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# Synthesis, characterization and spectroscopic studies of novel peripherally tetra-imidazole substituted phthalocyanine and its metal complexes, the computational and experimental studies of the novel phthalonitrile derivative

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# 1. Introduction

Phthalocyanines (Pcs), one of the most useful heterocyclic materials, can be introduced as tetraazapyrole derivatives. Although history of the Pcs is about 70 years, there are still many investigations on their technological applications in different scientific disciplines. Pcs and their metal complex derivatives, thanks to properties such as strong delocalized 18  $\pi$ -electronic structure, good thermal stability and visible area optical properties, are used in many technological investigations such as chemical sensors [1-3], electrochromic displaying systems [4], non-linear optics [5], solar cells [6], photo-voltaic optics, molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10], laser dyes [11], catalyst [12] and photodynamic therapy (PDT) [13]. The central cavities of Pc can complex with about 70 different elements. Depending on specification of elements; monomeric, axially ligated or dimeric phthalocyanines can be obtained. The cations fitting the central cavity of phthalocyanines form monomeric species [14], the larger cations form dimeric or axially ligated species [15-17].

# ABSTRACT

Compound (**3**) was synthesized by the reaction of 4-(4,5-diphenyl-1*H*-imidazol-2-yl) phenol and 4-nitrophthalonitrile in dry DMF in presence of  $K_2CO_3$  and obtained as single crystal form suitable for x-ray analysis. Vibrational assignments and electronic transitions of the compound (**3**) were calculated and compared with the experimental results. Compound (**4**) was obtained from compound (**33**), by heating at 160 °C for 24 h under N<sub>2</sub> atmosphere in dry N,N dimethyl aminoethanol. Compounds (**5–8**) were synthesized by the same method applied for the synthesis of compound (**4**) with addition of the corresponding metal salts (ZnCH<sub>3</sub>COO<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, CuCl<sub>2</sub>). Prepared phthalocyanines were purified by column chromotography using appropriate solvent system and characterized by elemental analysis <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV–vis, IR and mass spectra. Aggregation behavior of compound (**5**) was studied in different mixtures of sulfuric acid and DMSO.

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The main disadvantage of these valuable materials is their insolubility in majority of solvents due to intermolecular interactions between the macrocycles. The solubility of Pcs can be increased by various methods such as transforming into cationic species, axially substitution and perypheral/non-perypheral substitutions [18–21]. Especially peripherally and non-peripherally substituted phthalocyanines, depending on the structure of the substituent, are soluble in common organic solvents [22–26]. The most important advantage of Pcs compared to porphyrines is that their Q bands are at longer wavelengths and more intense. Thanks to the special optical properties of phthalocyanines, it's known that some phthalocyanines show biological activity against tumors [27].

On the other hand imidazole derivatives consisting of five membered ring system containing two nitrogen atoms are important heterocyclic compounds. These compound classes are used in many fields such as P38 MAP kinase [28], antivascular disrupting, antitumor activity [29], ionic liquids [30], anion sensors [31], electrical and optical materials [32–34]. Imidazole substituted porphyrines are important structures which are investigated for their optical, electronic and catalytic properties [35–37]. Additionally, imidazole substituted phthalocyanines can be used in different research areas such as phthodynamic therapy [38], electron transfer processes [39] and synthesis of polymeric phthalocyanines [40].

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Synthesis of phthalocyanines containing peripherally substituted imidazole ring is a promising enterprise in terms of developing new technological materials. In this study, a novel metal free phthalocyanine and its Zn-, Ni-, Co- and Cu- complexes containing peripherally highly conjugated imidazole substituent were synthesized. The aggregation behavior of ZnPc at different concentrations and in different solvents was also investigated. In addition, crystal structure of the novel phthalonitrile derivative (compound **3**) was explained and comparative investigation of vibrational and electronic transition features were performed theoretically and experimentally.

# 2. Experimental and computational details

All reactions were carried out under dry and oxygen free nitrogen atmosphere using schlenk system. DMF was dried and purified as described by Perrin and Armarego [41], 4-(4,5-diphenyl-1H-imidazol-2-yl) phenol (1) [42] and 4-nitrophthalonitrile (2) [43] were prepared as described in the literature. <sup>1</sup>H NMR/<sup>13</sup>C NMR spectra were recorded on a Varian XL-200 NMR spectrometer in CDCl<sub>3</sub>, DMSO d<sub>6</sub>, and chemical shifts were reported ( $\delta$ ) relative to Me<sub>4</sub>Si as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique. The MS and MS-MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. Methanol, chloroform and acetonitrile were used as solvents in mass analysis and all mass analysis were conducted in positive ion mode. Elemental analysis was performed on a Costech ECS 4010 instrument. UV-vis spectra were recorded by Perkin Elmer Lambda 25 spectrometer, using 1 cm path length cuvettes at room temperature. Melting points were measured by an electrothermal apparatus. All theoretical calculations were performed with gaussian 03W software package [44].

#### 2.1. Synthesis of the compounds (3-8)

2.1.1. 4-[4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy]phthalonitrile (3)

4-(4,5-diphenyl-1*H*-imidazol-2-yl) phenol (1) (1 g, 3.2 mmol) and 4-nitrophthalonitrile (2) (0.55 g, 3.2 mmol) were dissolved in dry DMF (10 ml) under N<sub>2</sub> atmosphere. After stirring for 10 min at 55 °C, dry finely powdered potassium carbonate (0.48 g, 3.5 mmol) was added portion wise within 2 h with efficient stirring. The reaction mixture was stirred under N<sub>2</sub> atmosphere at 55 °C for 5 days. Then the reaction mixture was poured into 250 ml ice-water and precipitate was filtered off, washed with water, diethylether and dried in vacuo. Residue was crystallized from acetone/ethanol solvent system., Colorless needle shape crystals, suitable for X-ray analysis were obtained. Yield 0.9 g (64%), mp: 274 °C.

