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# Selective Chemosensor Phthalocyanines for Pd<sup>2+</sup> ions; Synthesis, Characterization, Quantum Chemical Calculation, Photochemical and Photophysical properties

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# Selectivity of Chemosensor Phthalocyanines for Pd<sup>2+</sup> ions; Synthesis, Characterization, Quantum Chemical Calculation, Photochemical and Photophysical properties

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**Abstract:** In this study, ligand (1) was prepared by a nucleophilic displacement reaction of (4-bromophenyl)methanethiol with 4-nitrophthalonitrile according to literature and its novel type peripheral substituted tetra phthalocyanines [CuPc (2), ZnPc (3) and GaPc (4)] were prepared. The phthalocyanines obtained from compund (1) were characterized by FT-IR, <sup>1</sup>H-NMR, UV-Vis spectral data, elemental analysis, and MALDI-TOF. The novel phthalocyanines [CuPc (2), ZnPc (3) and GaPc (4)] were highly soluble in common organic solvents such as CHCl<sub>3</sub>, THF, CH<sub>2</sub>Cl<sub>2</sub>, DMSO and DMF. The effect of Pd<sup>2+</sup> ions on the fluorescence emission and UV-Vis spectra were performed with addition of increasing amounts of Pd<sup>2+</sup> ions. This functional phthalocyanines exhibited H-type aggregation versus Pd<sup>2+</sup> ions. Also, the molecular reactivity of the ligand (1) and related metallo phthalocyanines [CuPc (2), ZnPc (3) and GaPc (4)] were investigated and compared with the analysis of frontier molecular orbitals. In addition, photochemical and photophysical properties of these new phthalocyanines (fluorescence quantum yields, fluorescence behavior, singlet oxygen and photodegradation quantum yields) were studied in DMSO.

**Keywords**: Phthalocyanine, Metal sensor, Quantum Chemical Calculation, Photochemical, Photophysical

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#### 1. Introduction

Phthalocyanines (Pcs) are known not only as classical dyes in practical use but also as modern functional materials in scientific research and they have many extraordinary chemical and physical features based on an extensive delocalized  $18-\pi$  electron system [1]. Hence, the scientists have focused on the investigation of them for many decades in many fields such as chemical sensing [2], dye sensitized solar cells [3], electrochromic materials [4], nonlinear optics [5] and photodynamic therapy applications [6]. Nowadays, calculations such as measuring the photochemical and photophysical properties of phthalocyanines in order to investigate their roles in biological systems have been intensely carried out. These calculations are particularly important to test their usability in anticancer applications such as especially photodynamic therapy (PDT) which is a stimulating new approach to cancer treatment. Photodynamic therapy is a type of cancer treatment involving the use of photosensitisers (e.g. phthalocyanines) and a light source with singlet oxygen generation to kill cancer cells and shrink tumors [7, 8].

Phthalocyanines having attractive  $\pi$ - $\pi^*$  stacking interactions between their extended  $\pi$ -systems, tend to show high aggregation tendency in solution because of very low solubility **[9]**. The most important factor restricting phthalocyanines to find a usable application area is that their very low solubility in common solvents preventing the research for the chemical and physical properties of phthalocyanines for use in high technological applications such as the investigation of anticancer application **[10, 11]**. Their low solubility can be improved by attaching some functional groups such as long alkyl, alkoxy, phenoxy groups and crown ethers at peripheral and non-peripheral positions and/or by inserting some metal atoms in the inner core of ring **[12]**. The functional groups in phthalocyanine at peripheral or non-peripheral positions might exhibit a sensitivity to various metal ions such as Pd<sup>2+</sup> ions with the formation of H- or J-aggregates, causing significant changes in their optical properties. For decade, scientists have focused to develop various sensors for qualitative and quantitative detection of expensive or toxic metals by monitoring absorbance and fluorescent changes of phthalocyanines **[13, 14]**.

In this study, we have firstly made the synthesis of novel-type phthlocyanines [CuPc (2), ZnPc (3) and GaPc (4)] bearing "(4-bromophenyl)methanethiol" as functional groups at peripheral positions, creating it selective chemosensor for  $Pd^{2+}$  ions and then characterized by

elemental analysis, FT-IR, <sup>1</sup>H-NMR, UV-Vis and MS (Maldi-TOF) spectral data. Their aggregation behaviors and sensor properties for  $Pd^{2+}$  ions in the presence and absence of the other metal ions mixture[Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>] were studied by UV-Vis spectroscopy and fluorescence spectroscopy. Also, the molecular reactivity of the ligand (1) and related metallophthalocyanines were investigated and compared with the analysis of frontier molecular orbitals. Finally, We have investigated the effect of functional group "(4-bromophenyl)methanethiol" and the metal atoms [Zn(II) and Ga(III)] in the inner core of the ring on the photophysical and photochemical parameters of the phthalocyanines ZnPc (3) and GaPc (4) in DMSO (fluorescence lifetime and quantum yields, singlet oxygen and photodegradation quantum yields).

#### 2. Experimental

#### 2.1. Metarials and Methods

4-nitrophthalonitrile, (4-bromophenyl)methanethiol, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, GaCl<sub>3</sub>, Chloroform (CHCl<sub>3</sub>), Dimethylformamide (DMF), Methanol, tetrahydrofuran (THF), n-hexane, K<sub>2</sub>CO<sub>3</sub>, were purchased from commercial suppliers suh as Merck, Fluka, Aldrich and Alfa Aesar. The purity of the products were tested in each step by TLC. All reactions were carried out under a dry N<sub>2</sub> atmosphere. FT-IR spectra were recorded on a Perkin Elmer Spectrum two FT-IR (ATR sampling accessory) spectrometer. Fluorescence measurements were recorded by Hitachi S-7000 fluorescence spectrophotometer. Agilent Model 8453 diode array ultraviolet-visible (UV-Vis) spectrophotometer was used to take electronic spectra at room temperature. <sup>1</sup>H-NMR spectra were recorded on a Bruker 300 spectrometer instruments. Mass spectra were performed by MALDI SYNAPT G2-Si Mass Spectrometry.

