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Synthesis, Characterization and Thermal Behavior of New Bis-Metallophthalocyanines (Cu, Co, Zn, Ni) and Bis-Metal Free Phthalocyanine

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Abstract

The novel bis-metallophthalocyanines Cu(II) (4), Co(II) (5), Zn(II) (6), Ni(II) (7) and bis-metalfree-phthalocyanine (8) have been synthesized from 4,4'-(2-methyl-1,4-phenylenedioxy)diphthalonitrile (3), which can be obtained by the reaction of 4-nithrophthalonitrile (2) with 2-methylhydroquinone (1). Compound 3 has been characterized by elemental analysis, FT-IR, 1H-NMR and ^{13}C-NMR spectroscopies. 4-8 bis-phthalocyanine compounds have been characterized by the elemental analysis, UV/Vis, and FT-IR spectroscopies. The thermal properties of the bis-phthalocyanine compounds were examined by Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). TGA results showed that bis-phthalocyanine compounds have been thermal stability until 320- 410 °C.

KeywoKeywords: Phthalocyanine, Bis-phthalocyanine, Ball-type phthalocyanine, Hydroquinone, Macromolecule, Transition metal complexes, Thermal analysis

1. Introduction

Since the first metal-free phthalocyanines (H_2Pc) was obtained in 1907 [1], metallophthalocyanines (MPc) and metal-free phthalocyanines have been researched in detail for many years [2]. In recent years, phthalocyanines (Pc) have been found many application areas, for example; in nonlinear optics (NLO) as optical limiting [3, 4], in photodynamic cancer therapy (PDT) [5, 6, 7, 8], in gas sensing devices [9, 10, 11], as liquid crystals [12], as molecular semiconductors [13], as electrochromic substances [14].

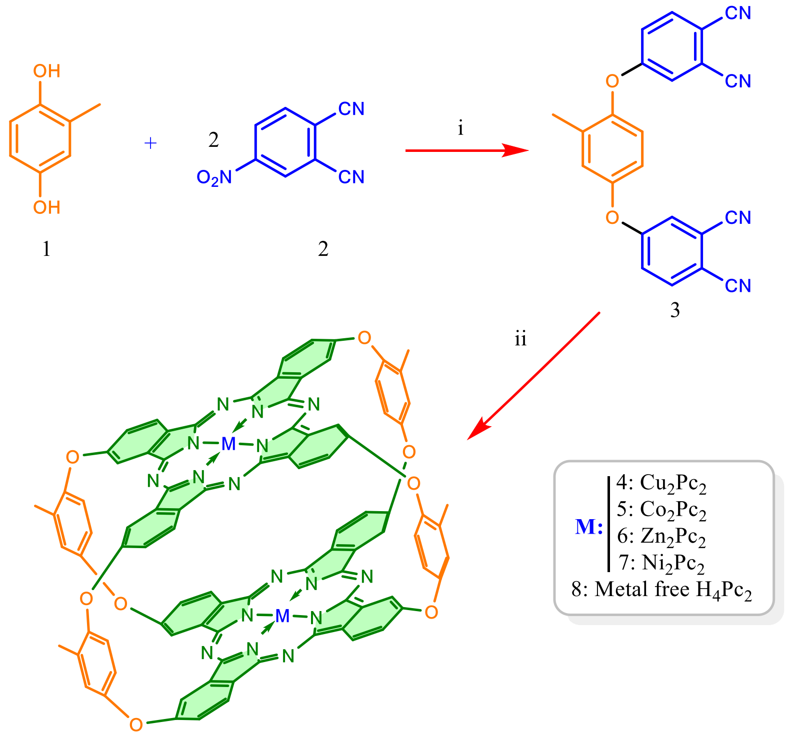
A new type of phthalocyanines, Ball-type phthalocyanines was published for the first time in 2002 [15] [16]. In later years, many studies have been made about the ball-type phthalocyanines.

2. Experimental

IR spectra of synthesized compound were taken with Perkin Elmer Spectrum One 1000 Series FT-IR spectrophotometer using KBr pellets. Electronic spectras were taken in H_2SO_4 with PG Instruments Ltd. T80+UV/Vis spectrophotometer. Elemental analyses were taken by Leco CHNS 930. ^{1}H-NMR and ^{13}C-NMR spectra were taken in dmso-d6 with an instrument Bruker DPX-400 MHz. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were taken by Shimadzu TA-60WS.

