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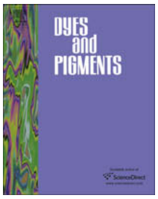

The microwave-assisted synthesis and structural characterization of novel, dithia-bridged polymeric phthalocyanines containing a substituted thiophenylamine Schiff base

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ABSTRACT

Novel polymeric metal-free and metallo(Cu(II), Co(II), Ni(II), Zn(II) and Pb(II))–phthalocyanine complexes were synthesized using microwave irradiation and the products were purified by several (crystallization and preparative thin layer) techniques. The newly prepared compounds were characterized by a combination of elemental analyses, IR, $^1H/^{13}C$ NMR, $^1H-^1H$ COSY, MS and UV–Vis spectroscopy. In order to better understand the spectroscopy data (especially for $^1H/^{13}C$ NMR and $^1H-^1H$ COSY techniques), computational calculations were used for characterization at DFT/6-31G(d) level. The electronic spectra exhibited an intense $\pi \rightarrow \pi^*$ transition with characteristic Q and B bands of the phthalocyanine core.

1. Introduction

The attributes of new substituted phthalocyanines commonly follows the lack of designed applications [1]. The interesting properties of Pcs are the presence of a highly conjugated π-electron system, eminent absorptivity in the near-IR region [2], a capability to exhibit changeable conductivity and photocatalytic effects [3]. As a result of newly synthesized compounds, in many fields such as chemical sensors, solar cells, electrochromism, batteries, photodynamic therapy, semiconductive materials and liquid crystals the importance of Pcs is increasing rapidly [4–7]. It is well known that choice of various metals and substituents powerfully affects the electrochemical and other properties of the metallophthalocyanine structures. Substitution of the α-fragment induces red shifting of the Q band due to the reducing aggregation problems than substitution at the β-fragment. Especially, the presence of more electronegative donor sulphur atom will pave the way for the shift of the Q band to even longer wavelengths. Pc complexes containing Pb metal show an extremely red-shifted Q band [7]. Since their discovery in 1950s, many of their intrinsic properties of Pcs are not discovered sufficiently [8,9]. Mainly polymeric phthalocyanines are prepared by cyclotetramerization reactions of bifunctional monomers such as tetracarbonitriles [10–13], diverse oxy-, arylenedioxy- and alkylenedioxy-bridged diphthalonitriles [14–18], other nitriles [19,20] or tetracarboxylic acid derivatives [21–24] in the existence of metals or metals salts.

In recent years, the synthesis of artificial receptors that are able to coordinate metal cations have increased [25,26]. Most of the consideration has focused on macrocyclic receptors that tend to bind with more than one transition metal ion [27–33]. Especially, in the early 1990s, due to the soft donor functionality of sulphur atom, several research groups such as Robson [34], Schroder [35] and Brooker and co-workers [36], in 2000, achieved similar researches aimed at introducing thiophenolate head units into Schiff base macrocycles. In all actions, the thiophenolate analogues are expected to reveal very different properties (e.g. redox and magnetic) due to the presence of the very polarisable thiophenolate donors and their interest in thiolatebridged metal active sites in biology.

In the last few decades rapid synthesis of polymeric Pcs by microwave irradiation or conventional methods had respectable amount of interest [37]. Microwave (MW) irradiation can increase the speed of many chemical methods. Especially, the reaction time

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and energy input are mostly reduced in contrast with the reactions that are run for a long time at high temperatures under conventional conditions [38,39]. The most successful applications of microwave irradiation are found to be related to the use of solvents and solvent-free systems, in which microwaves interact directly with reagents. Therefore, it can more efficiently accelerate chemical reactions [37,40]. Our previous articles describing a series of Pcs with a new macrocycle [41], four diazatetrathiamacrobicyclic [42], four-21 membered dithiacrown ether [2], and salen type Schiff base derivative bearing thiophene and triazole heterocyclic [43] macrocycles reported enhanced solubility of the product with bulky macrocycles on the periphery.

In this study, the synthesis, characterization and structural investigation of polymeric metal-free, Cu(II), Co(II), Ni(II), Zn(II), and Pb(II) phthalocyanines, which contain sulphur, nitrogen and oxygen donor atoms macrocyclic moieties, are described. This study also suggests the suitable combination of a substituted thiophenylamine by dithia-bridged Schiff base and phthalocyanine may allow new functionalized materials to be prepared, which are of importance for analytical chemistry as transition metal extraction agents.

2. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [44]. 2,2′-[ethane-1,2-diylbis(thio)]dianiline [2-({2-[(2-aminophenyl)thio]ethyl} thio)phenyl]amine **1** [45] and 4-nitrophthalonitrile **4** [46] was prepared according to the literature. ^1H NMR/^{13}C NMR and ^1H–^1H COSY spectra were recorded on a Varian XL-200 NMR spectrophotometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer in KBr pellets. The MS spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer equipped with pyridine–methanol as solvent. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument; the obtained values agreed with the calculated ones. UV–Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Beko MD 1500, 2.45 MHz domestic microwave oven was used in all synthesis reactions of the phthalocyanines. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.1. Synthesis

2.1.1. 2,2′-{Ethane-1,2-diylbis[thio-2,1-phenylenenitrilo(Z)methylylidene]}diphenol (3)

The salicylaldehyde **2** (0.44 g, 3.62 mmol) together with 3 drops of HCl in dry methanol (25 mL), was added to 2,2′-[ethane-1,2-diylbis(thio)]dianiline [2-({2-[(2-aminophenyl)thio]ethyl}thio)-phenyl]amine **1** (0.5 g, 1.81 mmol) in dry methanol (40 mL) and left for 3 h. The reaction mixture was refluxed for 24 h under N_2. The reaction was monitored by thin layer chromatography [chloroform]. At the end of this period, the mixture was cooled to room temperature, evaporated until it was completely dry under reduced pressure. The oily raw material was recrystallized from ethanol to give a light yellow crystalline powder and dried in a vacuum over P_2O_5. Yield: 0.78 g, (70.56%), mp: 185–186 °C.