#### 2.2. Photophysical and Photochemical Parameters

#### 2.2.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields ( $\Phi_F$ ) were determined in DMSO by the comparative method using by equation (1) [15, 16]

(1)

$$\Phi_{\rm F} = \Phi_{\rm F}({\rm Std}) \frac{{\rm F.A_{\rm Std.}n}^2}{{\rm F}_{\rm Std}.{\rm A.n}_{\rm Std}^2}$$

where F and  $F_{Std}$  are the areas under the fluorescence emission curves of the samples (4) and (5) and the standard, respectively. A and  $A_{Std}$  are the respective absorbances of the samples and standard at the excitation wavelengths, respectively.  $n^2$  and  $n_{Std}^2$  are the refractive indices of solvents used for the samples and standard, respectively. Unsubstituted ZnPc ( $\Phi_F = 0.20$ ) [17] was employed as the standard in DMSO. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

#### 2.2.2. Singlet oxygen quantum yields

Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) determinations are carried out using the experimental setup described in literature in DMSO [18-20]. Typically, a 3 mL portion of the respective standard ZnPc and sample (4-6) solutions (C= 1x10<sup>-5</sup> M) containing the singlet oxygen quencher was irradiated in the Q band region with the photoirradiation set-up described in the references [18-20].  $\Phi_{\Delta}$  values were determined in air using the relative method with ZnPc as standard in DMSO. 1,3-Diphenylisobenzofuran (DPBF) was used as chemical quencher for singlet oxygen. Equation (2) was employed for the determination of  $\Phi_{\Delta}$  values:

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}}$$
(2)

where  $\Phi_{\Delta}^{\text{Std}}$  is the singlet oxygen quantum yields for the standard ZnPc ( $\Phi_{\Delta}^{\text{Std}} = 0.67$  in DMSO) [21] and R and R<sub>std</sub> are the DPBF photobleaching rates in the presence of the respective samples (4-6) and standard, respectively. I<sub>abs</sub> and I<sup>std</sup><sub>abs</sub> are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by quencher (DPBF) in the presence of singlet oxygen, the concentration of quencher (DPBF) was lowered to ~3x10<sup>-5</sup> M [22]. Solutions of sensitizer (C= 1x10<sup>-5</sup> M) containing quencher (DPBF) were prepared in the dark and irradiated in the Q band region. DPBF degradation at 417 nm was monitored. The light intensity 6.21x10<sup>15</sup> photons s<sup>-1</sup> cm<sup>-2</sup> was used for  $\Phi_{\Delta}$  determinations.

#### 2.2.3. Photodegradation quantum yields

Photodegradation quantum yield ( $\Phi_d$ ) determinations are carried out using the experimental set-up described in the literature [18-20]. Photodegradation quantum yields were determined using equation (3) in DMSO.

$$\Phi_{d} = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{abs} \cdot S \cdot t}$$
(3)

where  $C_0$  and  $C_t$  are the samples concentrations before and after irradiation, respectively. V is the reaction volume,  $N_A$  the Avogadro's constant, S the irradiated cell area and t the irradiation time,  $I_{abs}$  is the overlap integral of the radiation source light intensity and the absorption of the samples. A light intensity of 2.17x 10<sup>16</sup> photons s<sup>-1</sup> cm<sup>-2</sup> was employed for  $\Phi_d$  determinations.

### 2.3. Quantum Chemical Calculation Method

Density Function Theory in complex calculations is widely used in recent studies. In the present study, DFT and HF calculations were carried out using Gaussian 9.0 Program [23]. In put files of studied molecules were prepared with Gauss View 5.0.8 [24]. All the calculations made were done by using B3LYP [25] and HF [26] basis sets in TÜBİTAK-TR Grid. All the atoms in the calculations were calculated in the sto-3g, 3-21 and lanl2dz sets. As it is well known the chemical reactivity of the molecules studied can be interpreted by looking at expressions such as chemical hardness ( $\eta$ ), electronegativity ( $\chi$ ), and chemical potential ( $\mu$ ) [27-36]. In the conceptual this theory, mentioned chemical properties are given as:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu(r)} \chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu(r)}$$
(4)

$$\eta = \frac{1}{2} \left( \frac{\partial E}{\partial N} \right)_{\nu(r)} = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{\nu(r)} \eta = \frac{1}{2} \left( \frac{\partial E}{\partial N} \right)_{\nu(r)} = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{\nu(r)}$$
(5)

As it is well-known ionization energy is the negative of the highest occupied molecular orbital energy and electron affinity is the negative of the lowest unoccupied molecular orbital energy.

$$\mu = \frac{E_{LUMO} + E_{HOMO}}{2} \quad \mu = \frac{E_{LUMO} + E_{HOMO}}{2} \tag{6}$$
$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad \eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{7}$$

The global electrophilicity index ( $\omega$ ) introduced are defined via eqn (8) by Parr et al. Using this index, it can be said that the electrophilic force of a chemical compound is related to electronegativity and chemical hardness. Nucleophilicity ( $\epsilon$ ) which is the inverse of the electrophilicity, is given via eqn (9).

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}$$

$$\varepsilon = \frac{1}{\omega} \varepsilon = \frac{1}{\omega}$$
(8)
(9)

#### 2.4. Synthesis

#### 2.4.1. 4-(4-bromobenzylthio)phthalonitrile (1)

This compound was prepared according to litrature [37].