2.1. Synthesis

In this study, first 2 compound was synthesized from 4-nitrophthalimide in accordance with the literature, followed by the reaction of compound 2 with compound 1, compound 3 were synthesized (Scheme 1i). And then bis-phthalocyanine compounds 4-8 were synthesized (Scheme 1, ii). Structures of the synthesized compounds have been characterized by TGA, DTA, melting point, FT-IR spectroscopy, UV/Vis spectroscopy, ^{1}H-NMR and ^{13}C-NMR spectroscopy.



Scheme 1. (i) Ar, K_2CO_3, DMF, 80 °C, (ii) Metal salts ($Cu(Ac)_2\cdot H_2O$, $Co(Ac)_2\cdot 4H_2O$, $Zn(Ac)_2\cdot 2H_2O$, $Ni(Ac)_2\cdot 4H_2O$, DMF, Ar, DBU, reflux.

2.1.1. Synthesis of 4,4'-(2-methyl-1,4-phenylenedioxy)diphthalonitrile (3)

Before starting of the reaction compound (**1**) and compound (**2**) were dried at 90 °C for 1 h. Compound 2 (4 g, 23.1 mmol) and compound (**1**) (1.434 g, 11.5 mmol) in 50 ml dry DMF was stirred at 80 °C under Ar atmosphere. K_2CO_3 (6.385 g, 46.2 mmol) was added into the reactin mixture nearly a period of 2 h. The reaction mixture was stirred at the same temperature for 42 h. The mixture was precipitated into 600 ml saltwater. Then precipitate was mixed into 300 ml %2 NaOH solutions for 2 h and it was filtered and washed several times with pure water, chloroform and ethanol. The new product was named as 4,4'-(2-methyl-1,4-phenylenedioxy)diphthalonitrile (**3**). Yield: 2.7 g (%62.2). M.p.: 204 C. IR (KBr pellet), ν (cm^{-1}): 3146-3020 (Ar-CH), 2979-2832 (Al-CH), 2232 (C≡N), 1599 (Ar-C=C), 1245 (C-O-C). Anal. Calc. for $C_{23}H_{12}N_4O_2$: C 73.40; H 3.21; N 14.89%. Found: C 73.25; H 3.15; N 14.70%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ, ppm: 8.17-8.13 (m, 2H), 7.90-7.89 (d, 1H), 7.81-7.80 (d, 1H), 7.56-7.53 (dd, 1H), 7.47-7.44 (dd, 1H), 7.30-7.26 (m, 2H), 7.18-7.15 (dd, 1H), 2.13 (s, 3H).

2.1.2. Synthesis of 2',10',16',24'-[tetrakis {4,4'-(2-methyl-1,4- phenylenedioxy)}] bisphthalocyaninato dicooper(II) (4)

A mixture of compound 3 (0.3 g, 0.80 mmol), $Cu(Ac)_2\cdot H_2O$ (0.159 g, 0.8 mmol) and 0.2 ml 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in 5 ml DMF in two necked reaction flask was stirred and refluxed under Ar atmosphere for 101 h. Green colored reaction mixture was filtered and washed with hot DMF and reaction mixture was precipitated in 250 ml water. The product was filtered and dried. Later, the product was solved in concentrated H_2SO_4 and precipitated in 250 ml water. The product was filtered and washed ethanol, acetone and chloroform. The resulting green colored product 4 was dried under vacuo at 80° C. This compound was soluble ever organic solvent. This compound was only soluble in concentrated H_2SO_4. Yield: 0.195 g (% 60). M.p.>320 °C. IR (KBr pellet), ν (cm^{-1}): 3058 (Ar-CH), 2990-2820 (Al-CH), 1600 (Ar-C=C), 1220 (C-O-C). UV-Vis (H_2SO_4), λ_{max}, (nm): 862, 757, 530. Anal. Calc. for $C_{92}H_{48}Cu_2N_{16}O_8$: C 67.68; H 2.96; N 13.73%. Found: C 67.12; H 2.80; N 13.50%.

