



Research Article

Novel flexible dithia-alkyl bridged homo-dimeric metal-free and metallophthalocyanines

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Keywords:
aggregation,
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synthesis,
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In this study, synthesis, characterization and investigation of spectroscopic properties in organic solvents of homo dimeric metal free and metallophthalocyanines have been carried out. The substituted di-phthalonitrile derivative as a starting material for the synthesis of phthalocyanines was prepared by the reaction of 4-nitrophthalonitrile and compound **1** in dry dimethylformamide/potassium carbonate. The cyclotetramerization of substituted diphthalonitrile derivative with phthalonitrile in 1:6.15 ratio gave the expected homo-dimeric metal-free phthalocyanine and with metal salts of Zn(II), Ni(II), Co(II) and Cu(II) gave binuclear Zn-, Ni-, Co- and Cu-phthalocyanines, respectively, in dimethyl aminoethanol/1,8-diazabicyclo [5.4.0] undec-7-ene system. The products were purified by crystallization and silica gel column chromatography. The newly prepared compounds were characterized by a combination of IR, ¹H / ¹³C-NMR, MS and UV-Vis spectroscopy. In addition, aggregation behaviors of all novel phthalocyanines were investigated. Aggregation properties of the metal free and metallophthalocyanines have been investigated in chloroform. Dimeric metal free and metallophthalocyanines did not show aggregation in chloroform at 4x10⁻⁶-16x10⁻⁶ mol/L concentration range. Furthermore, aggregation properties of Co-phthalocyanine have been investigated in chloroform, N,N-dimethyl formamide, dimethylsulfoxide, pyridine and tetrahydrofuran. Co-phthalocyanine complex showed monomeric behavior in mentioned solvents at 1x10⁻⁵ mol/L concentration.

TR

Yeni Esnek Ditiya-alkil Köprülü Homo-dimerik Metallsız ve Metalli ftalosyaninler

Anahtar Kelimeler:
agregasyon,
dimerik ftalosyanin,
ftalosyanin,
sentez,
spektroskopisi

Ö Z E T

Bu çalışmada, homo dimerik metal içermeyen ve metalofthalosyaninlerin organik çözücülerde spektroskopik özelliklerinin sentezi, karakterizasyonu ve araştırılması gerçekleştirilmiştir. Ftalosyaninlerin sentezi için başlangıç bileşiği olarak seçilmiş diftalonitril türevi, 4-nitroftalonitril ve bileşik **1**'in kuru dimetilformamid / potasyum karbonat içinde reaksiyonu ile hazırlandı. 1:6.15 oranında ftalonitril ile substitue diftalonitrilin siklotetramerasizasyonu, beklenen homo-dimerik metal içermeyen ftalosyanini ve Zn(II), Ni(II), Co(II) ve Cu(II) metal tuzları ile tetramerizasyonu da, binükleer Zn-, Ni-, Co- and Cu-ftalosyaninleri oluşturdu. Tüm bu reaksiyonlar, DMAE/1,8-diazabicyclo [5.4.0] undec-7-ene sisteminde gerçekleştirildi. Ürünler, kristallendirme ve silika jel kolon kromatografisi ile saflaştırıldı. Yeni hazırlanan bileşikler, IR, ¹H / ¹³C-NMR, MS ve UV-Vis spektroskopisinin kombinasyonu ile karakterize edildi. Ayrıca, tüm yeni ftalosyaninlerin agregasyon davranışları da araştırılmıştır. Metal içermeyen metalli-ftalosyaninlerin özellikleri kloroformda araştırılmıştır. Dimerik metal içermeyen metalli-ftalosyaninler kloroformda 4x10⁻⁶-16x10⁻⁶ mol/L konsantrasyon aralığında agregasyon göstermemiştir. Ayrıca kloroform, N,N-dimetil formamid, dimetilsülfoksit, piridin ve tetrahydrofuranda Co-ftalosyanin molekülünün agregasyon özellikleri araştırılmıştır. Co-ftalosyanin molekülü, 1x10⁻⁵ mol/L konsantrasyonda belirtilen çözücülerde monomerik davranış göstermiştir.