#### 2.4.2. [Cu] 2(3), 9(10), 16(17), 23(24) – Tetrakis-(4-bromobenzylthio)phthalocyanine (2)

The compound (1) (0.150 g, 0.46 mmol) and DBU (0.05 cm<sup>3</sup>) in hexanol (5 mL) was pulverized and heated with stirring at 120 °C for 30 minutes under N<sub>2</sub> atmosphere, then anhydrous CuCl<sub>2</sub> (0.030 g, 0.22 mmol) was added to the reaction medium. The temperature was raised to 150 °C and stirring for 6h. When the reaction is complete, the product was cooled to room temperature, and the solid was washed with hexane acetonitrile and MeOH to remove impurities. The green-blue product was isolated by silica gel column chromatography with CHCl<sub>3</sub>-MeOH (50/2 v/v) as eluent and then dried in vacuum. The novel phthalocyanine

[CuPc (2)] is soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMSO, THF and DMF. Yield 0.070 g (45.20%), Anal. calcd. for C<sub>60</sub>H<sub>36</sub>Br<sub>4</sub>CuN<sub>8</sub>S<sub>4</sub> (1380 g/mol): C, 52.21; H, 2.63; N, 8.12; S, 9.29. Found: C, 53.04; H, 2.96; N, 8.16; S, 9.13. FT-IR (KBr): v, cm<sup>-1</sup> 3053 (Ar-H), 2968, 2902 (Aliph-H), 1599, 1506, 1485, 1363, 1140, 1067, 1057, 1010 772, 743. UV-vis (THF):  $\lambda$ max, nm 687 (Q), 622 (n- $\pi$ \*, sh), 347 (B). MS (MALDI-MS, 2,5-dihydroxybenzoic acid as matrix): 1382.5 [M+H]<sup>+</sup>.

# 2.5.3. [Zn] 2(3), 9(10), 16(17), 23(24)-Tetrakis-(4-bromobenzylthio)phthalocyanine (3)

The compound (1) (0.150 g, 0.46 mmol) and DBU (0.05 cm<sup>3</sup>) in hexanol (5 mL) was pulverized and heated with stirring at 120 °C for 30 minutes under N<sub>2</sub> atmosphere, then anhydrous Zn(Acac)<sub>2</sub> (0.030 g, 0.22 mmol) was added to the reaction medium. The temperature was raised to 150 °C and stirring for 6h. When the reaction is complete, the product was cooled to room temperature, and the solid was washed with hexane acetonitrile and MeOH to remove impurities. The green-blue product was isolated by silica gel column chromatography with CHCl<sub>3</sub>-MeOH (50/2 v/v) as eluent and then dried in vacuum. The novel phthalocyanine [ZnPc (**3**)] is soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMSO, THF and DMF. Yield 0.074 g (47.50 %), Anal. calcd. for C<sub>60</sub>H<sub>36</sub>Br<sub>4</sub>ZnN<sub>8</sub>S<sub>4</sub> (1382 g/mol):C, 52.13; H, 2.63; N, 8.11; S, 9.28. Found: C, 52.57; H, 2.91; N, 8.23; S, 9.35. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 7.78–7.65 (m, 12H, Pc–H), 7.41–7.10 (m, 16H, Ar–H), 3.68 (s, 8H S-CH<sub>2</sub>–Ar). FT-IR (KBr): v, cm<sup>-1</sup> 3051 (Ar-H), 2922, 2872(Aliph-H), 1708, 1642 1597, 1484, 1438, 1302, 1233, 1132, 1068, 1035, 759, 742, 649. UV-vis (THF):  $\lambda$ max, nm 688 (Q), 620 (n- $\pi$ \*, sh), 358 (B). MS (MALDI-MS, 2,5-dihydroxybenzoic acid as matrix): 1383.8 [M+H]<sup>+</sup>.

### 2.5.4. [Ga] 2(3),9(10),16(17),23(24)-Tetrakis-(4-bromobenzylthio)phthalocyanine (4)

The compound (1) (0.150 g, 0.46 mmol) and DBU (0.05 cm<sup>3</sup>) in hexanol (5 mL) was pulverized and heated with stirring at 120 °C for 30 minutes under N<sub>2</sub> atmosphere, then anhydrous GaCl<sub>3</sub> (0.030 g, 0.17 mmol) was added to the reaction medium. The temperature was raised to 150 °C and stirring for 6h. When the reaction is complete, the product was cooled to room temperature, and the solid was washed with hexane acetonitrile and MeOH to remove impurities. The green-blue product was isolated by silica gel column chromatography with CHCl<sub>3</sub>-MeOH (50/2 v/v) as eluent and then dried in vacuum. The novel phthalocyanine

[GaPc (4)] is soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMSO, THF and DMF. Yield 0.052 g (32.60%), Anal. calcd. for C<sub>60</sub>H<sub>36</sub>Br<sub>4</sub>ClGaN<sub>8</sub>S<sub>4</sub> (1422 g/mol): C, 50.68; H, 2.55; N, 7.88; S, 9.02. Found: C, 51.11; H, 2.62; N, 7.85; S, 9.14. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ ppm: 7.85–7.68 (m, 12H, Pc–H), 7.43–7.19 (m, 16H, Ar–H), 3.73 (s, 8H S-CH<sub>2</sub>–Ar).FT-IR (KBr): v, cm<sup>-1</sup> 3052 (Ar-H), 2921, 2896 (Aliph-H), 1723, 1598, 1485, 1453, 1335, 1310 1123, 1068, 1010, 819, 765, 743. UV-vis (THF):  $\lambda$ max, nm 704 (Q), 637 (n-π\*, sh), 361 (B). MS (MALDI-MS, 2,5-dihydroxybenzoic acid as matrix): 1388.7 [M-CI+H]<sup>+</sup>.

#### 3. Results and discussion

### 3.1. Synthesis and spectroscopic characterization

As the first lietrature, step in this study, according to ligand, 4-(4bromobenzylthio)phthalonitrile and its new type copper, zinc, and gallium metallophthalocyanines (2-4) were synthesized. The new type phthalocyanines [CuPc (2), ZnPc (3) and GaPc (4)] were successfully accomplished by heating anhydrous CuCl<sub>2</sub>, ZnCl<sub>2</sub> and GaCl<sub>3</sub> metal salt with 4-(4-bromobenzylthio)phthalonitrile at 150-155 °C under N<sub>2</sub> atmosphere in the presence of DBU for 6h (Scheme 1).