2.1.3. Synthesis of 2',10',16',24'-[tetrakis {4,4'-(2-methyl-1,4- phenylenedioxy)}] bisphthalocyaninato dicobalt(II) (5)

A mixture of compound 3 (0.3 g, 0.80 mmol), $Co(Ac)_2{\cdot}4H_2O$ (0.198 g, 0.8 mmol) and 0.2 ml DBU in 5 ml DMF in two necked reaction flask was stirred and refluxed under Ar atmosphere for 32 h. Green colored reaction mixture was filtered and washed with hot DMF and reaction mixture was precipitated in 250 ml water. The product was filtered and dried. Later, the product was solved in concentrated H_2SO_4 and precipitated in 250 ml water. The product was filtered and washed ethanol, acetone and chloroform. The resulting green colored product 5 was dried under vacuo at 80 °C. This compound was soluble ever organic solvent. This compound was only soluble in der. H2SO4. Yield: 0.170 g (% 53). M.p.>380 °C. IR (KBr pellet), ν (cm^{-1}): 3111-2981 (Ar-CH), 2981-2820 (Al-CH), 1607 (Ar-C=C), 1219 (C-O-C). UV-Vis (H_2SO_4), λ_{max}, (nm): 837, 738, 546. Anal. Calc. for $C_{92}H_{48}Co_2N_{16}O_8$: C 68.07; H 2.98; N 13.81%. Found: C 67.50; H 3.15; N 14.02%.

2.1.4. Synthesis of 2',10',16',24'-[tetrakis {4,4'-(2-methyl-1,4- phenylenedioxy)}] bisphthalocyaninato dizinc (II) (6)

A mixture of compound 3 (0.3 g, 0.80 mmol), $Zn(Ac)_2{\cdot}2H_2O$ (0.175 g, 0.8 mmol) and 0.2 ml DBU in 5 ml DMF in two necked reaction flask was stirred and refluxed under Ar atmosphere for 24 h. Green colored reaction mixture was filtered and washed with hot DMF and reaction mixture was precipitated in 250 ml water. The product was filtered and dried. Later, the product was solved in concentrated H_2SO_4 and precipitated in 250 ml water. The product was filtered and washed ethanol, acetone and chloroform. The resulting green colored product 6 was dried under vacuo at 80 °C. This compound was soluble ever organic solvent. This compound was only soluble in concentrated H_2SO_4. Yield: 0.131 g (% 40). M.p.>410 °C. IR (KBr pellet), ν (cm^{-1}): 3120-2994 (Ar-CH), 2994-2821 (Al-CH), 1606 (Ar-C=C), 1213 (C-O-C). UV-Vis (H_2SO_4), λ_{max}, (nm): 845, 746, 526. Anal. Calc. for $C_{92}H_{48}Zn_2N_{16}O_8$: C 67.53; H 2.96; N 13.70%. Found: C 66.95; H 3.11; N 13.97%.

2.1.5. Synthesis of 2',10',16',24'-[tetrakis {4,4'-(2-methyl-1,4- phenylenedioxy)}] bisphthalocyaninato dinickel(II) (7)

A mixture of compound **3** (0.3 g, 0.80 mmol), $Ni(Ac)_2{\cdot}4H_2O$ (0.198 g, 0.8 mmol) and 0.2 ml DBU in 5 ml DMF in two necked reaction flask was stirred and refluxed under Ar atmosphere for 94 h. Green colored reaction mixture was filtered and washed with hot DMF and reaction mixture was precipitated in 250 ml water. The product was filtered and dried. Later, the product was solved in concentrated H_2SO_4 and precipitated in 250 ml water. The product was filtered and washed ethanol, acetone and chloroform. The resulting green colored product 7 was dried under vacuo at 80 °C. This compound was soluble ever organic solvent. This compound was only soluble in concentrated H_2SO_4. Yield: 0.119 g (% 37). M.p.>370 °C. IR (KBr pellet), ν (cm^{-1}): 3126-2988 (Ar-CH), 2988-2833 (Al-CH), 1598 (Ar-C=C), 1222 (C-O-C). UV-Vis (H_2SO_4), λ_{max}, (nm): 835, 736, 540. Anal. Calc. for $C_{92}H_{48}Ni_2N_{16}O_8$:: C 68.09; H 2.98; N 13.81%. Found: C 66.50; H 2.75; N 13.50%.