1. Introduction

Phthalocyanines (Pcs) are N4-macrocycles and have received widespread attention in the past century due to their exclusive chemical and physical properties [1]. Technological applications of phthalocyanines, such as semiconductors [2], electrochromic displays [3], chemical sensors [4], and catalysts [5–7], have motivated many researchers to synthesize various types of phthalocyanines. Due to the ability of almost all metals to

coordinate to the cavity of the Pc macrocycle, many metallophthalocyanines (MPc) have been synthesized so far [8-10].

Although the symmetrically substituted monomeric Pcs have many useful properties, scientists have tried to prepare novel asymmetric phthalocyanines. In this context homo- or hetero-multinuclear Pcs that have various bridges have attracted much attention [11-14]. Investigations have indicated that asymmetric binuclear Pcs having different substituents usually show different electrical and spectroscopic properties from their parent molecules. Although they have very important application properties, the main problem for asymmetrically substituted binuclear phthalocyanines is their purification difficulty. For this reason, there have been few reports on the synthesis of asymmetrically substituted phthalocyanines [15,16]. Recently our group has prepared asymmetrically substituted homo-dimeric metal-free and metallophthalocyanines [17]. Aggregation, coplanar association of the Pc

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rings due to the large planar π -conjugated systems, reduces the solubility and makes purification and characterization difficult. On the other hand, the aggregation reduces their photosensitizing efficiency and their ability to coat monolayer films onto electrode surfaces. Therefore, the preparation of the Pcs showing monomeric behavior in majority of solvents and investigation on the aggregation behaviors of them are important. In addition, Pcs that have sulphur atom at the periphery show excellent spectroscopic and photochemical properties [18].

On the basis of stated facts, unsymmetrically substituted binuclear phthalocyanines having long/flexible bridge containing Schiff base have been synthesized. Thereby by preventing the interaction of Pc macrocycles, the solubility and aggregation drawback may be overcome.

In this study, the synthesis, characterization and structural investigation of peripherally substituted homo-dimeric metal-free and metallophthalocyanines which contain dithia-alkyl bridged and Schiff base moieties are described. In addition, the aggregation behaviors of metal-free H₂Pc **5** and MPcs **6-9** in different solvents and at different concentrations were also investigated.

2. Materials and Methods

All reactions were carried out under dry and oxygen-free nitrogen atmosphere, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [19]. 2,2'-(1Z,11E)-5,8-dithia-2,11-diazadodeca-1,11-diene-1,12-diyl)diphenol (**1**) [20] and 4-nitrophthalonitrile (**2**) [21] were prepared according to the literature and phthalonitrile (**4**) was purchased from Merck. ¹H-NMR/¹³C-NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in deuterated chloroform (CDCl₃), and chemical shifts were reported (δ) relative to tetramethylsilane (Me₄Si) 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 with chloroform–methanol used as solvent. All experiments were performed in positive ion mode. UV–Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.1. Synthesis

2.1.1. 4,4'-(1Z,11Z)-5,8-dithia-2,11-diazadodeca-1,11-diene-1,12-diylbis(2,1-phenyleneoxy)diphthalonitrile (**3**)