Anal. Calc. for $C_{28}H_{24}N_2O_2S_2$: C, 69.39; H, 4.99; N, 5.78. Found: C, 69.26; H, 4.89; N, 5.91. IR (KBr tablet) υ_{max}/cm^{-1}: 3435 (–OH), 3049 (Ar–CH), 1612 (CH=N), 1468 (C–S), 1370 δ(–OH), 1279 (C–N), 1181 (C–OH), 1144 δ(C–N), 840 δ(C–S). ^1H NMR ($CDCl_3$), (δ: ppm): 13.25 (s, 2H, OH/D_2O exchangeable), 8.61 (s, 2H, CH=N), 7.42–7.37 (m, 4H, Ar–$H_{11\text{ and }18}$), 7.31 (d, 2H/Ar–H_{17}, $J = 8.99$ Hz), 7.26–7.17 (m, 6H/Ar–$H_{9,15\text{ and }16}$), 7.08 (d, 2H/Ar–H_8, $J = 9.06$ Hz), 6.95 (td, 2H/Ar–H_{10}, $J = 7.39$ and 1.15 Hz), 3.16 (s, 4H/CH_2). ^{13}C NMR ($CDCl_3$), (δ: ppm): 162.09 (CH=N), 161.21 (ArC–O), 147.06 (ArC–N), 133.47, 132.37, 131.34, 128.59, 127.53, 127.06, 119.09 (ArC–S), 118.52, 117.93, 117.47, 31.68 (–CH_2). MS (ESI), (m/z): Calculated: 484.0; Found: 485.48 $[M + 1]^+$.

2.1.2. 4,4′-{Ethane-1,2-diylbis[thio-2,1-phenylenenitrilo(Z)methylylidene-2,1-phenyleneoxy]}diphthalonitrile (5)

A mixture of 4-nitrophthalonitrile **4** (0.36 g, 2.07 mmol) and dry DMF (15 mL) was charged into a 200 mL three-necked flask and stirred at room temperature under nitrogen inert atmosphere. 2,2′-{ethane-1,2-diylbis[thio-2,1-phenylenenitrilo(*Z*)methylylidene]}-diphenol **3** (0.5 g, 1.03 mmol) was added to the solution and the temperature was increased up to 55–60 °C. Powdered K_2CO_3 (0.43 g, 3.1 mmol) was added to the system in eight equal portions at 15 min intervals with efficient stirring and the reaction system was stirred at the same temperature for 5 days. Aliquots were taken and checked periodically for completeness of the reactions and observed by thin layer chromatography (TLC) (chloroform). The reaction system was cooled and poured into ice-water and then mixed for 12 h. The mixture was filtered and dried in vacuum over P_2O_5 for 4 h and recrystallized from ethanol to give dark yellow crystalline powder. According to TLC result (chloroform), the product was observed as a single spot. Yield: 0.49 g, (62.8%), mp: 179–180 °C.

Anal. Calc. for $C_{44}H_{28}N_6O_2S_2$: C, 71.72; H, 3.83; N, 11.41. Found: C, 71.89; H, 3.70; N, 11.12. IR (KBr tablet) υ_{max}/cm^{-1}: 3071 (Ar–CH), 2230 (C≡N), 1600 (CH=N), 1481 (C–S), 1278 (C–N), 1180 (C–O), 1097 δ(C–N), 838 δ(C–S).

^1H NMR ($CDCl_3$), (δ: ppm): 8.51 (s, 2H, CH=N), 8.34 (d, 2H/Ar–H_4, $J = 6.04$ Hz), 7.74 (d, 2H/Ar–H_{11}, $J = 8.04$ Hz), 7.60 (t, 2H/Ar–H_{18}, $J = 7.20$ Hz), 7.43 (t, 2H/Ar–H_5, $J = 7.05$ Hz), 7.30 (s, 2H/Ar–H_1), 7.22 (m, 4H/Ar–$H_{9\text{ and }17}$), 7.18 (bd, 4H/Ar–$H_{10\text{ and }15}$), 7.06 (d, 2H/Ar–H_{16}, $J = 8.02$ Hz), 6.88 (d, 2H/Ar–H_8, $J = 8.05$ Hz), 3.13 (s, 4H/CH_2).

^{13}C NMR ($CDCl_3$), (δ: ppm): 161.53 (CH=N), 154.08 (ArC_6–O), 153.40 (ArC_7–O), 150.41 (ArC–N), 135.61, 133.53, 130.60, 129.77, 128.46, 127.82, 126.96, 126.90, 126.80, 121.63, 121.37, 121.11, 118.12, 117.88 (C≡N), 115.40 (ArC–S), 111.82 (C≡N), 109.98, 31.17 (–CH_2). MS (ESI), (m/z): Calculated: 736.86; Found: 737.46 $[M + 1]^+$.

2.1.3. Metal-free polymeric phthalocyanine (6)

A mixture of compound **5** (0.15 g, 0.20 mmol), dry dimethylaminoethanol (DMAE) (3 mL) and 1,8-diazaby-cyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was irradiated in a microwave oven at 175 °C, 350 W for 20 min. Then it was diluted with hot ethanol (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:0.1) as eluents to give dark green yield. Yield: 0.05 g, (31%), mp: 210 °C (decomposition).