2.1.6. Synthesis of 2',10',16',24'-[tetrakis {4,4'-(2-methyl-1,4- phenylenedioxy)}] bisphthalocyanine (8)

A mixture of compound **3** (0.3 g, 0.80 mmol) and 0.2 mL DBU in 5 ml DMF in two necked reaction flask was stirred and refluxed under Ar atmosphere for 125 h. Green colored reaction mixture was filtered and washed with hot DMF and reaction mixture was precipitated in 250 ml water. The product was filtered and dried. Later, the product was solved in concentrated H_2SO_4 and again was precipitated in 250 ml water. The product was filtered and washed ethanol, acetone and chloroform. The resulting green colored product 8 was dried under vacuo at 80° C. This compound was soluble ever organic solvent. This compound was only soluble in concentrated H_2SO_4. Yield: 0.141 g (% 47). M.p.>370° C. IR (KBr pellet), ν (cm^{-1}): 3122-3002 (Ar-CH), 3002-2817 (Al-CH), 1598 (Ar-C=C), 1241 (C-O-C). UV-Vis (H_2SO_4), λ_{max}, (nm): 910, 845, 740, 522. Anal. Calc. for $C_{92}H_{52}Zn_2N_{16}O_8$:: C 73.20; H 3.47; N 14.85%. Found: C 72.95; H 3.10; N 14.42%.

3. Result and Discussion

3.1. Synthesis and Characterization

Diphthalonitrile compound **3** and bis-phthalocyanine compounds **4, 5, 6, 7, 8** were synthesized according to methods shown in Scheme 1.

Metal bisphthalocyanine complexes **4-7** were obtained by using newly synthesized 3 compound with Co(II), Ni(II), Cu(II) and Zn(II) acetate salts in N,N'-Dimethylformamide (DMF) under Argon atmosphere. Metal free bisphthalocyanine compound 8 were also synthesized from **3** compound by the catalysis of 1,8-Diazabisiklo[5.4.0]undec-7-ene (DBU) base in N,N'-Dimethylformamide (DMF) under Argon atmosphere. Analysis of the phthalocyanine compounds were performed by micro analysis, FT-IR and UV-Visible spectroscopic techniques. Thermal behaiviour of the complexes were investigated by thermogravimetric analysis (TGA) and differancial thermal analysis (DTA) methods.

In the ^1H NMR and ^{13}C NMR spectrum of compound 3 which was taken in DMSO-d_6. These spectrums were appeared at Figure 1 and Figure 2. According to ^1H NMR the spectrum of 3 compound (Figure 1.), H6 and H_20 protons appeared at 8.17-8.13 ppm (m). H5 proton appeared at 7.90-7.89 ppm (d). H21 proton appeared at 7.81-7.80 ppm (d). H13 proton appeared at 7.56-7.53 ppm (dd). H14 proton appeared at 7.47-7.44 ppm (dd). H3 and H17 protons appeared at 7.30-7.26 ppm (m). H10 proton appeared at 7.18-7.15 ppm (dd). H15 protons appeared at 2.13 ppm (s).

The IR spectrum of (**3**) taken with KBR pellet showed that a C≡N peak at 2232 cm^{-1}, aromatic C-H peaks at 3146-3020 cm^{-1}, aliphatic C-H peaks at 2979-2832 cm-1, an aromatic C=C peak at 1599 cm-1 and C-O-C peak at 1245 cm^{-1}. The most characteristic feature of all Pc in IR spectrum is lost of the sharp C≡N peak of the reactant. All of compound in this my work was disappear the sharp C≡N peak at 2232 cm^{-1}. IR spectra of 4-8 compounds were showed (Table 1).