Anal.calc. for C<sub>29</sub>H<sub>18</sub>N<sub>4</sub>O: C, 79.44; H, 4.14; N, 12.78.

Found: C, 79.32; H, 4.20; N, 12.84.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>)(δ: ppm): 12.75 (s,1H, –NH), 8.19–8.15 (d, 2H, Ar–H), 8.10 (s, 1H/Ar–H), 7.88 (s, 1H/Ar–H), 7.48–7.40 (m, 11H/Ar–H), 7.32–7.27 (d, 2H/Ar–H).

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>) (δ: ppm): 161.48, 154.52, 145.43, 137.86, 137.05, 135.74, 131.67, 129.41, 129.10, 128.93, 128.53, 128.08, 127.76, 123.70, 123.04, 121.21, 117.45, 116.63, 116.11, 109.12.

MS (ESI), (*m*/*z*): Calculated: 438.48; Found: 439.29 [M + H]<sup>+</sup>.

#### 2.1.2. Synthesis metal free phthalocyanine (4)

Compound (3) (0.2 g, 0.45 mmol), 1.8-diazabicyclo [4.5.0] undec-7-ene (DBU) (3 drops) and dry N,N dimethyl aminoethanol (DMAE) (4 ml) were added in a Schlenk tube. The mixture was heated and stirred at 160 °C for 24 h under N<sub>2</sub> atmosphere. After cooling to room temperature, the reaction mixture refluxed in methanol (30 ml) to precipitate the product which was than filtered off. The green solid product was washed with hot ethanol, acetone

and dietyhl ether respectively, and dried in vacuo. The green solid product was purified by column chromotography with chloroform:methanol (100:2) as eluent. Yield: 59 mg (30%), mp > 300 °C.

Anal.calc. for C<sub>116</sub>H<sub>74</sub>N<sub>16</sub>O<sub>4</sub>: C, 79.34; H, 4.25; N, 12.76.

Found: C, 79.41; H, 4.12; N, 12.82.

IR (KBr tablet)  $v_{max}/cm^{-1}$ : 3285, 3049, 1603, 1486, 1469, 1448, 1231, 1166, 1091, 1010, 929, 873, 853, 763.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>) ( $\delta$ : ppm): 11.19 (bs, 4H, –NH), 8.20–7.85 (m, 20H, Ar–H), 7.68 (s, 12 H/Ar–H), 7.60–7.01 (m, 36 H/Ar–H).

MS (ESI) (*m*/*z*): Calculated: 1754.6; Found: 1755.8 [M + H]<sup>+</sup>

UV-vis (DMSO)  $\lambda_{max}/nm$ : [(10<sup>-5</sup>  $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 698 (4.72), 664 (4.68), 642 (4.26) 598 (4.01), 342 (4.47).

#### 2.1.3. The general procedure for the synthesis

of metallophthalocyanines (5–8)

A mixture of compound (**3**) (0.2 g, 0.45 mmol), related anhydrous metal salts ( $M = NiCl_2$  (15.42 mg, 0.12 mmol); CoCl\_2 (15.6 mg, 0.12 mmol); CuCl\_2 (16.0 mg, 0.12 mmol)) and Zn(CH\_3COO)\_2 (22.29 mg, 0.12 mmol), dry DMAE (4 ml) and DBU (3 drops) were mixed in a schlenk tube, then the mixtures were heated and stirred at 160 °C for 24 h under N<sub>2</sub> atmosphere. After cooling to room temperature, methanol (30 ml) was added, and then reaction mixtures were refluxed to precipitate the products which were then filtered off. The green solid products were washed using hot ethanol, acetone and diethylether respectively, and dried in vacuo. Purifications of the solid product were accomplished by column chromatography with silica gel. The chemical and physical characterizations of the final products **5–8** were given bellow.

2.1.3.1. Synthesis of zinc (II) phthalocyanine (5). Eluent

for column chromatography: chloroform:methanol (100:3). Yield: 112 mg (55%), mp >300 °C. Anal. Calc. for C<sub>116</sub>H<sub>72</sub>N<sub>16</sub>O<sub>4</sub>Zn: C, 76.58; H, 3.99; N, 12.32. Found: C, 77.01; H, 3.87; N, 12.01.

IR (KBr tablet)  $\upsilon_{max}/cm^{-1}$ : 3057, 1603, 1488, 1469, 1450, 1234, 1164, 1093, 1045, 968–945.

<sup>1</sup>H NMR (DMSO) (δ: ppm): 12.71 (bs, 4H, –NH), 8.86 (bs, 4H, Ar–H), 8.74–8.42 (m, 8H/Ar–H), 8.33 (bs, 8H/Ar–H), 7.68–7.67

(d 12 H/Ar-H), 7.53 (m 16 H/Ar-H), 7.38-7.34 (m, 18H/Ar-H).

MS (ESI) (*m*/*z*): Calculated: 1816.5; Found: 1817.6 [M + H]<sup>+</sup>.

UV–vis (DMSO)  $\lambda_{\text{max}}/\text{nm}$  [(10<sup>-5</sup>  $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)] : 680 (4.92), 612 (4.12), 357 (4.49).

2.1.3.2. Synthesis of Nickel (II) phthalocyanine (6). Eluent

for column chromatography: chloroform:methanol (100:4). Yield: 91 mg (44%), mp > 300 °C.