The structure of phthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) was verified by using some spectroscopic methods such as UV-Vis, FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI-MS as well as by elemental analysis. All the obtained results are compatible with the expected phthalocyanine structures.

After the cyclotetramerization reaction of 4-(4-bromobenzylthio)phthalonitrile, the disappearance of the sharp  $-C\equiv N$  vibration at 2229 cm<sup>-1</sup> proved the formation of the phthalocyanines (2-4). The FT-IR spectra of phthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) are similar outside of small stretching shifts (Fig. 1).

In UV-Vis spectra of the new synthesized phthalocyanine complexes (CuPc (2), ZnPc (3) and GaPc (4)), some characteristic absorptions were observed in the Q-band region (650-700 nm) arising from the  $\pi$ - $\pi$ \*transition from the HOMO to the LUMO of the Pc ring and in the B band region (300-400 nm) due to the deeper  $\pi$ - $\pi$ \*transitions. The Q-band absorptions of  $\pi$ - $\pi$ \* transition for all phthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) in THF were observed as

a single band of high intensity at 686, 687, 704 nm respectively. There was also a shoulder at the slightly higher energy side of the Q band for each phthalocyanine at 623, 621, 637 nm respectively (**Fig. 2**). The novel phthalocyanines [CuPc (**2**), ZnPc (**3**) and GaPc (**4**)] were also characterized by mass spectrometry. Mainly protonated ion peak of (**2**), (**3**) and (**4**) were apperared at high intensity. They are compatible with the calculated values in (**Fig. S1-S3**).

#### 3.2. Aggregation Studies

It has been well known that they have aggregation behavior since the research for phthalocyanine. Aggregation can be modified by changing some properties such as solvents, concentration, nature of functional group and temperature. The aggregation behaviors of CuPc (2), ZnPc (3) and GaPc (4) in the solvents were investigated by UV-vis spectroscopy at different concentrations. Figure 3 exhibits the UV-vis spectrum of the ZnPc (3) and GaPc (4) at different concentrations in THF as an example. These results proved that the formation of monomeric species in THF as a result of the observitaon of a single Q bands for the ZnPc (3) (Fig. 3A) and GaPc (4) (Fig. 3B). While the concentrations of CuPc (2), ZnPc (3) and GaPc (4) were increasing, the O band intensities increased. No new band formation was observed because of the aggregated species. The pH dependency on aggregation properties was also investigated. Aggregation behaviors of ZnPc (3) and GaPc (4) in THF were recorded by UVvis spectroscopy in various pH values. During the titration of ZnPc (3) with acid, the Q band intensity decreased and new aggregation bands were appeared at 651 and 734 nm. During the titration of ZnPc (3) with base, the Q band intensity did not significantly decrease, but the new aggregation band was appeared near the 750 nm (Fig. S4). During the titration of GaPc (3) with acid, the Q band intensity decreased and new band formation was not observed. During the titration of GaPc (3) with base, the Q band completely disappeared when the pH value exceeded 9 and a new band formation was not observed. (Fig. S5).

# **3.3.** Pd<sup>2+</sup> ions binding titration studies

It is well known that phthalocyanines substituted with appropriate functional group might exhibit optical sensitivity to metal ions [9]. In this study, it was investigated by UV-Vis spectroscopy whether or not the new synthesized phthalocyanines were optically sensitive to

 $Pd^{2+}$  ions. Thus, the effect of  $Pd^{2+}$  ions on CuPc (2), ZnPc (3) and GaPc (4) were studied by monitoring the absorbance changes in the UV-Vis spectra.

Each binding titration studies was carried out by addition of a solution of  $Pd^{2+}$  ions dissolved in MeOH in to the phthalocyanines solutions in MeOH/THF (10/90, v/v). The concentration of the metal salt was selected as a 10<sup>-6</sup> mol cm<sup>-3</sup>, while the concentration of metallo phthalocyanine was selected as a 10<sup>-8</sup> mol cm<sup>-3</sup>. The high concentration of the metal salt was selected to eliminate the absorption decreases of the bands due to the dilution.

After the addition of  $Pd^{2+}$  ions to the CuPc (2), ZnPc (3) and GaPc (4) solutions at room temperature, a color change from green to light-green happened. This proved that the formation of aggregated species between the phthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) and Pd<sup>2+</sup> ions.

Due to aggregated species, the solubility of metallophthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) decreased at the end of the titration compared to the monomeric species (Fig. 4).

As shown in **Fig. 4**, the Q, B and shoulder band absorptions effected as a result of the interaction of  $Pd^{2+}$  ions with the S-donor atoms in the metallophthalocyanines. While the Q band absorption intensities of the monomeric species (at 687 nm for (2), 688 nm for (3) and 704 nm for (4)) were decreasing by the addition of  $Pd^{2+}$  ions gradually, the absorption intensities of the aggregated species enhanced simultaneously (at 642 nm for (2), 646 nm for (3) and 670 nm for (4)). **Fig. 4** show that the binding of  $Pd^{2+}$  to the donor atoms of metallophthalocyanines (CuPc (2), ZnPc (3) results in pronounced effects on the Q- and B-bands in the UV–vis spectrum. This is due to the metal cation binding capability of the functional sulfur chains [12-14]. (Scheme 2)

The changes in the monomer and aggregation band intensity of metallophthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) were monitored as a function of mole amounts of Pd<sup>2+</sup>ions versus molar extinction coefficients ( $\epsilon$ ) (**Fig. 4**). Binding ratios of metallophthalocyanines (CuPc (2), ZnPc (3) and GaPc (4)) with Pd<sup>2+</sup>ions were found as 1:2, 1:2 and 1:1,5, respectively.