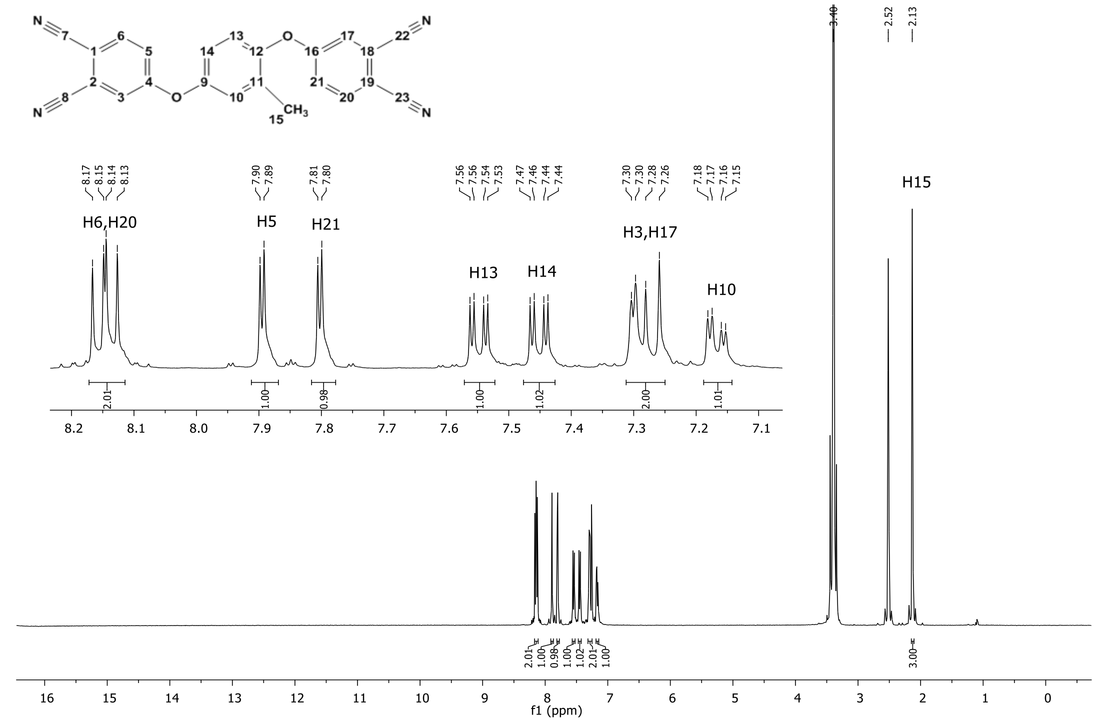


Figure 1. ^{1}H NMR spectrum of (**3**) compound in DMSO-d$_6$

When ^{13}C NMR spectrum of compound (**3**) was viewed, the aromatic carbons were appeared at 162-108 ppm and aliphatic carbon was appeared at 16,19 ppm.

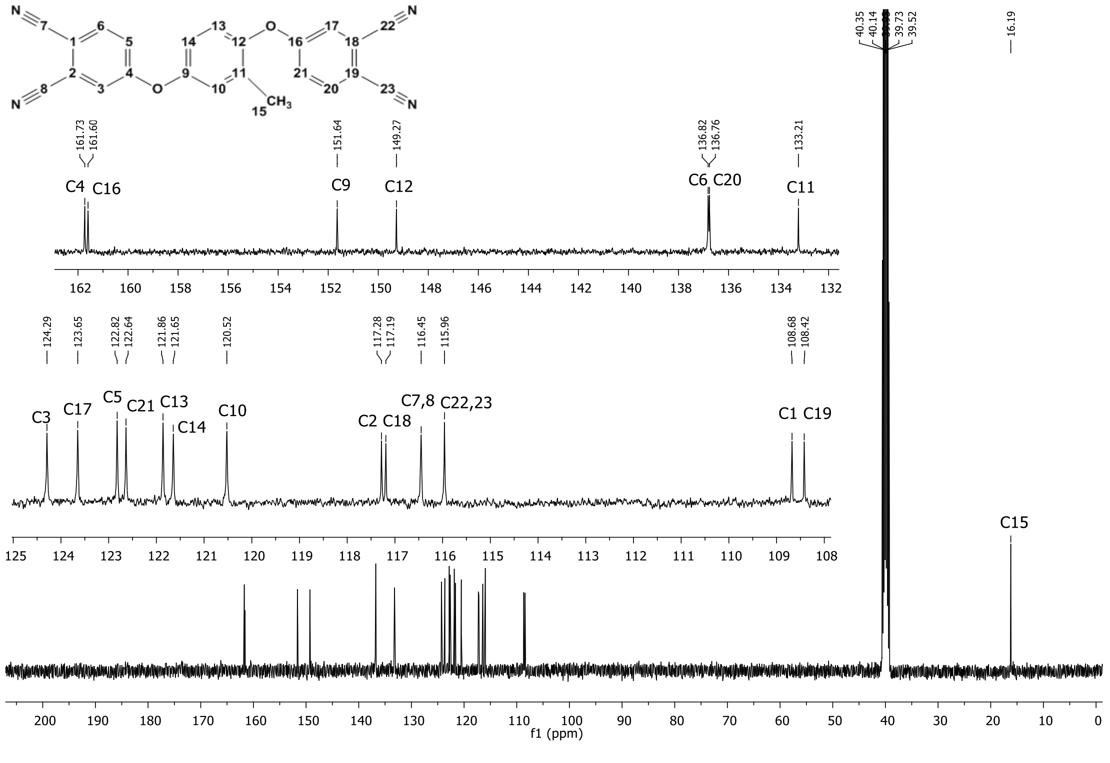


Figure 2. ^{13}C NMR spectrum of 3 compound in DMSO-d$_6$

Table 1. IR spectra peaks for bis-Phthalocyanine complexes (4-8).

