.23 (m, 12H, Ar–H), 3.86 (t, 16H, N–CH$_2$), 2.75 (t, 16H, S–CH$_2$), 2.68 (t, 16H, S–CH$_2$), 2.39 (s, 24H, CH$_3$), 1.75 (m, 8H, CH$_2$). ^{13}C NMR (DMSO): δ = 162.16, 151.43 (Ar–C), 144.76, 136.54, 134.88 (Ar–Ts–C), 130.15, 128.31 (Ar–Ts–CH), 125.43, 124.72, 122.66 (Ar–CH), 59.12, 58.48 (N–CH$_2$), 35.94, 33.16 (S–CH$_2$), 28.56 (CH$_2$). UV–Vis [(in pyridine) λ_{max}/nm10^{-5}ε (mol^{-1} cm^{-1})]: 710 (5.26), 677 (5.30), 615 (4.86), 343 (5.25) MS; m/z = 3078 [M + K + H_2O]$^+$.

*2.3. Zinc (II) phthalocyanine (**5**)*

Compound **3** (0.2 g, 0.265 mmol), anhydrous $ZnCl_2$ (0.009 g, 0.0662 mmol) and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture refluxed with ethanol (30 mL) to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. Yield: 75 mg (36%), mp: >300 °C. Anal. Calcd. (for imide end groups) ($C_{148}H_{140}N_{20}O_{24}S_{16}Zn$)$_n$ (%): C, 56.23; H, 4.46; N, 8.86; S, 16.23. Found: C, 56.77; H, 5.09; N, 9.38; S, 16.00. IR (KBr pellets): 3436 (imide N–H), 3058 (Ar–H), 2921–2857 (Aliph. C–H), 1774 (sym. C=O), 1717 (asym. C=O), 1651 (C=C), 1596, 1487–1347 (S=O), 1401 (CH$_2$–S–C). 1256 cm^{-1} (Ar–N–C). ^1H NMR ($CDCl_3$): δ = 7.94 (m, 12H, Ar–H), 7.69 (m, 16H, Ar–Ts), 7.43 (m, 16H, Ar–Ts), 7.18 (m, 12H, Ar–H), 4.14 (t, 16H, N–CH$_2$), 2.88 (t, 16H, S–CH$_2$), 2.72 (t, 16H, S–CH$_2$), 2.54 (s, 24H, CH$_3$), 1.62 (m, 8H, CH$_2$). ^{13}C NMR (DMSO): δ = 154.23, 152.90 (Ar–C), 134.01, 133.35, 131.61 (Ar–Ts–C), 129.81, 128.58 (Ar–Ts–CH), 124.61, 124.30, 123.39 (Ar–CH), 59.63, 59.57 (N–CH$_2$), 36.11, 35.01 (S–CH$_2$), 29.71 (CH$_2$). UV–Vis [(in pyridine) λ_{max}/nm10^{-5} ε(mol^{-1} cm^{-1})]: 690 (5.25), 624 (4.65), 358 (4.99). MS; m/z = 3180 [M + H_2O + 1]$^+$.

*2.4. Copper (II) phthalocyanine (**6**)*

Compound **3** (0.2 g, 0.265 mmol), anhydrous $CuCl_2$ (0.0089 g, 0.0662 mmol) and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture refluxed with ethanol (30 mL) to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. Yield: 58 mg (28%), mp: >300 °C. Anal. Calcd. (for imide end groups) ($C_{148}H_{140}N_{20}O_{24}S_{16}Cu$)$_n$ (%): C, 56.26; H, 4.47; N, 8.87; S, 16.24. Found: C, 56.65; H, 4.73; N, 9.03; S, 16.78. IR (KBr pellets): 3306 (imide N–H), 3060 (Ar–H), 2917–2862 (Aliph. C–H), 1778 (sym. C=O), 1718 (asym. C=O), 1597, 1469–1345 (S=O), 1404 (CH$_2$–S–C), 1278 cm^{-1} (Ar–N–C). UV–Vis [(in pyridine) λ_{max}/nm10^{-5} ε(mol^{-1} cm^{-1})]: 689 (5.33), 623 (4.91), 329 (5.08). MS; m/z = 3159 [M]$^+$.