Anal. Calc. for $C_{176}H_{114}N_{24}O_8S_8$(for C≡N end groups): C, 71.67; H, 3.90; N, 11.40. Found: C, 71.43; H, 4.12; N, 11.59. IR (KBr tablet) υ_{max}/cm^{-1}: 3192 (–NH), 3060 (Ar–CH), 2225 (C≡N), 1602 (CH=N), 1480 (C–S), 1273 (C–N), 1152 (C–O), 1096 δ(C–N), 875 δ(C–S). ^1H NMR ($CDCl_3$), (δ: ppm): 8.59 (s, 8H, CH=N), 8.38 (d, 8H/Ar–H_4, $J = 6.51$ Hz) 8.01–6.83 (m, 72H/Ar–H), 6.69 (d, 8H/Ar–H_8, $J = 7.05$ Hz), 3.03 (s, 16H, CH_2).^{13}C NMR ($CDCl_3$), (δ: ppm): 160.85 (CH=N), 155.01 (C_a), 154.21 (ArC_6–O), 153.44 (ArC_7–O), 149.69 (ArC–N), 136.53, 135.65, 132.67, 130.14, 129.70, 128.91, 127.42, 126.68, 126.13, 123.03, 122.82, 122.53, 118.05, 117.56 (C≡N), 116.53 (ArC–S), 114.30 (C≡N), 108.34, 32.46 (–CH_2). MS (ESI),

(m/z): Calculated: 2949.46; Found: 2950.23 $[M + 1]^+$. UV–vis (chloroform): λ_{max}/nm: $[(10^{-5} \log \varepsilon \, dm^3 \, mol^{-1} \, cm^{-1})]$: 688 (5.30), 663 (5.14), 620 (4.77), 341 (5.23), 323 (5.24), 308 (5.19), 294 (5.19), 281 (5.16), 231 (5.09).

2.1.4. *Cu(II)-containing polymer (**7**)*

A mixture of compound **5** (0.15 g, 0.20 mmol), anhydrous $CuCl_2$ (0.014 g, 0.10 mmol), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was irradiated in a microwave oven at 175 °C, 350 W for 6 min. Then it was diluted with hot ethanol (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:0.1) as eluents to give green yield. Yield: 0.09 g, (58%), mp: 230 °C (decomposition).

Anal. Calc. for $C_{176}H_{116}N_{20}O_{16}S_8Cu$(for imide end groups): C, 68.48; H, 3.79; N, 9.07; Cu, 2.06. Found: C, 68.71; H, 4.05; N, 9.26; Cu, 1.83. IR (KBr tablet) υ_{max}/cm^{-1}: 3368 (NH_{imidic}), 3061 (Ar–CH), 1722 (C═O), 1598 (CH═N), 1454 (C–S), 1273 (C–N), 1245 υ(C–N)/δ(–NH), 1119 (C–O), 1091 δ(C–N), 874 δ(C–S). UV–vis (chloroform): λ_{max}/nm: $[(10^{-5} \log \varepsilon \, dm^3 \, mol^{-1} \, cm^{-1})]$: 689 (5.23), 621 (5.24) MS (ESI), (m/z): Calculated: 3086.99; Found: 3088.25 $[M + 1]^+$.

2.1.5. *Co(II)-containing polymer (**8**)*

A mixture of compound **5** (0.15 g, 0.20 mmol), anhydrous $CoCl_2$ (0.013 g, 0.10 mmol), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. Then it was diluted with hot ethanol (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:0.1) as eluents to give dark green yield. Yield: 0.09 g, (59%), mp: 247 °C (decomposition).

Anal. Calc. for $C_{176}H_{116}N_{20}O_{16}S_8Co$(for imide end groups): C, 68.58; H, 3.79; N, 9.09; Co, 1.91. Found: C, 68.36; H, 4.02; N, 9.32; Co, 2.23. IR (KBr tablet) υ_{max}/cm^{-1}: 3360 (NH_{imidic}), 3054 (Ar–CH), 1722 (C═O), 1572 (CH═N), 1452 (C–S), 1350 (C–N), 1236 υ(C–N)/δ(–NH), 1155 (C–O), 1095 δ(C–N), 881 δ(C–S). UV–vis (chloroform): λ_{max}/nm: $[(10^{-5} \log \varepsilon \, dm^3 \, mol^{-1} \, cm^{-1})]$: 683 (5.28), 619 (4.84), 262 (5.23), 251 (5.25). MS (ESI), (m/z): Calculated: 3082.38; Found: 3100.07 $[M + H_2O]^+$.

2.1.6. *Ni(II)-containing polymer (**9**)*

A mixture of compound **5** (0.15 g, 0.20 mmol), anhydrous $Ni(CH_3COO)_2$ (0.018 g, 0.10 mmol), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was irradiated in a microwave oven at 175 °C, 350 W for 6 min. Then it was diluted with hot ethanol (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:0.1) as eluents to give dark green yield. Yield: 0.07 g, (46%), mp: 228 °C (decomposition).

Anal. Calc. for $C_{176}H_{116}N_{20}O_{16}S_8Ni$(for imide end groups): C, 68.58; H, 3.79; N, 9.09; Ni, 1.90. Found: C, 68.82; H, 3.67; N, 9.43; Ni, 2.11. IR (KBr tablet) υ_{max}/cm^{-1}: 3340 (NH_{imidic}), 3065 (Ar–CH), 1725 (C═O), 1598 (CH═N), 1454 (C–S), 1352 (C–N), 1234 υ(C–N)/δ(–NH), 1119 (C–O), 1096 δ(C–N), 884 δ(C–S). ^1H NMR ($CDCl_3$), (δ: ppm): 8.62 (s, 8H, CH═N), 8.15 (d, 8H/Ar–H_4, $J = 6.82$ Hz) 7.68–6.75 (m, 72H/Ar–H), 6.70 (d, 8H/Ar–H_8, $J = 7.03$ Hz), 2.95 (s, 16H, CH_2). ^{13}C NMR ($CDCl_3$), (δ:ppm): 168.11 (C_{imide}), 160.77 (CH═N), 154.48 (C_a), 154.37 (ArC_6–O), 151.18 (ArC_7–O), 149.29 (ArC–N), 135.59, 134.77, 133.59, 129.63, 129.24, 128.05, 127.39, 127.19, 126.53, 125.77, 125.38, 122,47, 117.89, 116.26 (ArC–S), 114.20, 32.4 (-CH_2). MS (ESI), (m/z): Calculated: 3082.14; Found: 3083.07 $[M + 1]^+$. UV–vis (chloroform): λ_{max}/nm: $[(10^{-5} \log \varepsilon \, dm^3 \, mol^{-1} \, cm^{-1})]$: 680 (5.26), 612 (4.84), 241 (5.13).