To a solution of 4-nitrophthalonitrile (**2**) (0.89 g, 5.14 mmol) in dry DMF (15 mL) compound **1** (1 g, 2.57 mmol) was added, and the temperature was increased up to 55-60 °C. Powdered K₂CO₃ (0.710 g, 5.14 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. The completion of the reaction was controlled by thin layer chromatography (TLC) [chloroform:methanol (10:1)]. The temperature of the system was lowered to room temperature, and the mixture was poured into ice-water and mixed overnight. The precipitate was filtered and dried in vacuum over P₂O₅ and recrystallized from ethanol to give dark brown crystalline powder. Yield: 0.86 g, (52.1%), mp: 271-273 °C. IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3050 $\nu(\text{Ar-CH})$, 2922-2852 $\nu(\text{aliph. CH})$, 2210 $\nu(\text{C}\equiv\text{N})$, 1604 $\nu(\text{C}=\text{N})$, 1522 $\nu(\text{C}=\text{C})$, 1462, 1350, 1260, 1204, 1109, 832. ¹H-NMR (CDCl₃), (δ : ppm): 9.03 (s, 2H, CH=N), 8.68-8.52 (d, 2H/Ar-H), 7.89-7.85 (d, 4H/Ar-H), 7.60-7.65 (m, 2H/Ar-H), 7.51-7.47 (d, 4H/Ar-H), 7.26-7.22 (d, 2H/Ar-H), 3.78-3.83 (t, 4H, NCH₂), 3.29-3.16 (m, 8H, SCH₂). ¹³C-NMR (CDCl₃), (δ : ppm): 161.16 (CH=N), 160.71, 157.11, 142.72, 136.81, 132.11, 131.44, 128.75, 128.03, 122.11, 120.91, 118.14, 116.35 (C \equiv N), 116.04 (C \equiv N), 110.61, 56.86 N(CH₂), 33.72 (SCH₂), 33.01 (SCH₂). MS (ESI), (m/z): Calculated: 640.17; Found: 641.44 [M+H]⁺.

2.1.2. Dimeric metal-free phthalocyanine (**5**)

The solution of compound **3** (0.20 g, 0.312 mmol), phthalonitrile (**4**) (0.25 g, 1.92 mmol) in dry N,N-dimethylaminoethanol (DMAE) (4 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) were heated and stirred in a glass sealed tube at 150 °C for 24 h. Then it was diluted with methanol. The precipitated product was filtered and then washed with hot ethanol, diethyl ether and dried in vacuum over P₂O₅. Then, the solid product was dissolved in chloroform and filtered. The filtrate was evaporated under reduced pressure and the obtained solid product was purified by column chromatography using silicagel, and dark green product was gathered by using chloroform/methanol (10:1) as eluent. Yield: 0.036 g, (8.2%), mp >300 °C (decomposition). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3255 (NH), 3049 $\nu(\text{Ar-CH})$, 2923-2853 $\nu(\text{aliph. CH})$, 1605 $\nu(\text{C}=\text{N})$, 1521 $\nu(\text{C}=\text{C})$, 1465, 1355, 1248, 1213, 1118, 845. ¹H-NMR (CDCl₃), (δ : ppm): 8.88 (bs, 2H, CH=N), 8.80-7.92 (bm, 22H/Ar-H), 7.76-7.44 (d, 8H/Ar-H), 7.22-7.12 (d, 8H/Ar-H), 3.92-3.51 (m, 4H, NCH₂), 3.28-3.15 (m, 8H, SCH₂). UV-Vis (Chloroform): λ_{\max}/nm : [(10⁻⁵ log ϵ dm³mol⁻¹cm⁻¹): 696 (4.76), 660 (4.69), 639 (4.39), 608 (4.21), 343 (4.85)]. MS (ESI), (m/z): Calculated: 1412.43; Found: 1413.57 [M+H]⁺.

2.1.3. The general procedure for synthesis of metallophthalocyanines (**6-9**)

Mixtures of compound **3** (0.20 g, 0.312 mmol), phthalonitrile (**4**) (0.25 g, 1.92 mmol), related metal salts Zn(OAc)₂ (0.114 g, 0.624 mmol); Ni(OAc)₂ (0.110 g, 0.624 mmol); CoCl₂ (0.081 g, 0.624 mmol); CuCl₂ (0.084 g, 0.624 mmol), dry DMAE (5 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) were heated and stirred in a glass sealed tube at 150 °C for 24 h. Then they were diluted with methanol, and precipitates were filtered and washed with hot ethanol, diethyl ether and dried in vacuum over P₂O₅. Then solid products were dissolved in chloroform and filtered. The filtrates were evaporated under reduced pressure, and the obtained solid products were purified by column chromatography using silicagel with appropriate solvent systems. The chemical and physical spectral characteristics of the products **6-9** are given below.