*2.5. Cobalt(II) phthalocyanine (**7**)*

Compound **3** (0.2 g, 0.265 mmol), anhydrous $CoCl_2$ (0.0086 g, 0.0662 mmol) and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture refluxed with ethanol (30 mL) to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. Yield: 66 mg (32%), mp: >300 °C. Anal. Calcd. (for imide end groups) ($C_{148}H_{140}N_{20}O_{24}S_{16}Co$)$_n$ (%): C, 56.35; H, 4.47; N, 8.88;

S, 16.26. Found: C, 56.49; H, 4.43; N, 8.48; S, 16.84. IR (KBr pellets): 3304 (imide N–H), 3062 (Ar–H), 2921–2862 (Aliph. C–H), 1775 (sym. C=O), 1718 (asym. C=O), 1595, 1470–1348 (S=O), 1404 (CH_2–S–C), 1248 cm^{-1} (Ar–N–C). ^1H NMR (DMSO): $\delta = 7.86$ (m, 12H, Ar–H), 7.64 (m, 16H, Ar–Ts), 7.54 (m, 16H, Ar–Ts), 7.29 (m, 12H, Ar–H), 4.37(t, 16H, N–CH_2), 2.78 (t, 16H, S–CH_2), 2.72 (t, 16H, S–CH_2), 2.43 (s, 24H, CH_3), 1.58 (m, 8H, CH_2). ^{13}C NMR (DMSO): $\delta = 157.89$, 156.34 (Ar–C), 132.35, 131.24, 130.02 (Ar–Ts–C), 128.58, 126.24 (Ar–Ts–CH), 123.97, 123.78, 121.58 (Ar–CH), 59.54, 59.51 (N–CH_2), 36.68, 35.24 (S–CH_2), 27.81 (CH_2). UV–Vis [(in pyridine) λ_{max}/nm10^{-5} ε(mol^{-1} cm^{-1})]: 671 (5.44), 608 (5.06), 302 (5.41). MS; $m/z = 3223$ $[M + 3Na + 1]^+$.

2.6. *Nickel(II) phthalocyanine (**8**)*

Compound **3** (0.2 g, 0.265 mmol), anhydrous $NiCl_2$ (0.0086 g, 0.0662 mmol) and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture refluxed with ethanol (30 mL) to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. Yield: 73 mg (35%), mp: >300 °C. Anal. Calcd. (for imide end groups) $(C_{148}H_{140}N_{20}O_{24}S_{16}Ni)_n$ (%): C, 56.35; H, 4.47; N, 8.88; S, 16.26. Found: C, 56.36; H, 4.54; N, 8.15; S, 16.78. IR (KBr pellets): 3285 (imide N–H), 3060 (Ar–H), 2919–2857 (Aliph. C–H), 1776 (sym. C=O), 1714 (asym. C=O), 1596, 1470–1347 (S=O), 1407 (CH_2–S–C), 1254 cm^{-1} (Ar–N–C). ^1H NMR (DMSO): $\delta = 7.86$ (m, 12H, Ar–H), 7.72 (m, 16H, Ar–Ts), 7.45 (m, 16H, Ar–Ts), 7.13 (m, 12H, Ar–H), 3.99 (t, 16H, N–CH_2), 2.86 (t, 16H, S–CH_2), 2.83 (t, 16H, S–CH_2), 2.39 (s, 24H, CH_3), 1.74 (m, 8H, CH_2). ^{13}C NMR (DMSO): $\delta = 150.95$, 148.30 (Ar–C), 142.05, 137.32, 134.98 (Ar–Ts–C), 130.07, 129.76 (Ar–Ts–CH), 125.68, 124.43, 122.86 (Ar–CH), 59.32, 58.35 (N–CH_2), 35.38, 32.27 (S–CH_2), 29.79 (CH_2). UV–Vis [(in pyridine) λ_{max}/nm10^{-5} ε(mol^{-1} cm^{-1})]: 683 (5.27), 617 (4.94), 305 (5.40). MS; $m/z = 3154$ $[M]^+$.