2.1.7. *Zn(II)-containing polymer (**10**)*

A mixture of compound **5** (0.15 g, 0.20 mmol), anhydrous $Zn(CH_3COO)_2$ (0.014 g, 0.10 mmol), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. Then it was diluted with hot ethanol (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:0.1) as eluents to give dark green yield. Yield: 0.08 g, (52%), mp: 235 °C (decomposition).

Anal. Calc. for $C_{176}H_{116}N_{20}O_{16}S_8Zn$(for imide end groups): C, 68.44; H, 3.79; N, 9.07; Zn, 2.12. Found: C, 68.54; H, 3.91; N, 9.15; Zn, 2.20. IR (KBr tablet) υ_{max}/cm^{-1}: 3360 (NH_{imidic}), 3054 (Ar–CH), 1717 (C═O), 1577 (CH═N), 1451 (C–S), 1385 (C–N), 1235 υ(C–N)/δ(–NH), 1120 (C–O), 1092 δ(C–N), 881 δ(C–S). ^1H NMR ($CDCl_3$), (δ: ppm): 8.61 (s, 8H, CH═N), 8.21 (d, 8H/Ar–H_4, $J = 6.80$ Hz) 7.70–6.79 (m, 72H/Ar–H), 6.69 (d, 8H/Ar–H_8, $J = 7.02$ Hz), 2.98 (s, 16H, CH_2). MS (ESI), (m/z): Calculated: 3088.86; Found: 3089.10 $[M + 1]^+$. UV–vis (chloroform): λ_{max}/nm: $[(10^{-5} \log \varepsilon \, dm^3 \, mol^{-1} \, cm^{-1})]$: 688 (5.25), 681 (4.60), 244 (5.04).

2.1.8. *Pb(II)-containing polymer (**11**)*

A mixture of compound **5** (0.15 g, 0.20 mmol), anhydrous PbO (0.023 g, 0.10 mmol), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. Then it was diluted with hot ethanol (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:0.1) as eluents to give green yield. Yield: 0.06 g, (37%), mp: 225 °C.

Anal. Calc. for $C_{176}H_{116}N_{20}O_{16}S_8Pb$(for imide end groups): C, 68.44; H, 3.79; N, 9.07; Found: C, 65.37; H, 4.24; N, 8.43. IR (KBr tablet) υ_{max}/cm^{-1}: 3362 (NH_{imidic}), 3054 (Ar–CH), 1720 (C═O), 1575 (CH═N), 1452 (C–S), 1384 (C–N), 1236 υ(C–N)/δ(–NH), 1152 (C–O), 1078 δ(C–N), 881 δ(C–S). ^1H NMR ($CDCl_3$), (δ: ppm): 8.60 (s, 8H, CH═N), 8.29 (d, 8H/Ar–H_4, $J = 6.81$ Hz) 8.07–7.075 (m, 72H/Ar–H), 6.77 (d, 8H/Ar–H_8, $J = 7.04$ Hz), 2.95 (s, 16H, CH_2). MS (ESI), (m/z): Calculated: 3230.65; Found: 3231.74 $[M + 1]^+$. UV–vis (chloroform): λ_{max}/nm: $[(10^{-5} \log \varepsilon \, dm^3 \, mol^{-1} \, cm^{-1})]$: 728 (5.25), 656 (4.81), 257 (5.17).