2.1.3.1. Binuclear Zn(II) phthalocyanine of clamshell type (**6**)

Solvent system: chloroform:methanol (12:1). Yield: 0.025 g, (5.2%), mp:>300 °C (decomposition). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3053 $\nu(\text{Ar-CH})$, 2922-2854 $\nu(\text{aliph. CH})$, 1608 $\nu(\text{C}=\text{N})$, 1524 $\nu(\text{C}=\text{C})$, 1449, 1361, 1244, 1214, 1118, 844. ¹H-NMR (CDCl₃), (δ : ppm): 8.75 (s, 2H, CH=N), 8.75-8.07 (bm, 22H/Ar-H), 7.84-7.56 (m, 8H/Ar-H), 6.94-6.56 (bd, 8H/Ar-H), 3.85-3.64 (m, 4H, NCH₂), 3.24-3.09 (m, 8H, SCH₂). UV-Vis (chloroform): λ_{\max}/nm : [(10⁻⁵ log ϵ dm³mol⁻¹cm⁻¹): 674 (5.27), 609 (4.55), 344 (5.09)]. MS (ESI), (m/z): Calculated: 1539.25; Found: 1540.89 [M+H]⁺.

2.1.3.2. Binuclear Ni(II) phthalocyanine (**7**)

Solvent system: chloroform:methanol (15:1). Yield: 0.043 g, (9%), mp:>300 °C (decomposition). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3053 $\nu(\text{Ar-CH})$, 2923-2854 $\nu(\text{aliph. CH})$, 1604 $\nu(\text{C}=\text{N})$, 1521 $\nu(\text{C}=\text{C})$, 1451, 1361, 1241, 1211, 1135, 853. ¹H-NMR (CDCl₃), (δ : ppm): 9.12 (s, 2H, CH=N), 8.87-8.56 (m, 22H/Ar-H), 7.84-6.91 (bm, 16H/Ar-H), 3.81-3.54 (m, 4H, NCH₂), 3.19-3.11 (m, 8H, SCH₂). UV-Vis (Chloroform): λ_{\max}/nm : [(10⁻⁵ log ϵ dm³mol⁻¹cm⁻¹): 678 (5.21), 610 (4.53), 342 (4.83)]. MS (ESI), (m/z): Calculated: 1524.27; Found: 1547.45 [M+Na]⁺.

2.1.3.3. Binuclear Co(II) phthalocyanine (**8**)

Solvent system: chloroform:methanol (15:1). Yield: 0.042 g, (8.8%), mp:>300 °C (decomposition). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3051 $\nu(\text{Ar-CH})$, 2925-2854 $\nu(\text{aliph. CH})$, 1607 $\nu(\text{C}=\text{N})$, 1520 $\nu(\text{C}=\text{C})$, 1451, 1363, 1237, 1214, 1134, 859. UV-Vis (chloroform): λ_{\max}/nm : [(10⁻⁵ log ϵ dm³mol⁻¹cm⁻¹): 666 (5.18), 603 (4.67), 326 (5.00)]. MS (ESI), (m/z): Calculated: 1526.26; Found: 1527.12 [M+H]⁺.