2.7. *Lead(II) phthalocyanine (**9**)*

Compound **3** (0.15 g, 0.1989 mmol), anhydrous $PbCl_2$ (0.014 g, 0.0497 mmol) and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture refluxed with ethanol (30 mL) to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. Yield: 41 mg (25%), mp: >300 °C. Anal. Calcd. (for imide end groups) $(C_{148}H_{140}N_{20}O_{24}S_{16}Pb)_n$ (%): C, 53.82; H, 4.27; N, 8.48; S, 15.53. Found: C, 53.32; H, 4.11; N, 8.70; S, 16.29. IR (KBr pellets): 3306 (imide N–H), 3059 (Ar–H), 2921–2861 (Aliph. C–H), 1778 (sym. C=O), 1725 (asym. C=O), 1596, 1482–1324 (S=O), 1399 (CH_2–S–C), 1248 cm^{-1} (Ar–N–C). ^1H NMR (DMSO): $\delta = 8.01$ (m, 12H, Ar–H), 7.59 (m, 16H, Ar–Ts), 7.55 (m, 16H, Ar–Ts), 7.47 (m, 12H, Ar–H), 4.43 (t, 16H, N–CH_2), 2.83 (t, 16H, S–CH_2), 2.76 (t, 16H, S–CH_2), 2.51 (s, 24H, CH_3), 1.64 (m, 8H, CH_2). ^{13}C NMR (DMSO): $\delta = 157.59$, 155.76 (Ar–C), 145.63, 139.98, 132.83 (Ar–Ts–C), 130.94, 127.96 (Ar–Ts–CH), 127.54, 125.86, 124.21 (Ar–CH), 54.51, 52.16 (N–CH_2), 35.16, 32.19 (S–CH_2), 31.23 (CH_2). UV–Vis [(in pyridine) λ_{max}/nm10^{-5} ε(mol^{-1} cm^{-1})]: 721 (5.36), 681 (5.08), 345 (5.19). MS; $m/z = 3306$ $[M + 3]^+$.

2.8. *The conversion of cyano end groups of the polymeric metal-free phthalocyanine into imido groups (**4a**)*