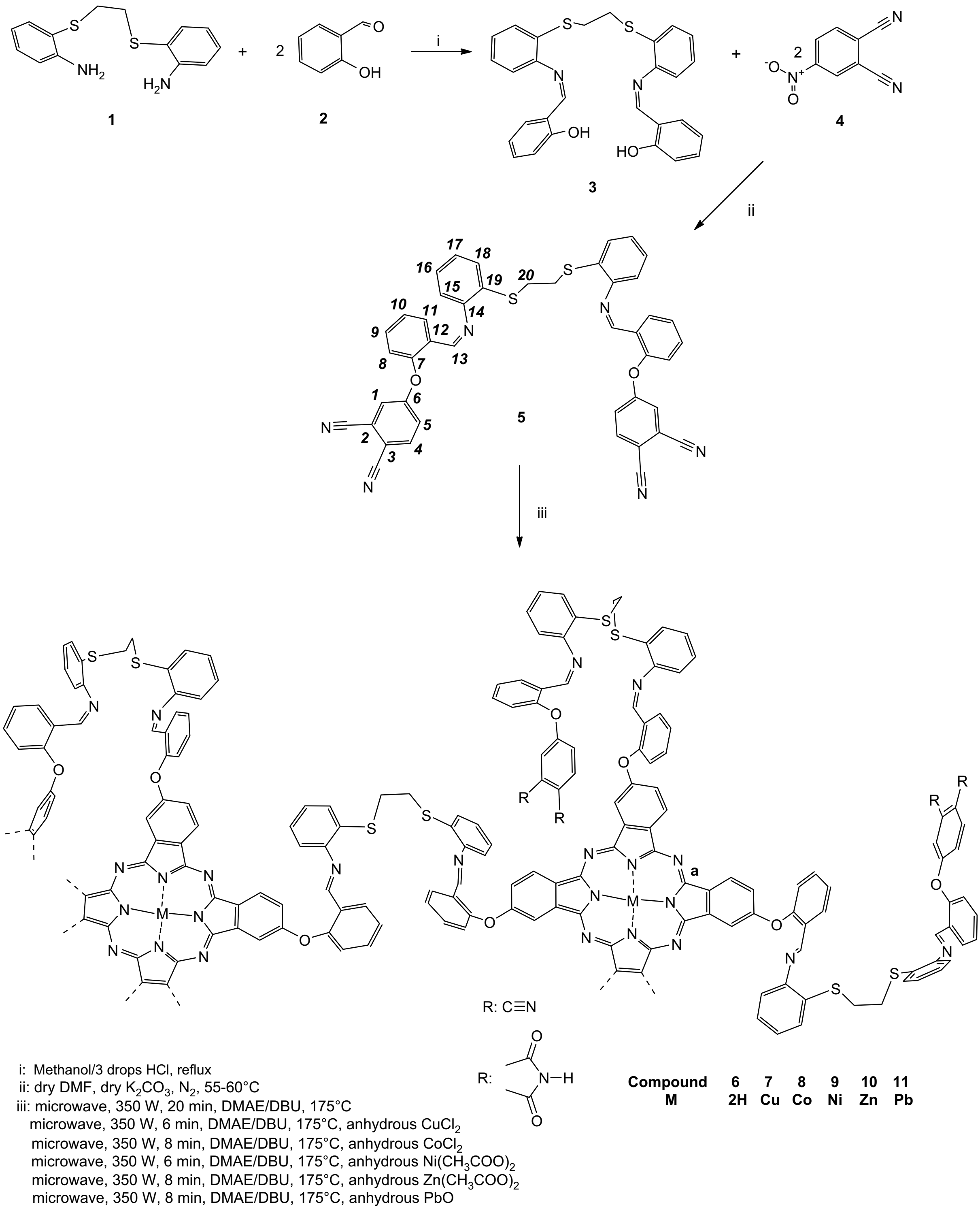
3. Results and discussion

3.1. *Outlook of the synthesized compounds*

The preparation of substituted dithia-bridged Schiff bases **3**, **5**, the target polymeric metal-free phthalocyanine **6** and metallophthalocyanines **7**, **8**, **9**, **10** and **11** are shown in Scheme 1. The structures of novel compounds were characterized by a combination of $^1H/^{13}C$ NMR, $^1H–^1H$ COSY, IR, UV–Vis, elemental analysis, MS spectral data and also by theoretical calculations at DFT/6-31G(d) level (for compound **5**).

3.2. *Spectroscopic characterization with theoretical assistance*

The condensation of **1** with salicylaldehyde in dry methanol at 1:2 ratio gave the expected salicylic Schiff base **3** in a high



Scheme 1. The synthesis of polymeric metal-free and metallophthalocyanines.

yield-(70.56%) [43]. In the IR spectrum of **3**, the disappearing of the intense absorption bands at υ_{as}(3388) and υ_{s}(3360) cm^{-1}, corresponding to the –NH2 groups, after the conversion to substituted Schiff base and the appearance of a new band at 1612 cm^{-1} corresponding to CH=N group, indicated that the combining has occurred. The rest of the spectrum of the Schiff base **3** resembles closely that of starting reactants **1** and **2** including the characteristic stretching/deformation vibrations of aliphatic, aromatic/aliphatic S and phenolic groups. ^{1}H NMR spectrum of **3** is almost identical with the IR spectrum, except for small changes and shifts. The difference between the two spectra of substituted amine **1** and the Schiff base **3** is due to the presence of iminic carbon CH=N at 8.61 ppm. Moreover, ^{13}C NMR spectrum of compound **3** clearly indicates the presence of CH=N group (162.09 ppm). The MS mass spectrum of compound **3** shows a molecular ion peak at $m/z = 485.48\ [M+1]^{+}$, supporting the proposed formula of this compound.