Anal.calc. for C<sub>116</sub>H<sub>74</sub>N<sub>16</sub>O<sub>4</sub>: C, 76.86; H, 4.00; N, 12.36.

Found: C, 76.75; H, 4.09; N, 12.38.

IR (KBr tablet)  $v_{max}/cm^{-1}$ : 3057, 1604, 1488, 1470, 1413, 1236, 1164, 1093, 1061, 958, 876, 765.

<sup>1</sup>H NMR (DMSO) (δ: ppm): 11.48 (bs, 4H, –NH), 8.55 (bs 6 H/Ar–H); 8.15 (bm 9 H/Ar–H); 8.0–7.7 (bm 11H/Ar–H); 7.7–7.18 (bm 36 H/Ar–H); 6.95 (s 2H/Ar–H); 6.55 (s 2 H/Ar–H); 6.5 (s 2 H/Ar–H).

MS (ESI) (*m*/*z*): Calculated: 1810.6; Found: 1811.6 [M + H]<sup>+</sup>.

UV–vis (DMSO)  $\lambda_{max}/nm$  [(10<sup>-5</sup>  $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)] : 672 (4.73), 606 (4.02), 332 (4.28).

2.1.3.3. Synthesis of Co (II) phthalocyanine (7). Eluent

for column chromatography: chloroform:methanol (100:5). Yield: 81 mg (40%), mp > 300 °C. Anal.calc. for C<sub>116</sub>H<sub>74</sub>N<sub>16</sub>O<sub>4</sub>: C, 76.58; H, 3.99; N, 12.32. Found: C, 77.01; H, 3.87; N, 12.01. IR (KBr tablet)  $v_{max}/cm^{-1}$ : 3048, 1603, 1486, 1468, 1403, 1233, 1163, 1091, 1051, 950, 869, 832, 765.

MS (ESI) (*m*/*z*): Calculated: 1811.5; Found: 1812.7 [M + H]<sup>+</sup>.

UV-vis (DMSO)  $\lambda_{\text{max}}/\text{nm} [(10^{-5} \epsilon, \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$  : 676 (4.83), 608 (4.06), 352 (4.42).

2.1.3.4. Synthesis of Cu (II) phthalocyanine (8). Eluent

for column chromatography with chloroform:methanol (100:3). Yield: 90 mg (44%), mp > 300 °C.

Anal.calc. for C<sub>116</sub>H<sub>74</sub>N<sub>16</sub>O<sub>4</sub>: C, 76.66; H, 3.99; N, 12.33.

Found: C, 76.78; H, 3.91; N, 12.29.

IR (KBr tablet)  $v_{max}/cm^{-1}$ : 3057, 1602, 1474, 1449, 1405, 1235, 1165, 1095, 1053, 950, 874, 834, 769.

MS (ESI) (m/z): Calculated: 1815.5; Found: 1816.7 [M + H]<sup>+</sup>; 1880.5 [M + ACN + Na]<sup>+</sup>.

UV-vis (DMSO)  $\lambda_{max}/nm$  [(10<sup>-5</sup>  $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)] : 676 (4.80), 608 (4.12), 342 (4.45).

2.2. Crystal structure of the compound (3)

For the crystal structure determination, the single crystal of the compound **3** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo  $K_{\alpha}$  radiation  $(\lambda = 0.71073 \text{ Å})$  and oscillation scans technique with  $\Delta \omega = 5^{\circ}$  for each image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with  $F^2 > 2\sigma(F^2)$ . Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc., 2005) software [45]. The structures were solved by direct methods using SHELXS-97 [46] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [46]. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. Crystal data for compound **3**: C<sub>29</sub>H<sub>18</sub>N<sub>4</sub>O, crystal system, space group: orthorhombic, *Pbna*; (no:60); unit cell dimensions: a = 8.8175(2), b = 17.4971(2), c = 31.4846(4) Å, volume: 4857.5(1) Å<sup>3</sup>; Z = 8; calculated density: 1.20 g/cm<sup>3</sup>; absorption coefficient: 0.075 mm<sup>-1</sup>; F(000): 1824;  $\theta$ -range for data collection 2.3–26.5°; refinement method: full-matrix least-square on F<sup>2</sup>; data/parameters: 4974/308; goodness-of-fit on  $F^2$ : 1.000; final *R* indices  $[I > 2\sigma(I)]$ :  $R_1 = 0.058$ , w $R_2 = 0.135$ ; *R* indices (all data):  $R_1 = 0.166$ ,  $wR_2 = 0.189$ ; largest diff. peak and hole: 0.143 and -0.164 e Å<sup>-3</sup>; Crystallographic data were deposited in CSD under CCDC registration number 837496. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc. cam.ac.uk/data\_request/cif.

# 2.3. Computational details

The molecular geometry of the compound (**3**) was optimized by using the DFT method with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) and the 6-311G(d)+ basis set [47,48]. All calculations were performed with the Gaussian 03W [44] software package. The harmonic vibrational frequencies were calculated at the same level of the theory for the optimized geometry of the compound (**3**). Absence of the imaginary frequency indicated that the structure was in global minimum and obtained vibrational frequencies were scaled by 0.9613 [49]. Vibrational frequency assignments were done by using Gauss-view molecular visualization software [50]. Tight convergence criterions were used at the geometric optimization and frequency calculation. Electronic absorbtion properties were studied using time-dependent density functional theory (TD-DFT) with PCM (Polarized continuum model) at the same level of theory and basis set for 50 singlet transitions in DMSO.