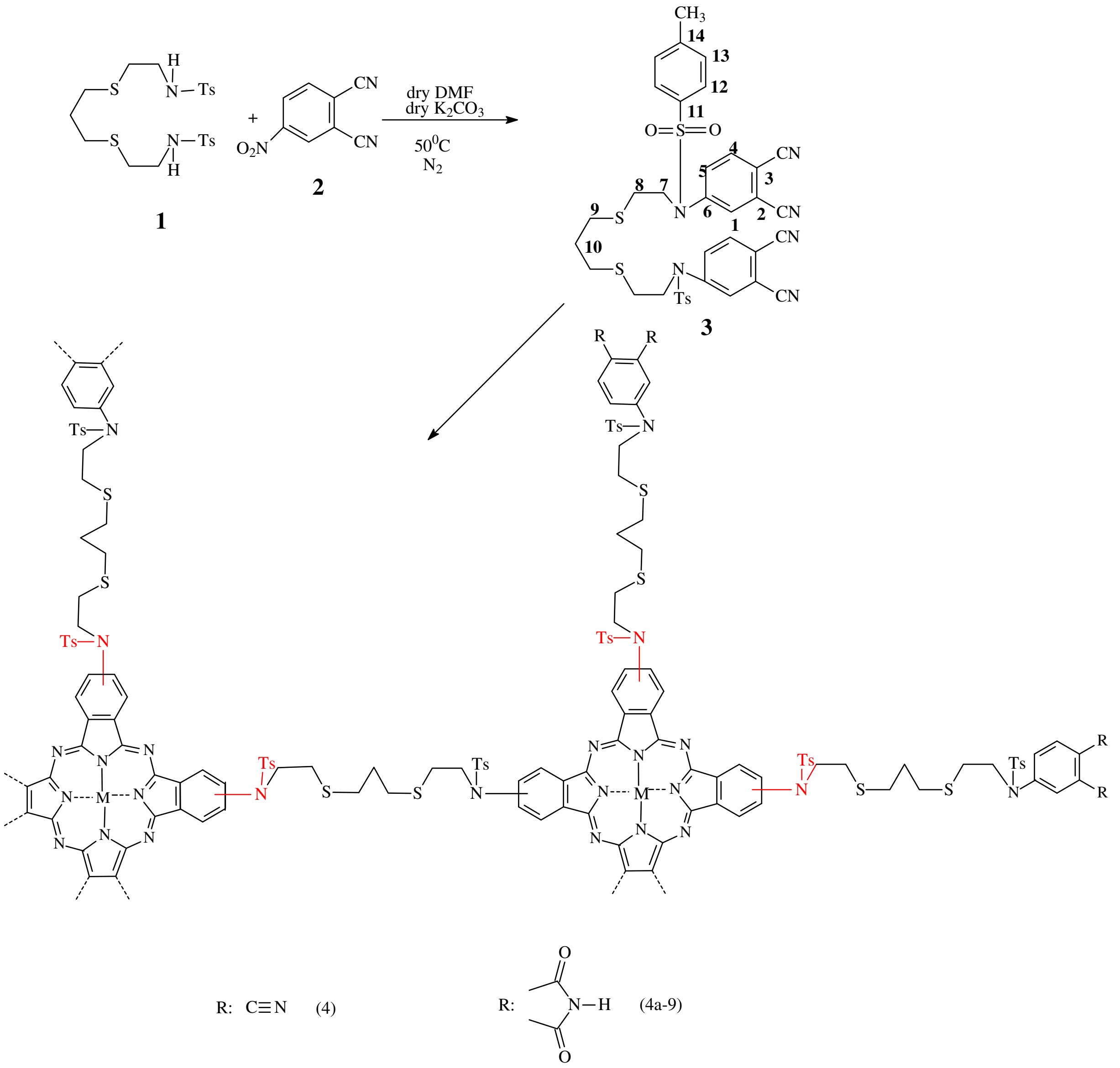
A sample of compound 4 (0.15 g, 0.0497 mmol) was dissolved in a minimum volume of H_2SO_4 (96 wt.-%) at room temperature. After 3–4 h of stirring, the reaction mixture was filtered. The filtered part was poured into excess amount of ice-water mixture. The dark green crude product was washed with distilled water until the residue washing water was neutral. Then the final product 4a was washed with ethanol and dried. Yield: 18 mg (46.2%). M.p: >300 °C. Anal. Calc. (for imide end groups) $(C_{148}H_{142}N_{20}O_{24}S_{16})_n$ (%): C, 57.38; H, 4.62; N, 9.04; S, 16.56. Found: C, 57.76; H, 4.84; N, 9.32; S, 16.09. IR (KBr pellets): 3392 (imide N–H), 3057 (Ar–H), 2923–2846 (Aliph. C–H), 1772 (sym. C=O), 1720 (asym. C=O), 1599, 1443–1399 (S=O), 1408 (CH_2–S–C), 1240 cm^{-1} (Ar–N–C). ^1H NMR (DMSO): $\delta = 7.74$ (m, 12H, Ar–H), 7.69 (m, 16H, Ar–Ts), 7.38 (m, 16H, Ar–Ts), 7.22 (m, 12H, Ar–H), 3.86(t, 16H, N–CH_2), 2.92(t, 16H, S–CH_2), 2.86(t, 16H, S–CH_2), 2.43 (s, 24H, CH_3), 1.68 (m, 8H, CH_2). ^{13}C NMR (DMSO): $\delta = 150.86$, 146.62 (Ar–C), 144.08, 134.28, 132.58 (Ar–Ts–C), 130.34, 127.86 (Ar–Ts–CH), 125.14, 124.76, 121.43 (Ar–CH), 59.32, 58.35 (N–CH_2), 35.28, 33.42 (S–CH_2), 25.79 (CH_2). MS; $m/z = 3098$ $[M + 1]^+$.