The compound **5** was obtained from the reaction of compound **3** to 4-nitrophthalonitrile **4** in dry K_2CO_3/dry DMF under N_2 atmosphere at 55–60 °C for 5 days. This is accomplished by a base catalyst nucleophilic displacement aromatic nitro group of 4-nitrophthalonitrile with the Schiff base **3** [43]. Similarly, comparison of the IR spectral data clearly indicated the presence of compound **5**. The –OH stretching/deformation of compound **3** at 3435/1370 cm^{-1} and NO_2 stretching of compound **4** at 1519 and 1333 cm^{-1} disappeared, and a new absorption band appeared at 2230 cm^{-1} ($C{\equiv}N$), indicating the reaction took place. In the ^1H NMR spectrum of dinitrile **5** a singlet at $\delta = 13.25$ ppm belonging to the phenolic –OH **3** disappeared after the conjunction reaction. The spectral data belonging to new formation indicated that the joining has occurred as predicted by the proposed structure. Separately, four doublets at ca. $\delta = 8.34$ (H_4), 7.74 ppm (H_{11}), 7.06 (H_{16}) and 6.88 (H_8), two triplets at ca. 7.60 (H_{18}) and 7.43 (H_5), a multiplet at ca. 7.22 ($H_{9\text{ and }17}$ as merged), a singlet at ca. 7.30 (H_1) and a broad doublet at ca. 7.18 ($H_{10\text{ and }15}$ as merged) ppm, are observed in the spectra respectively. Additionally, ^1H NMR spectrum of compound **5** showed a resonate due to iminic carbon ($-CH{=}N$) at 8.51 ppm, as expected. The ^1H–^1H COSY spectrum of compound **5** is shown in Fig. 1. The COSY spectrum confirms the expected assignments. Peaks at δ values 8.51, 7.30 and 3.13 ppm had no correlation pattern in the COSY, indicating the absence of interaction of these protons with any other proton. Contours are observed in the aromatic region only. The doublet at δ 8.34 ppm is assigned to H_4 proton. In the COSY spectrum, the spot at δ 8.34 ppm, met the off-diagonal peak at δ 7.43 ppm, assigned to the H_5 proton. This establishes the fact that the H_4 proton splits the peak assigned to the H_5 proton into three because they are neighboring protons. Similarly, H_{11} at δ 7.74 ppm correlates with H_9 proton at δ 7.22 ppm, H_{18} at δ 7.60 ppm correlates with H_{16} at δ 7.06 ppm, and H_{10} at δ 7.18 ppm couples with H_8 at δ 6.88 ppm, respectively, supporting the ^1H NMR data. The proton-decoupled ^{13}C NMR spectrum indicated the presence of nitrile carbon atoms in compound **5** at 117.88, 111.82 ppm, respectively. In order to support the ^1H NMR and ^1H–^1H COSY results, the E/Z notations about $CH{=}N$ of compound **5** at DFT/6-31G(d) level were performed [56]. DFT computations of **5** showed that there are three energy minima corresponding to mentioned E/E, Z/Z and E/Z conformations as anticipated. The computed ground-state energy for E/E position is 3.73 kcal mol^{-1} lower than that of the E/Z state and 10.27 kcal mol^{-1} lower than that of the Z/Z conformation (Fig. 2). According to the DFT energies, the E/E conformation should be therefore the most stable and the Z/Z the least stable conformer, with the E/Z having an intermediate stability. In E/Z form, one of the –CH protons attached to azomethinic groups is situated in plane, the other one is situated out of plane. As can be seen in Fig. 2, it is important that the distance of the iminic proton lying in plane to more electronegative atoms (oxygen and sulphur) is different than the distance of the iminic proton lying out of plane. Due to the different electromagnetic interactions, these protons should resonate at diverse regions. According to these facts, two different –CH signals should be present in the ^1H NMR spectrum of compound **5**, however only one –CH signal was observed. So, the E/Z conformation should be eliminated. All these data are well consistent with literature values [57]. Especially, the azomethinic CH and almost all aromatic protons lie out of plane more obviously in the E/E configuration. So, the out of plane positioning decreases shielding on the related protons and causes these protons to have more cycle in the aromatic region. The two-dimensional (^1H–^1H COSY) experiment suggested that the two species (E/E and Z/Z) did not interchange in the solution. The iminic protons at δ ca. 8.51 ppm did not show a cross-peak (at left or right) with any proton (see Fig. 1). This suggests that these two protons are not proximal with other protons. This is possible only when the molecule **5** adopts the E/E form [58]. It can be understood from the facts explained so far that, the E/E configuration being the most stable configuration well agrees with ^1H NMR results. Additionally, the MS mass spectrum of compound **5** shows a molecular ion peak at $m/z = 737.46$ $[M + 1]^+$, supporting the proposed formula for this compound.

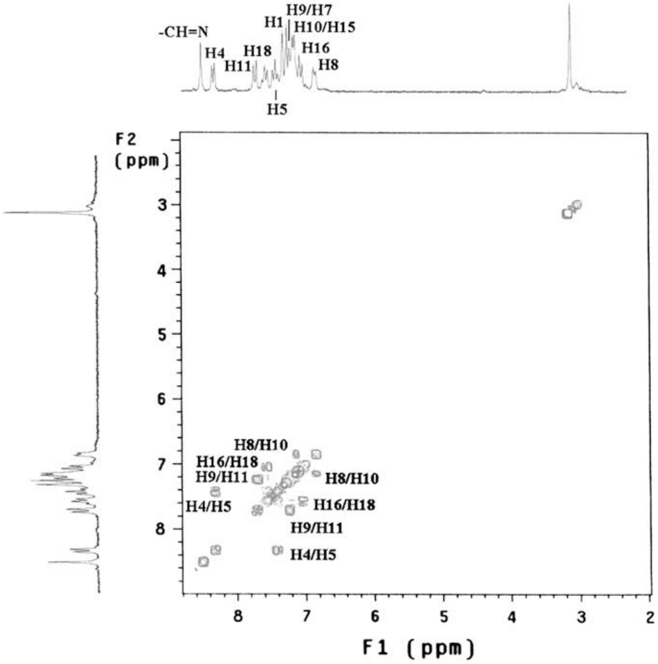


Fig. 1. Two-dimensional ^1H–^1H COSY spectrum of 5 in $CDCl_3$.

Five metal salts, $CuCl_2$, $CoCl_2$, $Ni(CH_3COO)_2$, $Zn(CH_3COO)_2$ and PbO, were used as templates for the formation of metallophthalocyanines. Especially, because it is known that phthalocyanines containing cobalt and copper templates can be used as effective catalysts in oxygenation [47] and oxyhalogenation processes [48]. In a typical experiment, the reactions were carried out by simply mixing and grinding substituted nitrile **5** with one of the metal salts, and then irradiating the mixtures in open vessels in the microwave reactor. All the substances used in the synthesis were solid, however, in order to initiate a chemical reaction under microwave conditions at least one of the substrates needs to be a melting solid which absorbs microwaves relatively well [37b].

The metal-free phthalocyanine **6** and metallophthalocyanines **7**, **8**, **9**, **10** and **11** were obtained directly by the reaction of substituted phthalodinitrile **5** with dry DMAE/DBU mixtures in case of metal-free phthalocyanine and by the reaction of substituted phthalodinitrile **5** with dry DMAE/DBU and related metal salts in case of metallophthalocyanines in microwave oven at 350 W for 6–20 min [43]. The solubility of the phthalocyanines was moderate in common organic solvents such as ethyl acetate, acetone, tetrahydrofurane and ethanol.

Detailed synthetic work by Wöhrle and co-workers on the optimization of the formation of polymeric phthalocyanine from 1,2,4,5-tetracyanobenzene indicated, relatively uniform macromolecules (i.e. networks with only nitrile end groups) were prepared from the bulk polymerization of nitrile by itself and similarly, relatively uniform macromolecules (i.e. networks with only imide end groups) were prepared from the bulk polymerization with convenient metal salts at elevated temperatures (200–400 °C) [11,14,49].

