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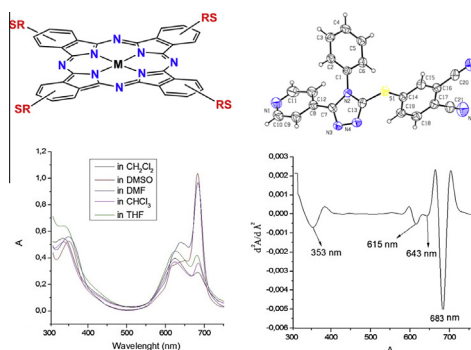
# Synthesis, aggregation and spectroscopic studies of novel water soluble metal free, zinc, copper and magnesium phthalocyanines and investigation of their anti-bacterial properties

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## HIGHLIGHTS

- The preparation of triazole substituted phthalonitrile.
- Synthesis of its corresponding metal free and metallophthalocyanines.
- The synthesis of quaternized phthalocyanine derivatives.
- The investigation of aggregation, thermal gravimetric and antibacterial properties.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, novel phthalonitrile derivative (**3**) was synthesized by the reaction between 4-nitrophthalonitrile (**2**) and a triazole derivative (**1**) containing pyridine moiety. Crystal structure of compound (**3**) was characterized by X-ray diffraction. New metal free and metallo-phthalocyanine complexes (Zn, Cu, and Mg) were synthesized using the phthalonitrile derivative (**3**). Cationic derivatives of these phthalocyanines (**5**, **7**, **9**, and **11**) were prepared from the non-ionic phthalocyanines (**4**, **6**, **8**, and **10**). All proposed structures were supported by instrumental methods. The aggregation behaviors of the phthalocyanines (**4–11**) were investigated in different solvents such as dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), chloroform and water. Water soluble cationic Pcs (**5**, **7**, **9**, and **11**) aggregated in water and sodium dodecyl sulfate was used to prevent the aggregation. The second derivatives of the UV-Vis spectra of aggregated Pcs were used for analyzing the Q and B bands of aggregated species. Thermal behaviors of the phthalocyanines were also studied. In addition, anti-bacterial properties of the phthalocyanines were investigated. We used four gram negative and two gram positive bacteria to determine antibacterial activity of these compounds. Compound **7** has the best activity against the all bacteria with 125 µg/mL of MIC value. Compounds **4**, **6**, and **10** have the similar effect on the bacteria with 250 µg/mL of MIC value.

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## Introduction

Phthalocyanines (Pcs) have many potential applications in many areas such as electrochemistry [1–6], chemical sensors [7,8], electrochromic devices, electrocatalysts [9], liquid crystals [10], antimicrobial agents and photodynamic therapy [11–14]. Insolubility is one of the most common problems in applications of Pcs. While non-substituted Pcs are insoluble in common organic solvents, non-ionic peripherally and non-peripherally Pcs mainly are soluble in DMSO, DMF, pyridine, tetrahydrofuran (THF) – slightly soluble methanol, ethanol, chloroform – and are not soluble in water, exceptionally polyethyleneglycol, carbohydrate, polyhydroxylated substituted Pcs [14]. Cationic (pyridinium) and anionic (carboxylate, sulfonate) forms of peripherally and non-peripherally Pcs usually are soluble in water. Synthesis of water soluble Pcs is important in terms of many technological applications. Another problem limiting the use of Pcs in tech-applications is aggregation phenomena resulting from co-planar interaction between the Pc rings. As a consequence of this interaction, monomeric Pcs change to their dimeric or higher order forms. Aggregation causing broadening and decreasing of the Q band absorption, depends on the concentration of solution, type of the solvent, nature of the substituent, the type of the metal ion in central cavity and temperature. [14–19].

In this work, novel peripherally substituted metal free, zinc, copper and magnesium Pc complexes bearing triazole moiety (**4**, **6**, **8**, **10**) and their cationic complexes (**5**, **7**, **9**, **11**) have been synthesized and investigated their spectroscopic properties, aggregation behaviors and thermal stabilities. The aim of this work is not only determination of aggregation behaviors of the novel Pc derivatives (**4–11**) and effect of sodium dodecyl sulfate (SDS) – anionic surfactant – on the aggregation behavior of them in water, but also are how to effect on bacterial growth or to determine their anti-bacterial activity.

## Experimental

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 [20], 4-Phenyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol (**1**) [21] and 4-nitrophthalonitrile (**2**) [22] 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 (δ) 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 spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. Methanol and chloroform 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. Thermal gravimetric analysis was performed with SI-TGA 6400 instrument in N<sub>2</sub> atmosphere and gas flow rate was set up to 20 ml/min. Temperature rate was set up to 10 °C /min. Melting points were measured by an electrothermal apparatus.