3. Result and discussion

Metal-free and metallophthalocyanine polymers were synthesized by a polymeric tetramerization reaction (Fig. 1). The first step in the synthetic procedure was to obtain N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1diyl))bis(N-(3,4-dicyanophenyl)-4-methylbenzenesulfonamide) **3**. This compound was prepared from 4-nitrophtalonitrile **2** and N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) **1** in DMF; K_2CO_3 was used as the base for this nucleophilic aromatic displacement. In the IR spectrum of **3**, the disappearance of NO_2 and NH stretches, along with the appearance of new bands at 2234 belonging to the C≡N group, are in agreement with the proposed structure. The ^1H NMR spectrum of a $CDCl_3$ solution of **3** was well resolved and showed that the formation of this macrocycle was accomplished. The chemical shifts belonging to the deuterium exchangeable NH groups at $\delta = 5.36$ ppm disappear after the condensation reaction between **1** and **2**. In the ^1H NMR spectrum of **3**, the NH group of compound **1** disappeared as expected. The ^{13}C NMR spectrum of **3** indicated the presence of nitrile carbon atoms in **3** at 114.70 (C≡N), ppm. FAB mass spectrum and elemental analysis also confirm the formation of desired compound **3**.

The metal-free phthalocyanine **4** derived from the corresponding tetracyano compound **3** was synthesized in 2-(dimethylamino) ethanol under nitrogen in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.232 g, 1.5 mmol).

Compound **4a** was obtained to use its characteristic data for analysis of the degree of polymerization. For this aim, the metal-free phthalocyanine was reacted with conc. H_2SO_4 at room temperature to give **4a** and the cyano end groups of the metal-free phthalocyanine were converted into imido end groups. In the IR spectrum of **4** characteristic peaks for phthalocyanines were observed. The peak at 3436 cm^{-1} is the characteristic metal-free phthalocyanine N–H stretching bands. Also, 2214 cm^{-1} (C≡N) band were present in the spectrum. The mass spectrum of this compound at $m/z = 3078$ $[M + K + H_2O]^+$ support the proposed formula for this structure. The elemental analysis were confirm desired compound **4**. In the IR spectrum of **4a**, the disappearance of the peak at 2214 cm^{-1} correspond to the cyano groups of **4** and the appearance of new peaks at 1772–1720 cm^{-1} correspond to imido groups confirm the conversion of the cyano groups into imido groups. The metallophthalocyanines **5**–**9** were obtained from tetracyano derivative **3** and corresponding anhydrous metal salts $ZnCl_2$, $CuCl_2$, $CoCl_2$, $NiCl_2$, and $PbCl_2$, respectively, by microwave irradiation in 2-(dimethylamino)ethanol for 10 min. The metal-free phthalocyanine was obtained under the same conditions in the microwave oven but only in low yield (18%) relative to the



Compound	4	4a	5	6	7	8	9
M	2H	2H	Zn	Cu	Co	Ni	Pb

Fig. 1. Synthesis of new network polymeric phthalocyanine polymers.

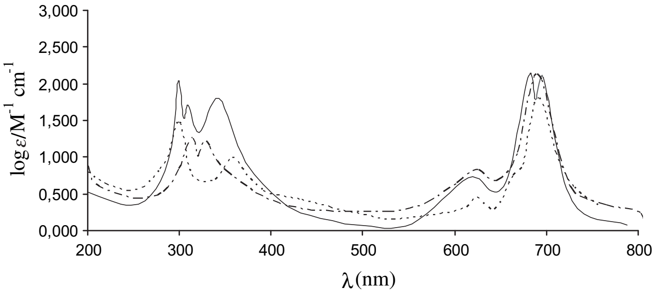


Fig. 2. UV–Vis spectra of H_2Pc(—), ZnPc(……) and CuPc(-.-.-.) complexes.