#### 3. Results and discussion

3.1. Synthesis and spectroscopic characterization of the compound (**3**) via complementary techniques

The synthetic route of compounds (1-4) is depicted in Fig. 1. Nucleophilic aromatic nitro displacement reaction of 4-nitrophthalonitrile with base catalyst has been carried out by many scientists [14,43]. Generally, nucleophilic substitution of a nitro group from an activated aromatic substrate can be effectively conducted by variety of strong nucleophiles under dipolar aprotic conditions, for example in DMF or DMSO [43]. In this respect, initial phthalonitrile derivative (3) was obtained from reaction between compound (1) and 4-nitrophthalonitrile (2) in dry DMF at 55 °C. Dry K<sub>2</sub>CO<sub>3</sub> was used for supplying basic reaction condition. After the crystallization of compound (3), yield of the product was moderate. All spectral data supported the proposed structure (3). According to IR spectral data, new vibration that appeared at 2231 cm<sup>-1</sup> clearly indicated that structure (**3**) contains nitrile group. Detailed IR analysis (experimental and theoretical) for the compound (**3**) is given in Section 3.1. In  $^{13}$ C NMR of (**3**), the new peaks at 116,63 ppm and 116,11 ppm belonging to nitrile carbons were evidence of the substitution. Mass spectral analysis of compound (3) showed that target compound was successfully prepared. Stable molecular ion  $[M + H]^+$  peak was seen at 439.29 in mass spectra of the compound (3). Also elemental analysis data of compound (3) was satisfactory.

# 3.2. Description of the crystal and optimized structure of the compound (**3**)

The ORTEP plot of title compound is shown in Fig. 2. Selected bond lengths and bond angles of the structure and the DFT calculation are compared in Table 1. The compound crystallizes in the orthorhombic space group *Pbna* (no:60), with eight molecules in the unit cell. It consists of 4-(4,5-Diphenyl-1*H*-imidazol-2-yl)-phenol and phthalonitrile units. The bond lengths of cyano,  $C \equiv N$  in the structure are in range of 1.134–1.143 Å.

Imidazole and C16/C21 phenyl rings are not strictly planar. They are considerably strained due to the substituted units. Dihedral angle formed by LSQ-planes is  $21.51(2)^{\circ}$ . As shown in Fig. 3, in the crystal, the N–H N intermolecular hydrogen bonds are formed along the *b*-axis between the imidazole groups of neighboring molecules [N3…N4<sup>i</sup>; 2.931(4) Å, N3–H3N; 0.86 Å, N3…H3N–N4; 155°, symmetry code; (i) 1/2 + x,y, 1/2-z ].

Geometrical parameters obtained from the computational study are acceptable when compared with the crystallographic results except for N3–H bond length and some dihedral angle. While N3–H bond length was found 0.859 A in crystallographic study, it was calculated as 1.010 A. This difference in the N3–H bond length may have brought about different N3–H vibrational frequencies in the experimental and theoretical vibrational spectra (in section 3.3.1). Most probably, the difference between the theoretical and experimental N3–H bond length is caused by intermolecular hydrogen bonding and molecular packing that was not considered in the theoretical calculation.

#### 3.3. Assignments of the vibrational modes of the compound (3)

The theoretical vibrational spectrum of substituted phthalonitrile ligand (3) was calculated using B3LYP method with 6-311G(d)+basis set [47,48]. The theoretical results of the compound (**3**) were



Fig. 1. Synthetic route for novel compounds.

compared with the experimental results. The vibration band assignments were studied by using Gauss-View molecular visualization program [50]. The frequency values computed at the calculation level contain known systematic errors. Therefore, 0.9613 was selected as the scaling factor [49]. Selected theoretical and experimental vibrational data are shown in Table 2. Selected vibrational frequencies have good correlation with corresponding experimental results except for N3-H stretching vibration as can be seen in Fig. 4.

#### 3.3.1. *C*–*H* and *N*–*H* vibrations

The experimental and theoretical FT–IR spectra of the compound are shown in Fig. 5. Some imidazole derivatives in solid phase show crystal interactions in vibrational spectra. Because of these interactions, some frequencies can be different from the gas



Fig. 2. Crystal sturucture of the compound (3).

phase. Imidazole derivatives contain strong intermolecular hydrogen bonds in solid phase. Although free N–H stretching vibration was expected to be about  $3400 \text{ cm}^{-1}$ , N3–H stretching vibration shifts to aromatic C–H stretching range

 Table 1

 Some selected geometrical parameters compared with crystallographic data.

Bond lenght A	X-ray	Calc.	Bond angle (°)	X-ray	Calc.
N3-H	0.859	1.008	H-N3-C8	125.4	124.0
N3-C8	1.371	1.383	N3-C8-C7	104.8	104.5
N3-C15	1.361	1.369	N3-C15-N4	110.4	110.2
N4-C7	1.393	1.375	N4-C7-C8	109.9	109.7
N4-C15	1.328	1.319	N4-C7-C6	118.8	120.1
01-C22	1.360	1.363	01-C22-C27	115.5	115.5
01–C19	1.401	1.395	01-C19-C18	119.9	118.9
C8–C7	1.383	1.393	C7-C8-C9	134.5	134.8
C8–C9	1.470	1.468	C8-C7-C6	131.3	130.2
C7–C6	1.471	1.473	C7-C6-C5	121.4	122.2
C29-C25	1.436	1.427	C8-C9-C14	119.7	120.4
C29-N2	1.143	1.155	N3-C15-C16	124	124.6
C14-C9	1.392	1.404	C15-C16-C21	119.7	118.8
C16-C15	1.452	1.462	C29-C25-C24	119	119.8
C16-C17	1.368	1.402	C27-C22-C23	120	120.2
C26-C27	1.373	1.393	C10-C11-C12	119.8	119.5
C26-C28	1.436	1.431	Dihedralangle (° )	X-ray	Calc.
C25-C24	1.389	1.399	C19-01-C22-C27	-173.7	175.8
C17-C18	1.383	1.391	01-C19-C20-C21	-176.5	-174.7
C10-C11	1.385	1.390	C10-C9-C8-N3	141.2	136.5
C22-C27	1.378	1.397	C21-C16-C15-N4	21.2	8.4
C18-C19	1.374	1.389	C9-C8-N3-C15	-177.7	-176.7
C13–C12	1.371	1.393	C14-C9-C8-C7	147.1	140.6
C28-N1	1.134	1.154	C9-C8-C7-C6	-6.1	-5.2



Fig. 3. Unit cell of the compound (3) view down along the *b*-axis.