Competitive studies of ZnPc (3) and GaPc (4) towards metal mixture  $[Ag^+, Cd^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}]$  in the presence and absence of Pd<sup>2+</sup> ions were carried out. The effect

of Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> ions on ZnPc (**3**) and GaPc (**4**) were studied by monitoring the absorbance changes in the UV-Vis spectra. As expected, during the titration with these metal ions, there was not observed to be significant change in the Q band intensity of (**3**) and (**4**) (**Fig. S6-Fig. S23**). But, new metallophthalocyanines (**ZnPc (3)** and **GaPc (4**)) demonstrated a highly selectivity towards Pd<sup>2+</sup>ions in both the presence and absence of competitive metal ions such as Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> (**Fig. 5**).

#### **3.4. Fluorescence measurements**

#### 3.4.1. Fluorescence spectra and fluorescence quantum yields

Fluorescence behaviors of the ZnPc (3) and GaPc (4) were investigated in DMSO at room temperature (Fig. 6A and 6B). The ZnPc (3) and GaPc (4) exhibited emission at 704 and 721 nm upon excitation at 620 and 637 nm, respectively (Table 1). The observed Stokes shifts of ZnPc (3) and GaPc (4) are 11 and 13 nm, respectively. As seen in Fig. 6, the excitation spectra were similar to absorption spectra in the complexes. The fluorescence spectra were mirror images of the excitation spectra for ZnPc (3) and GaPc (4). The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for all complexes recommends that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMSO [38, 39]. Complex (2) did not show fluorescence properties due to paramagnetic nature of Cu<sup>+2</sup> ion in Pc core. The fluorescence quantum yields ( $\Phi_F$ ) of the complexes 3 and 4 were studied in THF and the fluorescence quantum yields ( $\Phi_{\rm F}$ ) values were given in **Table 1**. The fluorescence quantum yields ( $\Phi_{\rm F}$ ) values of complexes 3 and 4 are 0.14 and 0.61 respectively. Considering metal effects on  $\Phi_{\rm F}$  values, ZnPc (3) showed the lower value (0.14) than GaPc (4) ( $\Phi_{\rm F}=0.61$ ) due to metal effect. The peripheral tetra-substituted Ga(III)Pc (4) shows marginally larger  $\Phi_{\rm F}$  values among the investigated Ga(III)Pcs. [40-44]. The pH dependency on fluorescence behaviors of the complexes 3 and 4 was also investigated in THF at room temperature. The fluorescence emission spectra of ZnPc (3) decreased when pH > 9 and pH < 6. No significant changes in fluorescence emission values were observed at pH 7, 8 and 9 (Fig. S24). The fluorescence emission spectra of GaPc (3) decreased when pH changed from 7 to 2. But, the fluorescence emission spectra of GaPc (3) sharply decreased when pH>9 (Fig. S25).

#### 3.4.2. Photochemical properties

Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) is a demonstration of singlet oxygen generation which is highly important for photocatalytic application such as PDT study. The  $\Phi_{\Delta}$  values were calculated using eq. (2). Singlet oxygen quantum yields were studied in DMSO as a chemical method by using 1, 3-diphenylisobenzofuran, (DPBF) as singlet oxygen quencher. Fig. 7 shows spectral changes observed during photolysis of complex 3 and 4 in DMSO in the presence of DPBF. The disappearance of DPBF was viewed by UV-Vis spectroscopy. The rate at which the DPBF degrades is related to the generation of singlet oxygen. Any change was not observed in the Q band intensities during the  $\Phi_{\Delta}$  assignments, verifying that compounds were not degraded during singlet oxygen studies [45]. The  $\Phi_{\Delta}$  values for 3 and 4 are 0.72 and 0.35 in DMSO. While the  $\Phi_{\Delta}$  value of zinc complex is higher than unsubstituted ZnPc ( $\Phi_{\Delta}$ = 0.67), gallium complex is lower than unsubstituted Ga(III)Pc ( $\Phi_{\Delta}$ = 0.41) in DMSO [46]. Insertion of 4-bromobenzylthio groups on the Pc rings increases the efficiency of singlet oxygen creation for 3 in DMSO. Besides, the highs  $\Phi_F$  value of complex 4 causes quenching of singlet oxygen generation by the metal ion effect. The amount of singlet oxygen produced by a photosensitizer is arranged by the efficiency of a spin-forbidden electronic transition from a singlet to a triplet state (ISC). The introduction of a larger and heavy atom into Pc core is known to have an influence over the rates of the ISC and is termed the heavyatom effect. A larger heavy-atom effect of Zn ion for complex 3 can be induced that, depending upon other possible competing photophysical pathways, may translate into increased singlet oxygen production [47].

Photodegradation is a process where phthalocyanine as photosensitizer is degraded under light irradiation owing to singlet oxygen attack. The stability of MPc is mostly required in the body at a fitting under light. The photodegradation stabilities of complexes **3** and **4** were determined in DMSO by monitoring the decrease in the intensity of the Q band under irradiation with increasing time (**Fig 8 for 3**). The photodegradation quantum yield ( $\Phi_d$ ) values for the complexes listed in **Table 1** are of the order of  $10^{-5}$ . Stable ZnPc molecules show values as low as  $10^{-6}$  and for unstable molecules, values of the order of  $10^{-3}$  have been reported [**48**]. The order of stability among the substituted complexes was **4** > **3** in DMSO.  $\Phi_d$  of Pc complexes (**3** and **4**) show good stability under the light applied which is very important for efficiently singlet oxygen formation.