Compounds	Ar-CH (cm^{-1})	Al-CH (cm^{-1})	Ar-C=C (cm^{-1})	C-O-C (cm^{-1})
4	3058	2990-2820	1600	1220
5	3111-2981	2981-2820	1607	1219
6	3120-2994	2994-2821	1607	1213
7	3126-2988	2988-2833	1598	1222
8	3122-3002	3002-2817	1598	1241

The UV-Vis absorption spectra of the bis-pc compounds showed characteristic Q and B bands. The Q-band observed for the compounds was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the bis-pc rings. The UV–Vis absorption spectra of the bis-pc compounds 4-7 in concentrated H_2SO_4 showed characteristic absorptions between 835 and 854 nm in the Q-band region. The UV–Vis absorption spectra of the bis-pc compounds 8 in der H2SO4 showed characteristic absorptions at 910 and 845 nm in the double Q-band region (Table 2). B band in the UV region between 522–546 nm were observed due to the transitions from the lower π levels to LUMO (Table 2). Small shoulders at 757, 738, 746, 736, and 740 nm are due to aggression [17]. The use of concentrated H2SO4 as a solvent caused the synthesized bis-pc compounds to shift to higher wavelengths than the regions where characteristic B and Q bands are observed in general organic solvents [18, 19]. The UV-Vis absorption spectra of bis-pc compounds 4-8 in H_2SO_4 at room temperature is shown in Figure.3.

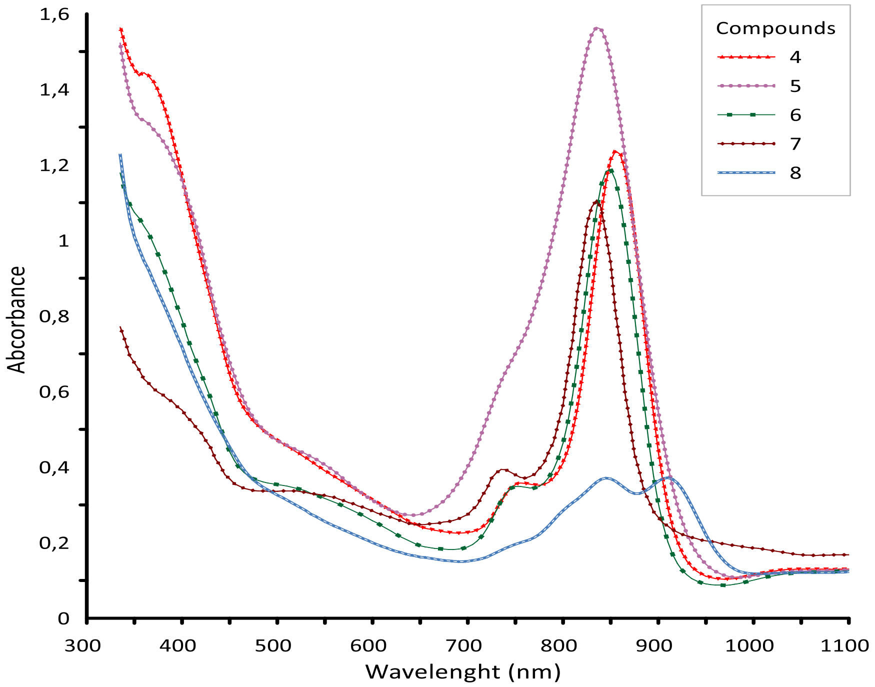


Figure 3. The UV-Vis absorption spectra of bis-phthalocyanine complexes (**4-8)** in H_2SO_4.

Table 2. UV–Visible absorption peaks in H_2SO_4 for bis-phthalocyanine complexes (**4-8**)

Compounds	Wavelenghts λ (nm)
4	854, 757, 530, 373
5	837, 738, 546, 383
6	845, 746, 526, 361
7	835, 736, 540, 393,306
8	910, 845, 740, 522, 367

3.2. Thermal analysis

Thermal analysis results show that all bisphthalocyanine compounds have thermal stability up to 320-410 °C. DTA data of the synthesized bisphthalocyanine compounds show that the compounds do not have a melting point, they begin to decompose without melting, and the decomposition has exothermic character. In addition, TGA data show that metalic bisphthalocyanine compounds decompose to metal oxides and the amounts of metal oxides formed are compatible with the formula structures of phthalocyanine compounds.