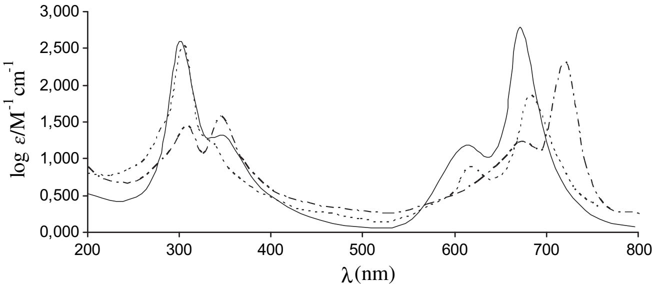


Fig. 3. UV–Vis spectra of CoPc(—), NiPc(……) and PbPc(-.-.-.) complexes.

metallophthalocyanines. Therefore **4** was obtained using the conventional heating conditions reported in the experimental section. The differences between the infrared spectra of the metal-free phthalocyanine and the metallophthalocyanine polymers 5–9 is clear from the absence of N–H stretching vibrations at 3436 cm^{-1} and 1090 cm^{-1} correspond to the inner core [32,33]. The end groups of the metal-free phthalocyanine polymer were cyano groups (2214 cm^{-1}) while the end groups of the metallophthalocyanine polymers were imido groups (1778–1714 cm^{-1}). The existence of imido groups in the case of metallophthalocyanine polymers was attributed to the presence of moisture during work-up. There was little shift to longer wavelength numbers in most of the IR bands of the metal complexes with respect to the metal-free analogues [34]. In the mass spectrum of, Zn, Cu, and Co, Ni, Pb phthalocyanines, the presence of molecular ion peaks at $m/z = 3180$ $[M + H_2O + 1]^+$, $m/z = 3159$ $[M]^+$, 3223 $[M + 3Na + 1]^+$, 3154 $[M]^+$, and $m/z = 3306$ $[M + 3H]^+$ respectively, confirmed the proposed structures. The elemental analysis were confirm desired compounds **5**, **6**, **7**, **8**, **9**.

Classical molecular weight determinations known in polymer chemistry are very difficult to conduct. This difficulty is due to the insolubility or very poor solubility of the polymers in organic solvents. Additionally, different arrangements of connected phthalocyanine rings in a polymer must be taken into account. Several isomers exists for a polymer molecule with a definite molecular weight. One possible procedure to determine of the degree of polymerization of polymers is IR spectroscopy [35]. We determined the degree of polymerization after converting the cyano end groups of the metal-free phthalocyanine polymer into imido end groups, due to the relatively good intensity of C=O imide groups to nitrile groups. After this, the ratios of the absorption intensities of (Ar–N–C) of the polymers (~1245 cm^{-1}) to asym. C=O groups of the imides (~1728 cm^{-1}) were calculated [compound/$\log_{10} I_{1245}/I_{1718}$: **4a**/0.62, **5**/0.92, **6**/0.90, **7**/0.73, **8**/0.86, **9**/0.88]. The polymerization degrees follow the order: **5** > **6** > **9** > **8** > **7** > **4a**. On the other hand, the IR spectrum of **4** shows a low degree of polymerization due to the high intensity of the nitrile groups [36].

The low solubility of the polymers only enabled spectra to be recorded in pyridine. The UV–Vis absorption spectra of these polymers exhibit Q and B bands, which are the characteristic bands for phthalocyanine polymers.

The split Q bands in **4**, which are characteristic for metal-free phthalocyanines, were observed at $\lambda_{max} = 677$ and 615 nm (Fig. 2). These Q band absorptions show the monomeric species with D_{2h} symmetry and due to the phthalocyanine ring relate to the fully conjugated 18π electron system [37–39]. In addition, in the UV region at around 340 nm and called the Soret (or B) band, arising from the deeper π levels → LUMO transition between an a_{2u} and the same orbitals and extending to the blue of the visible spectrum, is generally much less intense. The presence of absorption band in **4** in the near UV region at $\lambda_{max} = 343$ nm shows Soret region B bands which have been ascribed to the deeper π–π* levels of LUMO transitions [40].