 $(3100-3000 \text{ cm}^{-1})$  because of the strong intermolecular hydrogen bonding causing polymeric association through imidazole rings [51,52]. The theoretical N–H stretching vibration was observed at 3506 cm<sup>-1</sup> because the theoretical vibration calculation was performed for a single molecule in vacuum media.

The aromatic structures show characteristic C–H stretching vibrations at 2900-3150 cm<sup>-1</sup> range. In the present study, there were many aromatic C–H stretching vibrations at around

# 3100–2900 range in the experimental IR spectra, the superimposition of the aromatic C–H stretching vibrations resulted in broad absorption band. Similarly, according to theoretical data, many aromatic C–H stretching vibrations as well known "group frequencies" were observed at around 3090–3034 cm<sup>-1</sup> [49,53].

The aromatic structures show C–H in plane bending and C–H out of plane bending vibrations in the range of 1300-1000 and 1000-750 cm<sup>-1</sup> respectively. C–H in plane bending

#### Table 2

Experimental and calculated vibrational assignments of the compound (3).

Vibrational mode	Vibrations (Exp). cm <sup>-1</sup>	Vibrations (theo.)	Intensity
		scaled 0.9613 cm <sup>-1</sup>	-
υ (N3–H)		3506	36.7
$v_{sym} C-H (C23-H) + (C24-H)$		3090	0.8
υ C–H (C27–H)		3089	1.0
υ <sub>sym</sub> C–H (C21–H)+ (C20–H)		3087	1.5
υ C–H (C14–H), (C13–H), (C12–H), (C11–H), (C10–H)	3057	3064	39.9
υ <sub>asym.</sub> C–H (C21–H), (C20–H)		3063	12.5
υ C–H (C5–H), (C4–H), (C3–H), (C2–H), (C1–H)	3049	3058	52.3
υ C–H (C14–H), (C13–H), (C12–H), (C11–H), (C10–H)		3053	25.6
u <sub>asym</sub> C–H (C1–H), (C2–H), (C4–H), (C5–H)		3045	15.4
υ <sub>asym</sub> C–H (C17–H), (C18–H)		3044	25.8
v C28≡N1 (meta position)		2251	21.3
v C29≡N2 (para position)	2231	2244	84.3
υ C=C (C17–C18), (C20–C21)		1590	93.1
υ C==C (C1-C2), (C4-C5)		1585	29.4
υ C==C (C10-C11), (C13-C14)		1582	41.7
v C = C (C23 - C24), (C26 - C27) + vC15 = N4 (imidazole ring)	1595	1574	374.2
υ C=C (C26–C25),(C22–C23),(C7–C8), $\nu$ C15 = N4 (imidazole ring) + $\beta$ (N3–H)	1563	1531	154.6
υ C=C (C19–C20), (C17–C16), (C7–C8) (C16–C15)	1542	1503	219.9
υ C==C (C26–C25) + β C–H (C14–H), (C13–H), (C12–H), (C11–H), (C21–H),	1482	1462	827.0
(С20–Н), (С17–Н), (С18–Н), (С27–Н), (С23–Н)			
Ar $\nu$ C=C (C27–C26) + $\beta$ C–H (C23–H)	1423	1393	190.0
υ C–O (O1–C22) + β C–H (C27–H),(C23–H), (C24–H)	1288	1259	669.2
β C–H (C27–H), (C24–H) + υ C–O (C22–O1)	1250	1224	1353.8
β C–H (C27–H), (C24–H) + υ C–O. (C19–O1)			
Phenyl ring breathing mode + $\upsilon$ (C7–N4) + $\beta$ C–H (C5–H), (C4–H), (C3–H),	1213	1185	767.7
(C2–H), (C10–H), (C11–H), (C3–H)			
β C–H (C17–H), (C18–H), (C21–H), (C20–H),(C27–H), (C23–H), (C24–H) +	1173	1149	161.6
β C–H (C17–H), (C18–H), (C21–H), (C20–H), (C1–H), (C3–H) (C4–H)	1087	1070	60.0
$(C13-H) + \beta(N3-H) + Ar C-C-C$ in plane bending			
$\beta$ C–H (C14–H), (C13–H), (C12–H), (C11–H), (C10–H), (C1–H) (C3–H) (C4–H) + $\beta$ (N3-H)	1062	1058	
Ar C–C–C in plane bending	1017	992	51.8
γ C–H (C27–H), (C23–H), (C24–H) + Ring breathing	953	934	195.4
ω C–H (C21–H), (C17–H), (C20–H), (C18–H)	857	835	180.0
γ С–Н (С27–Н), (С23–Н), (С24–Н)	833	814	138.6
γ C–H (C14–H), (C11–H), (C2–H), (C3–H), (C4–H)	767	747	267.3
$\omega$ (C6–C14) phenyl ring	696	681	255.3
$\omega$ (C15–C1) phenyl ring		678	264.2

v: stretching, $\beta$ : in plane bending,  $\gamma$ :out of plane bending,  $\omega$ : out of plane wagging.