# 3.4.3. Fluorescence quenching studies of ZnPc (3) and GaPc (4) by Pd<sup>2+</sup> ions.

The effect of  $Pd^{2+}$  ions on the fluorescence emission of ZnPc (3) and GaPc (4) were investigated upon addition of increasing amounts of Pd<sup>2+</sup> ions and the fluorescence spectra were recorded in THF. ZnPc (3) and GaPc (4) show maximum emissions at 704 and 721 nm after excitation at 685 nm and 700 nm, respectively (Fig. 9). The titration with increasing amounts of  $Pd^{2+}$  ions influenced the emission spectra of ZnPc (3) and GaPc (4) by causing the blue shift quenching of fluorescence intensity, which can be used as a selective chemosensor for  $Pd^{2+}$  ions. The alkyl thia units of ZnPc (3) and GaPc (4) having donor sulphur atoms in their structures are possible interaction sites for  $Pd^{2+}$  ions [49]. This change in fluorescence response of ZnPc (3) and GaPc (4) exhibits that the H-aggregation of ZnPc (3) and GaPc (4) also plays a major role on fluorescence quenching, indicating the complex formation between Pd<sup>2+</sup> ions and the metallophthalocyanine [ZnPc (3) and GaPc (4)] [50]. It is well-known that J-aggregates of phthalocyanines are fluorescent whereas H-aggregates are not. In Haggregates, the lower state is much stabilized. So the transition from the excited state to the ground state is very fast and happens mostly between the excitonic bands with vanishing dipole moments as a result of which most of the energy losses are non radiative like thermal losses. Due to this reason the H-aggregates have very low florescence which is difficult to measure by regular techniques [51, 52]. Competitive studies of ZnPc (3) and GaPc (4) towards metal ion mixture [Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>] in the presence and absence of Pd<sup>2+</sup>ions were carried out. The effect of Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>ions on ZnPc (3) and GaPc (4) were studied by fluorescence spectra in THF. As expected, during the titration with these metal ions, there was not observed to be significant change in the fluorescence intensity of ZnPc (3) and GaPc (4). Some related figures were given in Fig. S26-S31. At the same time, addition of metal mixture on ZnPc (3) and GaPc (4) did not lead to the fluorescence quenching in the emission spectrum (Fig. 10). But, the presence of Pd<sup>2+</sup> ions and metal ion mixture led to significant fluorescence quenching of ZnPc (3) and GaPc (4) (Fig. 10). So, the new metallophthalocyanines (ZnPc (3) and GaPc (4)) may be said to be a highly selectivity towards Pd<sup>2+</sup>ions in both the presence and absence of competitive metal ions such as  $Ag^+$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Hg^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$  (**Fig. 10**).

#### 3.5. Quantum chemical calculation results

The obtained result via quantum chemical studies in this study are given in detail below by Gaussian Soft Ware. Chemical reactivity parameter such as  $E_{HOMO}$ ,  $E_{LUMO}$ ,  $\Delta E$  (HOMO-

LUMO energy gap), chemical hardness, softness, electronegativity, proton affinity, electrophilicity and nucleophilicity are a very important parameter in the theoretical calculations. These parameters are useful tools to compare activity of molecules.

In this study, the molecular reactivity of the molecules studied was investigated and compared with the analysis of frontier molecular orbitals. There are two frontier molecular orbitals, namely HOMO and LUMO. HOMO is Highest Occupied Molecular Orbital and LUMO is lowest unoccupied molecular orbital. The energy of HOMO is related to the electron donor ability of the molecule. HOMO's high energy value indicates that tends to give electrons to molecules with low energy and empty molecular orbitals. If the molecules have higher HOMO energy value, the molecules have more electron donating ability. On the other hand, the value of the LUMO energy shows the ability of electron accepting. The energy value of LUMO is related to the electron acceptability of the molecules have lowest LUMO energy value, the molecules have more electron accepting ability.

In consideration of previous exploitations, The HOMO-LUMO energy gap ( $\Delta E$ ) is the difference between the LUMO of the metal and the HOMO of the ligand. The energy gap value is a very important parameter that is indicated molecular reactivity. The molecule with the lower energy gap value is more reactive. If the HOMO value of the ligand is assumed to be constant, the complex formed with the ligand of metal atoms with the smaller LUMO value is formed more easily [53]. As a result of calculated HOMO and LUMO energy levels given for studied compounds in table 2 and table 3. Furthermore, the order of increasing reactivity is: GaPc (4)>CuPc (2)>ZnPc (3).

Chemical hardness Chemical hardness is defined the resistance against electron cloud polarization or deformation of chemical species [54]. Hard and soft Acid-Base (HSAB), which is based on the concept of chemical hardness, is a very useful method to predict the direction of chemical reactions [55, 56]. As a result of the Koopman theory [57], both softness and hardness are explained using HOMO and LUMO orbital energy values. When molecular hardness increases, electron donation becomes more difficult. On the other hand, soft molecules are good active molecule, because soft molecules very easy donation electron.

The electrophilicity index ( $\omega$ ) indicates the tendency of the active molecule to accept the electrons. The electrophilicity index is a very important parameter that is frequently used in

the analysis of chemical reactivity of molecules. Nucleophilicity ( $\epsilon$ ) is physically the inverse of electrophilicity ( $1/\omega$ ). As it is well known that a molecule that has large electrophilicity value isn't active molecule against metal atom while a molecule that has large nucleophilicity value is active molecule.

Electronegativity is an important parameter that gives information about the reactivity of the molecules. As the electronegativity value of the ligands increases, the ligand attracts more of its electrons. If electronegativity of the molecule has the highest value, reactivity of this molecule is the lowest. Because molecules have high electronegativity values give difficult electrons.