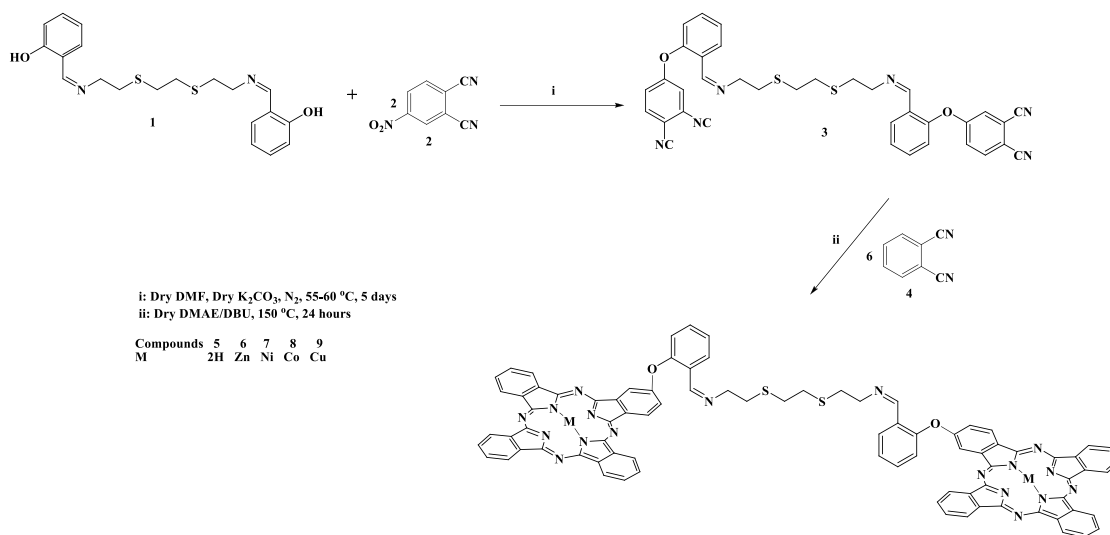


Fig. 1. Synthetic route of novel compounds

2.1.3.4. Binuclear Cu(II) phthalocyanine (9)

Solvent system: chloroform:methanol (8:1). Yield: 0.045 g, (9.4%), mp:>300 °C (decomposition). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3051 $\nu(\text{Ar-CH})$, 2925-2852 $\nu(\text{aliph. CH})$, 1606 $\nu(\text{C=N})$, 1517 $\nu(\text{C=C})$, 1448, 1363, 1244, 1151, 865. UV-Vis (chloroform): λ_{\max}/nm : $[(10^{-5} \log \epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$: 666 (4.92), 601 (4.26), 328 (4.68). MS (ESI), (m/z): Calculated: 1534.26; Found: 1535.95 [M+H]⁺.

3. Results and Discussion

The scheme of the synthesis of novel compounds is shown in Fig. 1. The compounds were characterized by the help of ¹H/¹³C-NMR, IR, UV-Vis and MS spectral data.

3.1. Synthesis of di-phthalonitrile derivative (3)

Substitution of the nitro group of the phthalonitrile derivatives with strong nucleophiles have been achieved by many scientists to date [22,23]. This type of substitution reactions has been performed by the help of a base such as K₂CO₃ in dipolar aprotic solvents for example DMF or DMSO [24,25]. In this respect, initial phthalonitrile derivative 3 was obtained from reaction between the diphenol derivative 1 and 4-nitrophthalonitrile (2) in dry DMF at 55 °C. Dry K₂CO₃ was used to supply basic reaction condition. According the IR spectral data of compound 3, the absence of the -OH vibration of compound 1 at 3230 cm⁻¹ and the presence of the C≡N vibration belonging to compound 3 at 2210 cm⁻¹ proved that the substitution has occurred. On the other hand, in ¹H-NMR spectrum, there was no signal concerning the OH proton of compound 1 at 10.72 ppm. Besides, the new signals of nitrile carbons of compound 3 at 116.35 and 116.04 ppm in ¹³CNMR assist the IR spectra. In addition, in mass spectral analysis of 3, stable molecular ion [M+H]⁺ peak at 641.44 proved that the target compound successfully prepared.

3.2. Synthesis of metal free (5) and metallophthalocyanines (6-9)

In spite of the presence of various methods on the synthesis of Pcs in literature, scientists commonly use cyclotramerization of substituted phthalonitrile or 1,3-diimino-1H-isoindoles [26-29]. Besides selecting the precursor, choosing the reaction conditions is important. A general method is the use of strong non-nucleophilic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in high boiling solvents such as N,N-dimethylaminoethanol (DMAE), n-hexanol etc. [30].