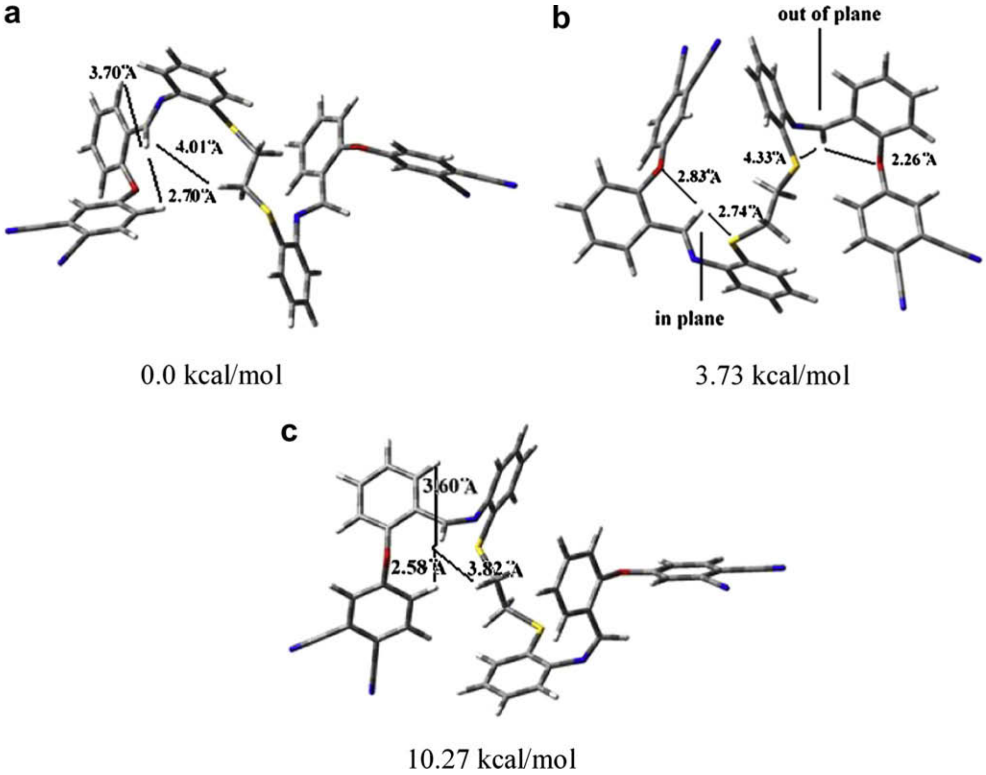


Fig. 2. (a) *E*/*E* (b) *E*/*Z* and (c) *Z*/*Z* calculated (DFT/6-31G(d)) relative steric energies of conformations of 5.

The IR spectrum of the metal-free phthalocyanine polymer **6** was slightly broadened and reduced in intensity, which could be attributed to a difficulty in grinding the sample to a small particle size. Characteristic peaks for phthalocyanines were observed. The peaks at 3192, 1096 and 1037 cm^{-1} are the characteristic metal-free pc –NH stretching and pyrrole ring vibration modes. In addition, a medium weak CH═N absorption at 1602 cm^{-1} was detected. In the ^1H NMR spectrum of compound **6** the typical shielding of inner core protons could not be observed due to the probable strong aggregation (especially for our molecules, because of multiple number of aromatic benzenes) of the molecules [50]. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton suggested the significant absorbance characteristic of the proposed structure. The MS mass spectrum of compound **6** showed a molecular parent ion peak at $m/z = 2950.23$ $[M + 1]^+$, supporting the proposed formula for this compound. Elemental analysis was satisfactory.

The IR spectra of metallophthalocyanine polymers **7**–**11** were very similar, with the exception of the metal-free phthalocyanine polymer **6** which showed an –NH stretching band at 3192 cm^{-1} due to the inner core [51]. This band is especially beneficial for the characterization of metal-free phthalocyanine polymers, as there is little frequency dependence on ring substitution and this is not overlapped by strong tetranitrile monomer absorptions [11,14,49]. This band disappeared in the spectra of the metallophthalocyanine polymers. The ^1H NMR spectra of the compounds **9**, **10** and **11** were almost identical to those of the metal-free phthalocyanine (**6**). The differences in the ^1H NMR spectra of H_2Pc, NiPc and ZnPc were the broad signals encountered in the case of compound **9** and **10** as a result of the aggregation of phthalocyanine cores at the considerable high concentration used for NMR measurements [52]. In addition, in the ^{13}C NMR spectrum of **9**, the peaks corresponding to nitriles at 117.56 and 114.30 ppm disappeared, and a new signal corresponding to imide carbon at 168.11 ppm appeared, confirming that the metallophthalocyanines **7**–**11** had imide end groups [9,11,14,38,49]. In the mass spectra of compounds **7**–**11**, the parent molecular ion peaks were observed at $m/z = 3088.25$ $[M + 1]^+$ for Cu(II), 3100.07 $[M + H_2O]^+$ for Co(II), 3083.07 $[M + 1]^+$ for Ni(II), 3089.10 $[M + 1]^+$ for Zn(II) and 3231.74 $[M + 1]^+$ for Pb(II), these peaks verified the proposed structures.

The UV–Vis absorption spectra of the phthalocyanine system exhibited characteristic Q and B bands. Phthalocyanines **6**–**11** showed typical electronic spectra with two strong absorption bands. One of them is in the visible region at about 600–700 nm (Q band), which is attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. The other band is in the UV region at about 300–400 nm (B band), arising from the deeper π-levels → LUMO transition [1,43]. The electronic absorption spectrum of compound **6** in chloroform at room temperature is shown in Fig. 3. The Q band is split, as expected, and there are two strong bands in the visible region. The split Q band, which is characteristic for metal-free phthalocyanines, was observed at λ_{max} 688 and 663 nm, indicating the structure with D_{2h} symmetry [43,53]. On the other hand, such split Q band absorptions are due to $\pi \rightarrow \pi^*$ transitions of these fully-conjugated 18π-electron systems. In addition, a third band is observed at 620 nm to the blue side of the double Q band of the metal-free compound. This band, in addition to the broadness of the spectrum, is an indicator of strong intramolecular interactions between the phthalocyanine rings, probably due to the strongly aggregated cofacial structure.