The Gibbs free energy  $(\Delta G)$  was calculated using below equation:

$$\Delta E = E_{\text{M-Lcomplex}} - \left[ E_{\text{M2+}} + 4 \sum E_{\text{Ligand}} \right]$$
$$\Delta E = E_{\text{M-Lcomplex}} - \left[ E_{\text{M2+}} + 4 \sum E_{\text{Ligand}} \right]$$
(10)

where  $E_{M-Lcomplex} E_{M-Lcomplex}$  is the energy of the metal complex,  $E_{Ligand} E_{Ligand}$  is the energy of the ligand and  $E_{M2+} E_{M2+}$  is energy of the metal ion [58]. The Gibbs free energy ( $\Delta G$ ) has three possibilities for the numerical value. The first state, if the Gibbs free energy ( $\Delta G$ ) numerical value of the reaction is less than zero, the reaction is spontaneous. Second state, If the numerical value of the Gibbs free energy ( $\Delta G$ ) of the reaction equals zero, then the reaction is in equilibrium. Third state, If the numerical value of the Gibbs free energy ( $\Delta G$ ) response is greater than zero, the reaction is spontaneous. In **table 4**, we see the Gibbs free energy ( $\Delta G$ ) of metal-complexes that is calculated in equation (10). The complex has the most negative the Gibbs free energy ( $\Delta G$ ) value is easier to occur than the others in Fig. 11. The order in which the reactions are spontaneous is as follows: GaPc (4)>ZnPc (3)>CuPc (2).

As it is well known that the molecular electrostatic potential (ESP) of ligand in **Fig. 12** is given to indicate the total charge distribution (electron + nuclei) of the molecule and correlates with dipole moments, electronegativity, partial charges and chemical reactivity. The relative polarity of the molecules is indicated with a visual method. An electron density isosurface of ligand is indicated the size, shape, charge density and site of chemical reactivity

of molecules with electrostatic potential surface **[27-36]**. In the electrostatic potential, different colors refer to charge in different values: The red color represents the most negative electrostatic potential, while the blue color represents the most positive electrostatic potential, the green color represents the electrostatic potential of the zero potential region.

The potential increases in the order red < orange < yellow < green < blue. As can be understood from this definition, the molecular electrostatic potential (ESP) have been plotted using the computer software Gauss view [24] in 6-311++G\*\* basis set.

#### 4. Conclusion

In the present work, we have demonstrated the synthesis and characterization of new metallophthalocyanines (CuPc ZnPc and GaPc (4)) containing (2), (3) (4bromophenyl)methanethiol substituted groups. Chemical structures of the new synthesed metallo phthalocyanines (CuPc (2), ZnPc (3), GaPc (4)) were characterized by elemental analysis, FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and UV-Vis spectral data. Their aggregation behaviors and sensor properties for Pd<sup>2+</sup> ions were studied by UV-Vis spectroscopy and fluorescence spectroscopy. The titration with increasing amounts of  $Pd^{2+}$  ions in the presence and absence of the other metal ions mixture [Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>] influenced the emission spectra of ZnPc (3) and GaPc (4) by causing the blue shift quenching of fluorescence intensity, which can be used as a selective chemosensor for  $Pd^{2+}$  ions. Photochemical and photophysical properties of ZnPc (3), GaPc (4) are useful for photocatalytic application such as photodynamic therapy agents for cancer treatments. Especially, the singlet oxygen quantum yields give an indication of the efficiency of the potential of these photosensitizers in PDT applications

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Synthetic route of the metallo phthalocyanines CuPc (2), ZnPc (3), GaPc (4) i:

#### **Figure Caption**

Scheme 1.

K<sub>2</sub>CO<sub>3</sub>, 4-nitrophthalonitrile, (4-bromophenyl)methanethiol, DMF, 40 °C, 3 days. ii: metal salts (CuCI<sub>2</sub>, ZnCI<sub>2</sub> or GaCI<sub>3</sub>, DBU, ca. 150-155 °C, for 6-8h. **Fig. 1**. The FT-IR spectra of the synthesized phthalocyanines (CuPc (2), ZnPc (3), GaPc (4)). UV-Vis spectra of the metallo phthalocyanines (CuPc (2), ZnPc (3), GaPc (4)) Fig. 2. in THF. Absorption spectra of ZnPc (3) and GaPc (4) in DMSO at different **Fig. 3.** concentrations (inset: plot of absorbance versus concentration). **Fig. 4.** UV-Visible spectra of CuPc (2), ZnPc (3) and GaPc (4) in THF during the titration with Pd<sup>2+</sup> ions and mole amounts of Pd<sup>2+</sup>ions versus molar extinction coefficients (ɛ) UV-Vis responses of ZnPc (3) and GaPc (4) towards metal mixture  $[Ag^+, Cd^{2+},$ Fig 5.  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Hg^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ] in the presence and absence of  $Pd^{2+}$  ions Absorption, excitation and emission spectra of the complex 3 (A) and 4 (B) in Fig. 6 **DMSO** A typical spectrum for the determination of singlet oxygen quantum yield of Fig. 7 the complex ZnPc (3) and GaPc (4) in DMSO. Fig. 8 A typical spectrum for the determination of photodegradation oxygen quantum yield of the complex GaPc (4) in DMSO Fluorescence emission spectra of ZnPc (3) and GaPc (4) in THF during the Fig. 9. titration with  $Pd^{2+}$  ions. Fig. 10. Fluorescence emission spectra of ZnPc (3) and GaPc (4) towards metal mixture  $[Ag^+, Cd^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}]$  in the presence and absence of Pd<sup>2+</sup> ions Fig. 11. Representations of the metallo phthalocyanines (CuPc (2), ZnPc (3), GaPc (4)) in which the ligand is formed by different metal atoms. Fig. 12. The optimized structures, HOMO, LUMO and electrostatic potential structures of ligand using DFT/B3LYP/6-31++G(d,p).

Compound	Q band $\lambda_{max}$ , (nm)	Excitation $\lambda_{Ex}$ (nm)	Emission λ <sub>Em</sub> (nm)	Stokes shift (nm)	$\Phi_{F}$	$\Phi_{\sf d}$ (10 <sup>-5</sup> )	$\mathbf{\Phi}_{\Delta}$			
ZnPc (3)	693	698	704	6	0,14	2.1	0,72			
GaPc (4)	708	716	721	5	0,61	0,63	0,35			
ZnPc	-	-	-	-	0,20 <sup>a</sup>	2.61	0,67 <sup>b</sup>			
GaPc	-	-	-	-	0,300 <sup>c</sup>	0,09 <sup>c</sup>	0,41 <sup>c</sup>			
<sup>a</sup> Data from ref. [17], <sup>b</sup> Data from ref. [21], <sup>c</sup> Data from ref. [46].										