Fig. 4. Correlation between experimental and calculated vibrational data of the compound (3).

vibrations were calculated at 1393, 1259, 1224, 1185, 1149, 1070 cm<sup>-1</sup>. The vibrations calculated at 934, 835, 814, 747 cm<sup>-1</sup> were assigned to C–H out of plane bending vibrations. All experimental C–H vibrations were in good agreement with the theoret-ical results [52,54–56].

# 3.3.2. C=C aromatic ring vibrations

Aromatic C=C stretching vibrations of the phenyl ring appeared in the range of 1625–1430 cm<sup>-1</sup>. In our study, the frequencies were observed at 1574, 1531, 1503, 1462, 1393 cm<sup>-1</sup> theoretically and at 1595, 1563, 1542, 1482, 1423 cm<sup>-1</sup> experimentally. Generally determination of the C=N aromatic vibrations are difficult; several vibrational types are seen in the region of the aromatic carbon–carbon ring vibration. C]C aromatic stretching vibrations calculated at a range of 1574–1393 cm<sup>-1</sup> were in good agreement with the experimental data at a range of 1595–1423 cm<sup>-1</sup>. Due to the dense C=C phenyl stretching vibrations, C=N stretching vibrations at 1574 and 1531 cm<sup>-1</sup> [52,54,57].



Fig. 5. Theoretical and experimental vibrational spectra of the compound (3).

The C–C–C in plane bending and ring breathing mode of benzene are observed at  $1010 \text{ cm}^{-1}$  and  $992 \text{ cm}^{-1}$ . These vibrations calculated at 1017 and 953 cm<sup>-1</sup> respectively were in agreement with the experimental results at 992 and 934 cm<sup>-1</sup> [54,56,58].

#### 3.3.3. *C*–*N* and *C*–*O* vibrations

The experimental C=N stretching mode was observed at 2230 cm<sup>-1</sup> as a single sharp band while in theoretical C=N stretching vibrations were observed as a sharp and intense band at 2244 and weak shoulder at 2251 cm<sup>-1</sup> [57]. The low intense band at 2251 cm<sup>-1</sup> was not observed in the experimental spectrum. The reason for this may be the proximity of the 2244 and 2251 cm<sup>-1</sup> bands causing them seem as a single band. Due to the dense C=C phenyl stretching vibrations, C=N stretching vibrations were observed together with C]C aromatic stretching vibrations at 1574 and 1531 cm<sup>-1</sup> [52,54,57].

 $C_{Ar}$ —O stretching vibrations calculated at the range of 1224–1149 cm<sup>-1</sup> were in good agreement with the experimental data and literature [57].

#### 3.3.4. Electronic absorption spectra of the compound (3)

Electronic absorption spectrum of the compound (**3**) was recorded in the 200–600 nm range in DMSO and absorption bands were observed at 224, 263 and 321 nm in UV region, respectively (Fig. 6). In order to explain electronic transition and to compare with the experimental spectrum, TD-DFT study was performed for 50 singlet transitions. The solvent effect on the theoretical electronic transitions was studied with the PCM (polarized continuum model) in DMSO. The computed electronic transition values, such as absorption wavelength, oscillator strengths and experimental values are given in Table 3. As can be seen in the theoretical and experimental results, since there is no transition in visible region, compound (3) is colorless. On the



Fig. 6. Theoretical and experimental UV-vis spectrum of the compound (3) in DMSO.

 Table 3

 Experimental and theoretical transitions and orbital contributions.

Experimental transitions		Theoretical transitions			
Wavelength (nm)	log ε	Wavelength (nm)	Oscillator strength	Electronic transition modes and orbital contributions	
224	4.43	220.2	0.3721	$\begin{array}{l} \text{H-4} \rightarrow \text{L+3 (19\%)} \\ \text{H-7} \rightarrow \text{L+2 (18\%)} \\ \text{H-6} \rightarrow \text{L (11\%)} \\ \text{H-5} \rightarrow \text{L+2 (7\%)} \end{array}$	
		220.8	0.1462	$H-4 \rightarrow L+3 (30\%)$ $H-3 \rightarrow L+3 (28\%)$ $H-4 \rightarrow L+2 (11\%)$	
		232.0	0.1712	$\begin{array}{l} H\text{-}3 \rightarrow L\text{+}1\ (27\%) \\ H\text{-}5 \rightarrow L\text{+}1\ (22\%) \\ H\text{-}6 \rightarrow L\text{+}1\ (11\%) \\ H\text{-}6 \rightarrow L\ (6\%) \\ H\text{-}6 \rightarrow L\ +2\ (5\%) \\ H\text{-}3 \rightarrow L\ +2\ (5\%) \end{array}$	
263	4.05	247.2 253.4	0.22 0.34	$H-1 \rightarrow L+2 (60\%)$ $H-1 \rightarrow L+2 (25\%)$ $H-1 \rightarrow L+1 (33\%)$	
321	4.23	303.8 (4.09ev) 326.7 (3.80ev) 332.3(3.74ev) 407.5 (3.05ev)	0.36 0.48 0.43 0.02	$\begin{array}{l} H \to L{+}3 \; (97\%) \\ H \to L{+}2 \; (83\%) \\ H \to L{+}1 \; (83\%) \\ H \to L{+}1 \; (89\%) \end{array}$	

contrary to the theoretical spectrum, absorbtion band about at 400 nm was not seen in experimental spectrum. This situation can be explained by very low oscillator strength of the corresponding transition [55].