### Synthesis of the compounds (**3–11**)

#### 4-Phenyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-mercapto phthalonitrile (**3**)

4-Phenyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol (**1**) (0.81 g, 3.2 mmol) and 4-nitrophthalonitrile (**2**) (0.55 g, 3.2 mmol) were dissolved in dry N,N-dimethylformamide (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 vacuum. Residue was crystallized from acetone/petroleum ether solvent system. Pale yellow solid was obtained. Yield 0.86 g (70.6%), IR (ATR tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3098, 3070, 3037, 2228, 1582, 1546, 1493, 1460, 1428, 1364, 1328, 1315, 1288, 1257, 1215, 1126, 1071, 1007, 991, 916, 864, 838, 773, 739, 722, 689. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), (δ: ppm): 8.63–8.58 (d, 2H/Ar–H), 8.04–7.99 (t, 3H/Ar–H), 7.74–7.72 (d, 2H/Ar–H), 7.56–7.49 (m, 3H/Ar–H), 7.37–7.34 (d, 2H/Ar–H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>), (δ: ppm): 154.31, 150.63, 147.46, 141.73, 135.51, 134.76, 134.21, 133.89, 132.60, 132.30, 131.05, 130.36, 128.23, 122.23, 116.13, 116.02, 115.74. MS (ESI), (m/z): [M+H]<sup>+</sup> Calculated: 381.1 Found: 381.3.

#### General procedure for the synthesis of nonionic metal-free and metallophthalocyanines (**4**, **6**, **8**, **10**)

Compound (**3**) (0.38 g, 1 mmol), dry N,N-dimethylaminoethanol (DMAE) (4 ml), 1,8-diazabicyclo [4.5.0]undec-7-ene (DBU) (3 drops) and for metallophthalocyanines (MPcs) equivalent amounts of corresponding anhydrous metal salts (Zn(OAc)<sub>2</sub>, CuCl<sub>2</sub>, and MgCl<sub>2</sub>) were added in a schlenk tube. The mixtures were heated at reflux temperature for 24 h under N<sub>2</sub> atmosphere. Then the mixtures were refluxed in methanol (30 ml) to precipitate the products which were then filtered off. The green solid products were washed with hot ethanol acetone and diethyl ether and dried in vacuo. The raw products were purified by silica gel column chromatography.

*Metal free Pc (4)*. Elution solvent system: Chloroform: methanol (100:2) as eluent. Yield: 113 mg (30%). Calc. for C<sub>84</sub>H<sub>50</sub>N<sub>24</sub>S<sub>4</sub>: C, 66.21; N, 22.24; S, 8.42 Found: C, 66.01; N, 23.95; S, 7.88 IR (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 3288, 3057, 1601, 1497, 1429, 1327, 1007, 827, 746, 695. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), (δ: ppm): 8.42–8.32 (bm, 8H/Ar–H), 8.10–8.02 (bm, 16H/Ar–H), 7.84–7.68 (bs, 4H/Ar–H), 7.38–7.28 (bm, 16H/Ar–H), 7.10–7.24 (bs 4H/Ar–H). MS (ESI), (m/z): [M+H]<sup>+</sup>. Calculated: 1511.7 (100%); Found: 1512.8. UV-vis (CHCl<sub>3</sub>)  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 706 (5.09), 670 (5.05), 655 (4.71), 628 (4.57), 345 (4.92).

*Zn(II)Pc (6)*. Elution solvent system: chloroform: methanol (100:3) as eluent. Yield: 150 mg (37.8%). IR (ATR  $\nu_{\max}/\text{cm}^{-1}$ ): 3061, 1602, 1495, 1431, 1384, 1307, 1098, 908, 828, 749, 695. Calc. for C<sub>84</sub>H<sub>48</sub>N<sub>24</sub>S<sub>4</sub>Zn: C, 63.57; N, 21.18; S 8.08 Found: C, 63.48; N 21.49; S, 8.88 <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), (δ: ppm): 8.50–8.38 (bm, 8H/Ar–H), 8.12–8.02 (bm, 16H/Ar–H), 7.86–7.7 (bs, 4H/Ar–H), 7.42–7.30 (bm, 16H/Ar–H), 7.12–7.22 (bs 4H/Ar–H) MS (ESI), (m/z) [M+H]<sup>+</sup> calculated: 1585.3 (100%); found 1585.6. UV-vis (DMSO)  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 687 (4.98), 620 (4.72), 362 (4.98).

*Cu(II)Pc (8)*. Elution solvent system: chloroform:methanol (100:5) as eluent. Yield: 123 mg (31%). IR (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 3056, 1602, 1496, 1430, 1396, 1310, 1257, 1143, 1100, 919, 745, 691. Calc. for C<sub>84</sub>H<sub>48</sub>N<sub>24</sub>S<sub>4</sub>Cu: C 63.64; N 21.21; S, 8.09 Found: C 64.49; N, 21.12; S 8.42 MS (ESI), (m/z) [M+H]<sup>+</sup> calculated: 1584.3 100%; found 1584.4. UV-Vis (DMSO)  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 683 (4.97), 648 (4.69), 362 (4.70).

*Mg(II)Pc (10)*. Elution solvent system: chloroform:methanol (100:2) as eluent. Yield: 114 mg (28.5%). IR (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 3043, 1604, 1496, 1431, 1329, 1134, 1092, 1009, 970, 856, 828, 771, 748, 695. Calc. for C<sub>84</sub>H<sub>48</sub>N<sub>24</sub>S<sub>4</sub>Mg: C 65.26, N 21.74, S 8.30 Found: C 66.02, N 21.55, S 8.50. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), (δ: ppm): 8.36–8.22 (bm, 8H/Ar–H), 8.01–7.88 (bm, 20H/Ar–H), 7.38–7.29 (bm, 16H/

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