In the electronic spectra of all metallophthalocyanines **7**–**11** in chloroform at room temperature, intense Q absorption bands were observed at ca. between 680 and 728 nm for all complexes and another band was observed in the UV region at ca. between 241 and 289 nm (B band) arising from the deeper π-levels → LUMO transition (Figs. 3 and 4). It shows an additional weak vibrational satellite band at ca. between 64 and 72 nm to the blue side of the

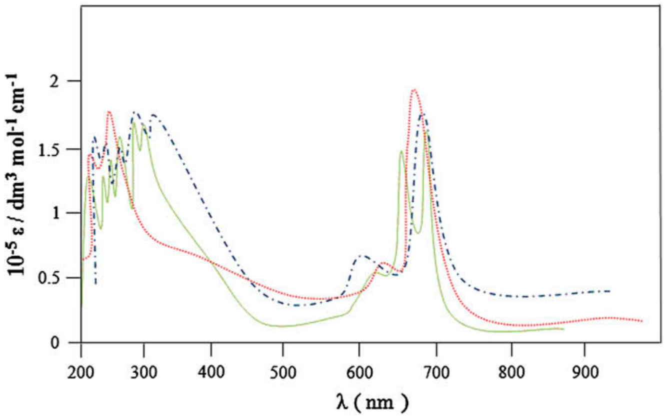


Fig. 3. UV–vis spectra of compounds **CuPc** corresponds to dark blue (-.-.) line, **CoPc** corresponds to red (….) line and **H$_2$Pc** corresponds to light green (–) line in CHCl$_3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

normal Q band as a result of exciton coupling between the phthalocyanine units [54]. Although the Q bands shifting to the red region, in the spectra of all complexes are not split, this is usually due to aggregation of phthalocyanine units, as expected. Well-defined absorptions with shoulder-type shifting to the blue region might also be interpreted in terms of intramolecular interactions between the phthalocyanine rings. The energies, relative intensities and broadening of the observed bands are in accordance with the pattern that would be anticipated on the basis of the excitation coupling theory for the phthalocyanine complexes. This result is typical of metal complexes of substituted and unsubstituted phthalocyanines with D$_{4h}$ symmetry [1,43].

4. Computational method

All quantum chemical calculations were carried out using the Gaussian 03W software package [56]. The input structures of compound **5** were optimized using with combination of MM+ and PM3 methods [43]. Then the obtained ground-state geometry was fully optimized in vacuo with the DFT/6-31G(d) method [43] and Becke's three-parameter hybrid functional (B3) with the nonlocal Lee-Yang-Parr theoretical correlation (LYP) [55] method. For all three conformations (*E*/*E*, *Z*/*Z* and *E*/*Z*), the PES scan for dihedral angles, C12-C13-N-C14 and their symmetry C12′-C13′-N′-C14′ was carried out at 10° intervals in the range 0–360° at the DFT level. The vibrational frequency calculations were performed for all the studied conformations to check the structure stabilities that correspond to the minima in the potential energy surface.

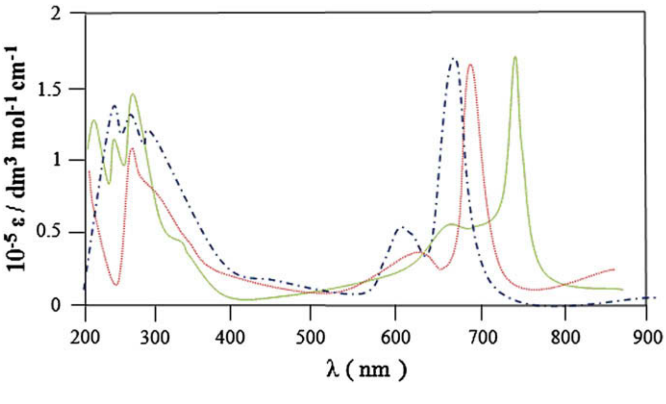


Fig. 4. UV–vis spectra of compounds; **Ni** corresponds to dark blue (-.-.) line, **Zn** corresponds to red (….) line and **Pb** corresponds to light green (–) line in CHCl$_3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Conclusion

In this study, we have reported on the preparation of a new phthalodinitrile derivative by microwave irradiation. This compound is used as a base for the preparation of a novel Substituted Thiophenylamine Schiff Base dithia-bridged with a polymeric metal-free phthalocyanine and five metallophthalocyanines. In the first stage, substituted Schiff Base analogue is obtained from condensation of **1** and **2** in dry MeOH. Then, compound **5** is synthesized from a 2:1 mixture of **3** and **4** in the presence of DMF/K$_2$CO$_3$ as key structure to give expected pcs. In the final stage, all phthalocyanines reflecting this study are obtained from the fusion of precursor **5** and related metal salts in dry DMAE/DBU catalyst mixtures (for all metallophthalocyanines) and obtained from the condensation of precursor **5** by itself in dry DMAE/DBU habitat (for metal free).

The preparations of the new products are supported by elemental analyses, IR, ^{1}H/^{13}C NMR, two-dimensional ^{1}H–^{1}H COSY, MS and UV–Vis spectroscopy, and also by theoretical efforts in DFT/6-31G(d) level. Additionally, when the phthalocyanines are substituted with alkylthia chains, the Q bands shift to longer wavelengths. Furthermore, especially, in the case of the coordination of Pb(II) with the phthalocyanine core, the Q band absorption occurred at a longer wavelength for compound **11**, compared to other derivatives.

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