The UV–vis absorption spectra of metallophthalocyanines **5**, **6** (Fig. 2), **7**, **8**, and **9** (Fig. 3) in pyridine show intense Q absorption at $\lambda_{max} = 690$, 689, 671, 683 and 721 nm, respectively with a weaker absorptions at 624, 623, 608, 617 and 681 nm, respectively. The single Q bands in metallo derivatives **5**, **6**, **7**, **8**, and **9** are characteristic. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [41]. B band absorptions of **5**, **6**, **7**, **8**, and **9** were observed at $\lambda_{max} = 358$, 329, 302, 305 and 345 nm, respectively, as expected.

The thermal behaviour of the metallophthalocyanines were investigated by TG/DTA. Although the thermal stabilities of phthalocyanines are well known, the phthalocyanines compounds are not stable above 286 °C. The initial and main decomposition temperatures are given in Tables 1–4. The initial decomposition temperature decreased in the order: **4** > **9** > **7** > **8** > **5** > **6**.

Table 1
Thermal properties of the polymeric phthalocyanines.

Compound	M	Initial decomposition temperature in °C	Main decomposition temperature in °C
4	2H	396	481
5	Zn	304	398
6	Cu	286	360
7	Co	356	451
8	Ni	307	377
9	Pb	371	417

Table 2
The spectral IR data of new compounds.

Compound	γ (N–H)	γ (Ar–H)	γ (Aliph. C–H)	γ (C≡N)	γ (S=O)
3	–	3070	2925–2856	2234	1489_1387
4	3436	3058	2921–2851	2214	1465–1158
5	3296 Imide N–H	3062	2921–2857	–	1487–1347
6	3306 Imide N–H	3060	2917–2862	–	1469–1345
7	3304 Imide N–H	3062	2921–2862	–	1470–1348
8	3285 Imide N–H	3060	2919–2857	–	1470–1347
9	3306 Imide N–H	3059	2921–2861	–	1482–1324

Table 3
Electronic spectra of metal-free phthalocyanine and phthalocyanine complexes in Pyridin.

Compound	λ_{max}/nm$10^{-5}\varepsilon(mol^{-1}\ cm^{-1})$			
4	710(5.26)	677(5.30)	615(4.86)	343(5.25)
5	690(5.25)	624(4.65)	358(4.99)	
6	689(5.33)	623(4.91)	329(5.08)	
7	671(5.44)	608(5.06)	302(5.41)	
8	683(5.27)	617(4.94)	305(5.40)	
9	721(5.36)	681(5.08)	345(5.19)	

Table 4
Some analytical data and physical properties of the new compounds.

Compounds	Empirical formula	Color	Formula wt	M.p. (°C)	Yield %
3	$C_{37}H_{34}N_6O_4S_4$	Brown	754	197–199	82
4	$(C_{148}H_{138}N_{24}O_{16}S_{16})_n$	Dark green	3021	>300	37
5	$(C_{148}H_{140}N_{20}O_{24}S_{16}Zn)_n$	Dark green	3161	>300	36
6	$(C_{148}H_{140}N_{20}O_{24}S_{16}Cu)_n$	Dark green	3159	>300	28
7	$(C_{148}H_{140}N_{20}O_{24}S_{16}Co)_n$	Dark green	3154	>300	32
8	$(C_{148}H_{140}N_{20}O_{24}S_{16}Ni)_n$	Dark green	3154	>300	35
9	$(C_{148}H_{140}N_{20}O_{24}S_{16}Pb)_n$	Dark green	3303	>300	25

4. Conclusions

A tetranitrile monomer **3** was synthesized by nucleophilic aromatic substitution of N,N′-(2,2′-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) **1** onto 4-nitrophthalonitrile **2**. The metal-free phthalocyanine polymer **4** was prepared by the reaction of the tetranitrile monomer **3** in the presence of 2-(dimethylamino)ethanol. Metallophthalocyanine polymers were prepared by reaction of the tetranitrile **3** with the chlorides of zinc (II), copper (II), cobalt (II), nickel (II), lead (II), by microwave irradiation in the presence 2-(dimethylamino)ethanol at 175 °C, 350 W for 10 min. The thermal stabilities of the phthalocyanine compounds were determined by thermogravimetric analysis. The initial decomposition temperature decreased in the order: **4** > **9** > **7** > **8** > **5** > **6**.

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