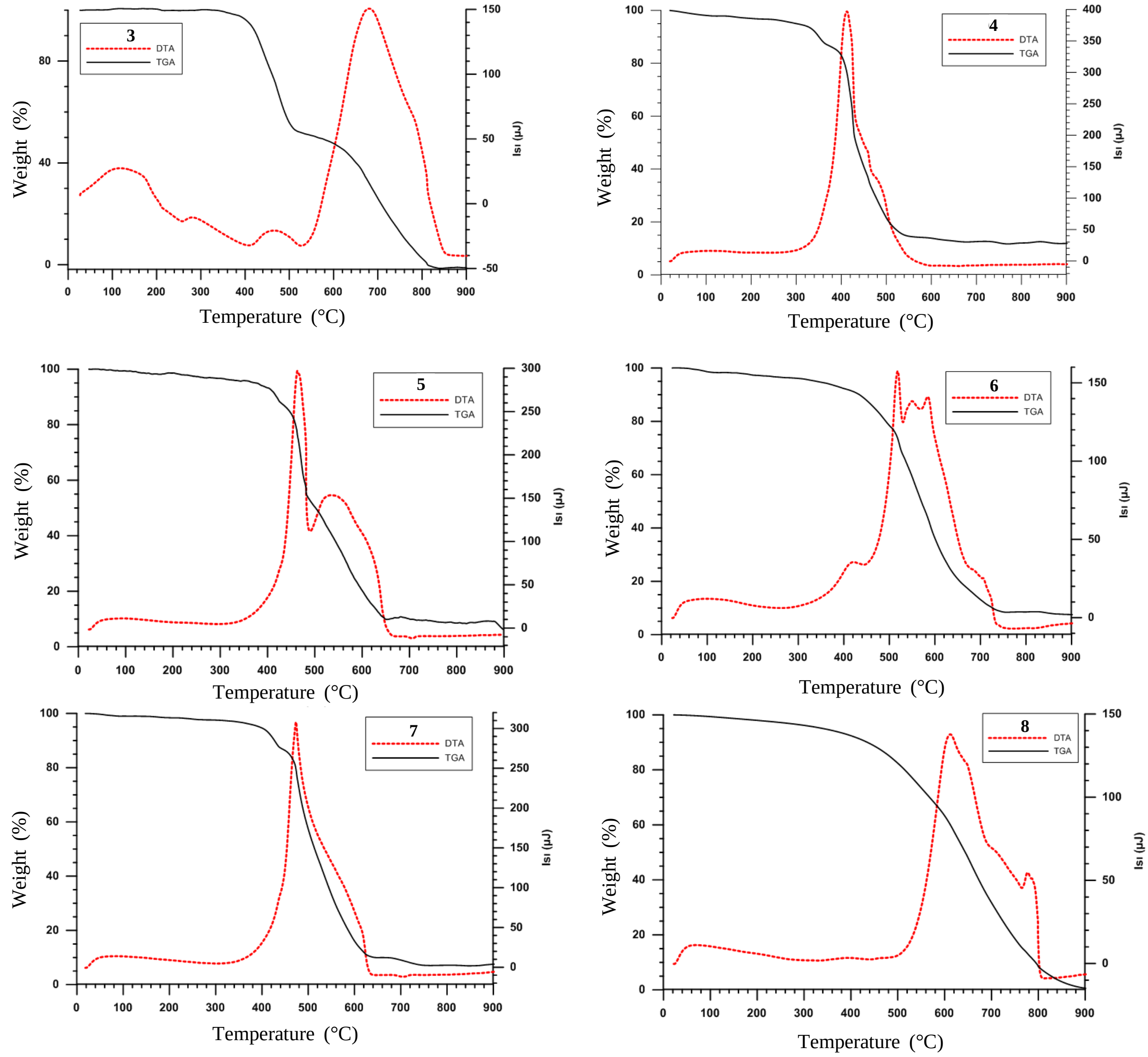


Figure 4 TGA and DTA of ligand (**3**) and bis-phthalocyanine metal complexes (**4-8**)

Author Contribution

Authors contributed equally.

Conflict of Interests

The authors declare that there is no conflict of interest.

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