The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) called as frontier orbitals determine the chemical reactivity of the compound. HOMO orbitals are nucleophilic center while LUMO orbitals are electrophilic center and the gap between the energy of HOMO and LUMO determine the chemical stability of the compound [58]. 3D plots of some important HOMOs and LUMOs of the compound (**3**) are shown in Fig. 7. As can be seen in Fig. 7, the HOMO orbital is localized on the phenyl and especially imidazole ring and LUMO orbital is localized on the phthalonitrile ring.

# 3.3.5. Synthesis of metal free (4) and metallophthalocyanines (5–8)

Although there are many synthetic methods for preparing substituted phthalocyanines in literature [59–62] authors generally prefer cyclotetramerization of substituted phthalonitrile or 1,3-diimino-1*H*-isoindoles [14,63]. Peripherally substituted phthalocyanines are prepared from the cyclotetramerization of 4-substituted phthalonitrile and non-peripherally substituted phthalocyanines are prepared from 3-substituted ones. Tetra substituted phthalocyanines prepared from either 4-substituted or 3-substituted phthalonitriles are obtained as a mixture of four different possible isomers (C<sub>4b</sub>, C<sub>2v</sub>, C<sub>s</sub> and D<sub>2b</sub>).

In this study, 4-substituted phthalonitrile (**3**) was used as the initial compound for synthesis of the metal-free- and metal-lophthalocyanines (Zn, Ni, Co, Cu) and no effort was given to separate the isomeric mixture. All new phthalocyanines were characterized by IR, <sup>1</sup>H NMR, mass spectrometry, elemental analysis and UV/Vis. All spectral data in Section 2 support the proposed structures (**4**–**8**). In the IR spectra of all novel phthalocyanines, the -C=N vibration of compound (3) disappeared, the absence of -C=N vibration in the phthalocyanine IR spectral data supports the proposed target structures. The rest of the spectra are similar to that of compound (**3**). The main difference between the IR spectral data of metal-free and metallophthalocyanines is the inner core -NH vibration for metal free phthalocyanine (4) that was observed at 3285 cm<sup>-1</sup>.



**Fig. 7.** Some important electronic transition of the compound (**3**).

The <sup>1</sup>H NMR spectra of (**7**) and (**8**) could not be determined because of the presence of paramagnetic cobalt and copper ions [64]. The <sup>1</sup>H NMR spectra of phthalocyanines (**4**), (**5**) and (**6**) were obtained in DMSO-*d*6 at room temperature. The spectra of the compounds were very similar. In <sup>1</sup>H NMR spectra, except for N–H protons of imidazole moieties, all protons were observed at aromatic region. For metal free phthalocyanine (**4**), imidazole N–H protons were observed at 11.19 ppm as a broad singlet and the typical shielding of inner core protons could not be observed due to the strong aggregation between phthalocyanine molecules [65]. For ZnPc (**5**) and NiPc (**6**) respectively, imidazole NH protons were observed at aromatic region. In addition, mass spectra and elemental analysis results of the compounds (**4**–**8**) were in good correlation with proposed structure.

# 3.3.6. UV-vis absorption spectra of the compound (4-8)

All of the phthalocyanines were soluble in most of the organic solvents such as chloroform, THF, dichloromethane, DMF, DMSO and pyridine. For the metallophthalocyanines (5-8) in DMSO, the Q bands caused by  $\pi \rightarrow \pi^*$  transitions were observed at 680, 672, 676 and 676 nm respectively (Figs. 8 and 9). The shoulders neighboring the Q band of these metallophthalocyanines were observed at: 612 for (5),606 for (6), 608 for (7) and 608 for (8). For Q band regions of metallophthalocyanines, the longer wavelength absorptions are due to the monomeric species and shorter wavelength absorptions (shoulders) are due to the aggregated species [66]. So, in DMSO at  $1 \times 10^{-5}$  mol dm<sup>-3</sup> concentration, monomeric behavior of metallophthalocyanines was proved by the dominance of the longer wavelength absorptions. The B bands arising from deeper  $\pi$  levels to LUMO were observed at: 357, 332, 352 and 342 nm for (5, 6, 7) and (8) respectively (Figs. 8 and 9). Differently from metallophthalocyanines, the Q band absorption of metal-free phthalocyanines splits into two strong absorption bands as  $Q_x$  and  $Q_y$  in visible region. In DMSO, the splitting Q band absorption of compound (4) was observed at 698 and 664 nm with shoulders at



Fig. 8. UV–vis spectra of compound (6), (7) and (8) in DMSO at  $1 \times 10^{-5}$  mol dm<sup>-3</sup>.

642 and 598 nm, which is an evidence of non-degenerate  $D_{2h}$  symmetry. Additionally, B-band of compound (**4**) was observed at 342 nm (Fig. 10).

Aggregation, usually defined as a coplanar association of rings from monomer to dimer or higher order complexes, is dependent on the concentration, nature of the solvent, nature and connection of the substituents, coordinated metal ions and temperature [67]. The aggregation behavior of the zinc(II)phthalocyanine (**5**) was investigated at different concentrations in DMSO and also in different solvents (Figs. 9 and 11). The intensity of *Q*-band maxima is directly proportional with the concentration and no new band that was sign of aggregation was observed. The zinc(II)phthalocyanine did not show aggregation and Beer–Lambert law was obeyed between the concentrations  $1.6 \times 10^{-5}$  and  $4 \times 10^{-6}$  mol dm<sup>-3</sup>(Fig. 9).