In this area, researchers mainly use cross-condensation of two different substituted phthalonitriles to obtain unsymmetrically substituted Pcs [31,32]. When two phthalonitriles (A and B) statistically react together in ratio 3:1, the crude product will be

mainly mixture of the symmetric Pc (AAAA) and the expected 3:1 Pc (AAAB) and a little other cross-condensation products [33,34]. However, it is known that purification of the desired product (AAAB) is quite difficult from these mixtures of phthalocyanines.

In this context, in order to reduce the purification problems, phthalonitrile (4) has been chosen and used excessively because the solubility of the unsubstituted symmetric Pc in common organic solvents is very low.

The unsymmetrical metal free phthalocyanine 5 was synthesized by statistical cross-condensation of a 1:6.15 molar ratio of 3 and 4 in DMAE/DBU by heating under reflux for 24 h. In case of metallophthalocyanines, the substituted diphthalonitrile 3 and phthalonitrile (4) with four metal salts, Zn(CH₃COO)₂, Ni(CH₃COO)₂, CoCl₂ and CuCl₂ were used for the formation of 6, 7, 8 and 9, respectively. Before the chromatographic purifications, to remove the unsubstituted Pc (AAAA), the crude products were dissolved in chloroform and filtered. The solubility of the asymmetrically substituted dimeric phthalocyanines were good in common organic solvents such as chloroform, ethyl acetate, DMF and DMSO.

The spectroscopic characterization of the newly synthesized compounds includes ¹H-NMR, IR, UV/Vis and mass spectral measurements, and the results were in accordance with the proposed structures. Cyclotramerization of dinitriles 3 and 4 gave Pcs 5-9, which was confirmed by the disappearance of the sharp C≡N vibration at 2210 cm⁻¹ in their IR spectra. The main difference between the IR spectral data of metal-free and metallophthalocyanines is that the inner core -NH vibration for metal free phthalocyanine 5 observed at 3255 cm⁻¹. The formation of metal free Pc was proved with given stretching vibration. The rest of the spectra of the Pcs 5-9 were similar to that of 3.

The ¹H-NMR spectra of 8 and 9 could not be determined because of the presence of paramagnetic cobalt and copper atoms [35]. In the ¹H-NMR spectrum of compound 5 the typical shielding of inner core protons could not be observed due to the probable strong aggregation at NMR measurement concentration. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton represent the significant absorbance characteristics of the proposed structures. In ¹³CNMR spectra of the compounds 5-7, the absence of the signals of the nitrile carbons of compound 3 at 116.35 and 116.04 ppm proves that the cyclotramerizations have occurred. In addition, the mass spectra of Pcs 5, 6, 7, 8 and 9 showed molecular parent ion peaks at m/z = 1413.57 [M+H]⁺, 1537.89 [M+H]⁺, 1547.45 [M+Na]⁺, 1527.12 [M+H]⁺ and 1535.98 [M+H]⁺, respectively, supporting the proposed formula for these compounds.

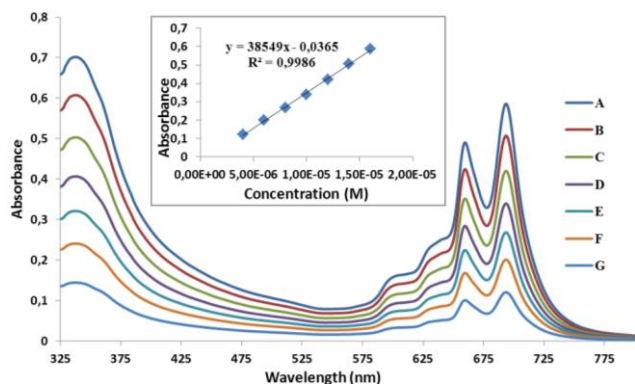


Figure 2. UV-Vis spectra of compound **5** in CHCl_3 at different concentrations (16×10^{-6} - 4×10^{-6} mol/L).

3.3. UV-Vis absorption spectra

When compared to other characterization methods, UV/Vis spectroscopy gives more information about phthalocyanine formation. The UV-Vis spectra of all phthalocyanines consist of two bands. One around 600-750 nm called as Q band is due to the $\pi \rightarrow \pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of phthalocyanine ring. The other one is called as B band at around 300-450 nm arising from deeper π levels to LUMO transitions. For metal-free phthalocyanine derivatives, Q-bands split to doublet (Q_x and Q_y) because of non-degenerate D_{2h} symmetry, and for metallated species, the Q bands are observed as singlet due to degenerate D_{4h} symmetry.

In the UV-Vis spectra of metal free phthalocyanine **5** in chloroform, splitted Q-band was observed at 696 and 660 nm with shoulders at 639 and 608 nm (Fig. 2). For metallophthalocyanines **6-9** in chloroform, the Q-bands were observed at 674, 678, 666 and 666 nm, respectively, as singlet form with shoulders at 609, 610, 603 and 601 nm, respectively (Figs. 3-6). The Q-bands of CoPc **8** and CuPc **9** are more blue-shifted (10 nm) than that of ZnPc **6** and NiPc **7** (Figs. 3-6). The term aggregation is depicted as coplanar association of rings progressing from monomer to dimer and higher order complexes, and it is dependent on the concentration of the solution, types of central metal ions, nature of the solvent, nature and connection of the substituents and temperature. For Q band regions, the sharper and the more intense Q-bands than the bathochromically shifted shoulders are the evidence of monomeric behavior. As can be seen from Figs. 2-6, the metal-free **5** and metallophthalocyanines **6-9** are monomer in chloroform at 4×10^{-6} - 16×10^{-6} mol/L concentration range, and the phthalocyanine rings of the dimeric Pcs do not affect each other.

Additionally, to better investigate the aggregation behavior of novel compounds, absorption spectra of all Pcs at different concentrations and different solvents were measured. As can be seen in Figs. 2-6, metal-free **5** and metallophthalocyanines **6-9** showed monomeric behaviors in chloroform between 4×10^{-6} and 16×10^{-6} mol/L concentration range, and Lambert-Beer's law was obeyed between this concentration range. In addition, the aggregation behavior of CoPc **8** in different solvents at 1×10^{-5} mol/L concentration has been investigated. CoPc **8** did not aggregate in chloroform, DMF, DMSO, pyridine and tetrahydrofuran (Fig. 7). Furthermore, Q-band maxima of CoPc **8** in chloroform more shifted bathochromically (~ 8 nm) then in other solvents (Fig. 7).

4. Conclusion

In this paper, the preparation of a new type of flexible dithia-alkyl bridged homo-dimeric metal-free and metallophthalocyanines (Zn, Ni, Co and Cu) has been reported. In the first step, di-phthalonitrile derivative **3** was synthesized from a mixture of **1** and **2** (1:2) in the presence of DMF/ K_2CO_3 as key structure to give expected Pcs. Then dimeric metal free and metallophthalocyanines **5-9** were synthesized by the interaction of di-phthalonitrile **3** with excess of

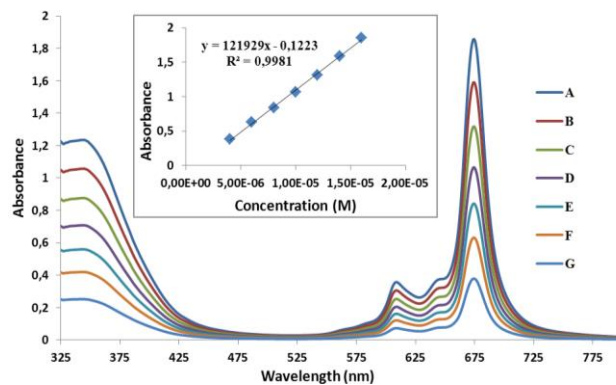


Figure 3. UV-Vis spectra of compound **6** in CHCl_3 at different concentrations (16×10^{-6} - 4×10^{-6} mol/L).