The absorbtion spectra of zinc(II) phthalocyanine (**5**) in different solvents at  $1 \times 10^{-5}$  mol dm<sup>-3</sup> concentration are shown in Fig. 11. In the absorbtion spectra of phthalocyanines; for monomeric species,



Fig. 10. UV–vis spectra of compound (4) in DMSO at  $1 \times 10^{-5}$  mol dm-3.

the Q band is observed as a sharp peak with a shoulder at the higher energy side, while for aggregated species, the shoulder shifts to red with increasing intensity and Q band is observed as a broad peak with lower intense. In consequence, ZnPc (**5**) showed monomeric behavior in DMSO, DMF, THF, pyridine and dioxane and aggregated in chloroform, benzene, 1,2-dichloroethane, dichloromethane and toluene at a concentration of  $1 \times 10^{-5}$  mol dm<sup>-3</sup> (Fig. 11).

Guttmans donor and acceptor number are used to explain lewis basicty and acidity of the solvents [68]. The aggregation behavior of the compound (**5**) in different solvents are closely related with donor and acceptor number. According to the spectroscopic data, aggregation was not observed in the solvents that donor number is higher than acceptor number. On the contrary, in solvents that acceptor number higher than donor number, aggregation was observed (Table 4). Possible causes for this situation is strong interaction between metal center (Zn) and solvent molecules with electron donor character.



Fig. 9. Absorption spectra of the compound (5) in DMSO at different concentrations.



**Fig. 11.** Absorption spectra of the compound (**5**) in different solvents. Concentration =  $1 \times 10^{-5}$  mol dm<sup>-3</sup>.

 Table 4

 Donor and acceptor number of some solvents [68].

Solvent	Donor number	Acceptor number	Compound ( <b>5</b> ) in solution
Pyridine	33.1	14.2	Non-aggregate
DMSO	29.8	19.3	Non-aggregate
DMF	26.6	16.0	Non-aggregate
Dioxane	14.3	10.3	Non-aggregate
THF	20.0	8.0	Non-aggregate
Dichlorometan	1.0	20.4	Aggregate
Toluene	0.1	8.2	Aggregate
Benzene	0.1	8.2	Aggregate
1,2-dichloroethane	0	16.7	Aggregate
Chloroform	0	23.1	Aggregate



Fig. 12. Spectral changes for the first protonation of compound (5) increasing concentration of  $H_2SO_4$  in DMSO.  $H_2SO_4$  concentrations as follows: 0.47, 0.94, 1.88, 2.35, 2.82 mol dm<sup>-3</sup>.

Zn(II) phthalocyanines ring system has four nitrogen atoms called "meso-nitrogens". These nitrogens can be protonated in acidic media. Mono-, di-, triprotonation of the nitrogen atoms cause decrease in the symmetry. The O band splits and a new band appears in the bathochromic region. Tetraprotonation of zinc phthalocyanine reverts back to D<sub>4h</sub> symmetry, but the Q band is still red shift. The shift of the Q band to red is an important property for photodynamic therapy (PDT) and photo sensing application. Peripherally substituted phthalocyanines isn't resistant against high concentration of sulfuric acid, so their "di-", "tri-", "tetra-" protonated forms cannot be prepared [69,70]. In our study, we investigated protonation behavior of the compound (5) by using sulfuric acid in DMSO. We studied on five different solutions containing  $10^{-6}$  M compound (5) and 0.47-0.98-1.88-2.35-2.82 M sulfuric acid respectively. As can be seen in Fig. 12, while the Q band intensity was decreasing, the intensity of the new bathochromic band was increasing because of the first protonation of the compound (5). When sulfuric acid concentration was increased above 2.82 M, compound (5) began to decompose so, di-, tri-, and tetra- protonation forms of compound (5) couldn't be obtained.

# 4. Conclusion

In this paper, we report the preparation of a new type of metal free and metallophthalocyanines (Zn, Ni, Co and Cu). At first stage, compound (**3**) was synthesized from a mixture of (**1**) and (**2**) (1:1) in the presence of DMF/K<sub>2</sub>CO<sub>3</sub> and obtained as single crystal form suitable for X-ray analysis. In addition, geometric structure of the compound (**3**) was optimized theoretically and compared with the X-ray crystallographic data. Vibrational assignments and electronic transitions of the compound (**3**) were calculated and compared with the experimental results. It was found that the theoretical results agreed with the experimental results. In the final stage, metal free and metallophthalocyanines were synthesized by the interaction of the compound (**3**) in DMAE/DBU and corresponding

metal salts. The structures of the new products (3-8) are characterized by elemental analysis, IR, UV-vis, <sup>1</sup>H NMR and Mass spectrometry. Furthermore, aggregation behavior of the compound (5) was researched in different solvents and also at different concentrations in DMSO. Substituted ZnPc (5) aggregated in chloroform, dichloromethane. 1.2-dichloroethane, benzene and toluene, while non-aggregated in DMSO, DMF, pyridine, THF, dioxane at  $1 \times 10^{-5}$  mol dm<sup>-3</sup> concentrations. The effect of the solvent donor and acceptor number to aggregation behavior of the compound (5) was investigated. It was observed that there was no aggregation in solvents of higher donor number. ZnPc (5) showed monomeric behavior between the concentrations of 4  $\times$   $10^{-6}$ and  $16\times 10^{-6}\,mol\;dm^{-3}$  in DMSO. The protonation behavior of the compound (5) in acidic media was studied at different sulfuric acid concentration in DMSO. The new band observed about at 720 nm in UV-vis spectrum of the compound (5) was evidence that one of the meso nitrogens on the phthalocyanine ring system was protonated. Once the concentration of the sulfuric acid in the solution was higher than 2.82 M, as expected, abnormal bands observed in the spectrum were signs of the decomposition of the compound (5).

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