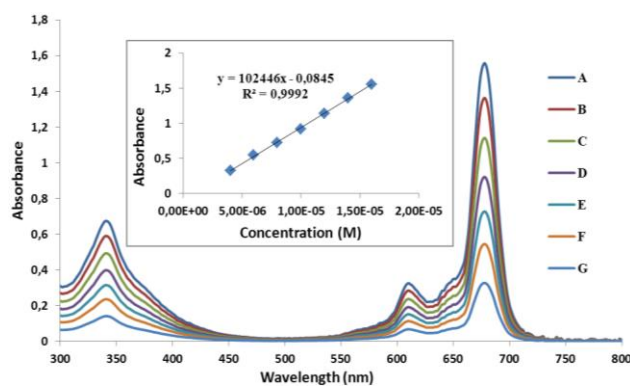


Figure 4. UV-Vis spectra of compound **7** in CHCl_3 at different concentrations (16×10^{-6} - 4×10^{-6} mol/L).

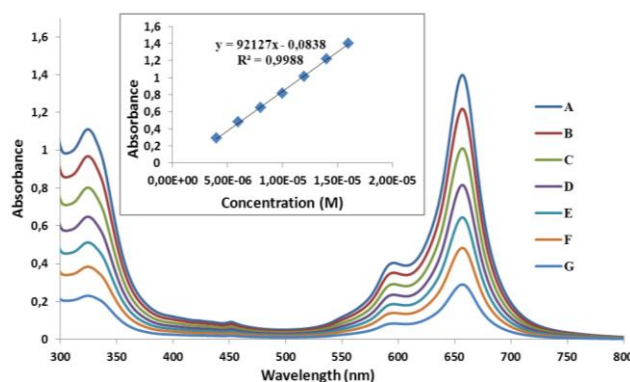


Figure 5. UV-Vis spectra of compound **8** in CHCl_3 at different concentrations (16×10^{-6} - 4×10^{-6} mol/L).

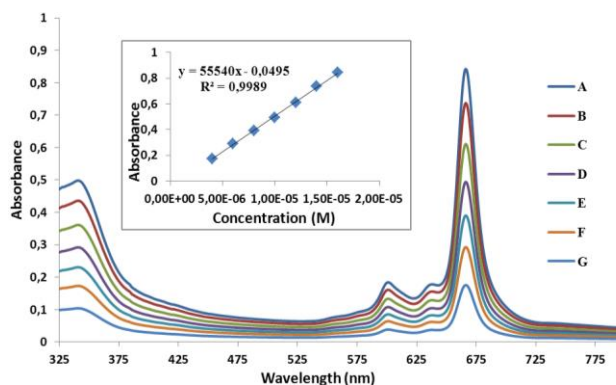


Figure 6. UV-Vis spectra of compound **9** in CHCl_3 at different concentrations (16×10^{-6} - 4×10^{-6} mol/L).

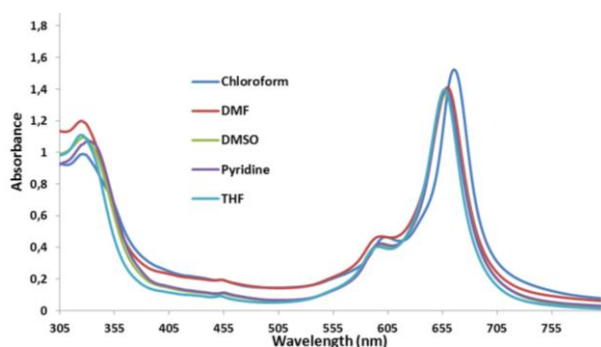


Figure 7. UV-Vis spectra of compound **8** in different solvents at 1×10^{-5} mol/L concentration.

phthalonitrile (**4**) in DMAE/DBU and corresponding metal salts. The preparations of the new products were supported by IR, UV-Vis, $^1\text{H}/^{13}\text{C}$ -NMR and mass spectra. All Pcs showed monomeric behaviors in chloroform between 1.6×10^{-6} – 4×10^{-6} mol/L concentration range. Furthermore CoPc **8** also indicated monomer behavior in different solvents at 1×10^{-5} mol/L concentration. The monomeric character of all phthalocyanines is an indication that they can be easily used in many fields such as the PDT (photodynamic therapy), electronics industry and as sensor.

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