Table 1 Spectral, Photophysical and photochemical properties of (3) and (4)

	E <sub>HOMO</sub>	E <sub>LUMO</sub>	Ι	А	ΔE	η	σ	PA	χ	ω	Dipol	Energy
B3LYP/STO-3G	-4,28011	0,20409	4,28011	-0,20409	4,48420	2,24210	0,44601	2,03801	-2,03801	0,92625	1,07962	-98440,43945
B3LYP/3-21G	-6,72371	-2,22373	6,72371	2,22373	4,49998	2,24999	0,44445	4,47372	-4,47372	4,44762	0,22484	-99066,49850
B3LYP/ LANL2DZ	-6,91474	-2,62265	6,91474	2,62265	4,29209	2,14604	0,46597	4,76870	-4,76870	5,29823	0,18874	-19305,75080
HF/ STO-3G	-7,00263	4,63114	7,00263	-4,63114	11,63378	5,81689	0,17191	1,18575	-1,18575	0,12085	8,27442	-98272,54213
HF/3-21G	-9,35589	1,32221	9,35589	-1,32221	10,67810	5,33905	0,18730	4,01684	-4,01684	1,51104	0,66180	-98881,44626
HF/ LANL2DZ	-9,43263	0,89172	9,43263	-0,89172	10,32435	5,16218	0,19372	4,27045	-4,27045	1,76638	0,56613	-19172,36550
Table 3. E <sub>HOMO</sub> , E <sub>LUMO</sub> and zero point energy for metal atoms (Ev)												

 Table 2. Calculated quantum chemical parameters for 4-(4-bromobenzylthio)phthalonitrile (Ev)

			<b>B3lyp</b>	$\rightarrow$		Hartree-Fock	
		STO-3G	3-21G	LANL2DZ	STO-3G	3-21G	LANL2DZ
	<b>E</b> <sub>HOMO</sub>	-0,78193	-0,97418	-1,18816	-1,20899	-1,31872	-1,46884
Cu <sup>2+</sup>	E <sub>LUMO</sub>	-0,75592	-0,74542	-0,73739	-0,60103	-0,56918	-0,58239
	Thermal Free Energies (G)	-44101,90200	-44396,51231	-5308,47607	-44074,62379	-44358,40567	-5282,40567
	E <sub>HOMO</sub>	-1,12455	-1,17009	-1,16785	-1,29900	-1,30630	-1,32011
Ga <sup>3+</sup>	E <sub>LUMO</sub>	-1,03308	-1,03741	-1,01026	-0,85937	-0,87563	-0,90509
	<b>Thermal Free Energies (G)</b>	-64098,95281	-64534,59281	-411,17547	-64050,55428	-64475,31838	-404,76787
	E <sub>HOMO</sub>	-0,94443	-1,00448	-1,32916	-1,06054	-1,36704	-1,51511
$Zn^{2+}$	E <sub>LUMO</sub>	-0,84378	-0,76087	-0,73250	-0,64775	-0,57889	-0,59664
	Thermal Free Energies (G)	-47829,55892	-48157,91779	-1759,01736	-47797,91937	-48118,02517	-1704,89964

**Table 4.** The Gibbs free energy ( $\Delta G$ ) for complex

	B3LYP /SDD	B3LYP /6-311G	B3LYP/3-21g	HF/SDD	HF/6-311G	HF/3-21g
CuPc (2)	-16092,14063	-16195,23302	-3034,24623	-16066,34082	-16166,37156	-3013,23273
ZnPc (3)	-16228,43081	-16333,41913	-2903,70208	-16203,21581	-16304,51379	-2881,91957
GaPc (4)	-16827,59195	-16936,21000	-2855,20937	-16801,53882	-16906,61997	-2835,17123
				AS?		
			AN			
		R C				



Scheme 1. Synthetic route of metallophthalocyanines Cu (2), Zn (3), Ga (4) i: K<sub>2</sub>CO<sub>3</sub>, 4-nitrophthalonitrile, (4-bromophenyl)methanethiol, DMF, 40 °C, 3 days. ii: metal salts (CuCI<sub>2</sub>, ZnCI<sub>2</sub> or GaCI<sub>3</sub>, DBU, ca. 150-155 °C, for 6-8h.



Scheme 2 Proposed schematic diagram for H-aggregation of metallophthalocyanines Cu (2), Zn (3), Ga (4)



Fig. 1 The FT-IR spectra of the synthesized phthalocyanines (2–4).



Fig. 2. UV-Vis spectra of the metallophthalocyanines (CuPc (2), ZnPc (3), GaPc (4)) in THF



**Fig. 3** Absorption spectra of ZnPc (**3**) and GaPc (**4**) in DMSO at different concentrations(inset: plot of absorbance versus concentration).



Fig. 4. UV-Visible spectra of CuPc (2), ZnPc (3) and GaPc (4) in THF during the titration with  $Pd^{2+}$  ions and mole amounts of  $Pd^{2+}$ ions versus molar extinction coefficients ( $\epsilon$ )





**Fig. 5**. UV-Vis responses of ZnPc (3) and GaPc (4) towards metal ion mixture  $[Ag^+, Cd^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}]$  in the presence and absence of Pd<sup>2+</sup> ions



Fig. 6 Absorption, excitation and emission spectra of the complex 3 (A) and 4 (B) in DMSO

![](_page_33_Figure_1.jpeg)

Fig. 7 A typical spectrum for the determination of singlet oxygen quantum yield of the complex 3 and 4 in DMSO.

![](_page_34_Figure_1.jpeg)

**Fig. 8** A typical spectrum for the determination of photodegradation oxygen quantum yield of the complex **4** in DMSO.

![](_page_35_Figure_1.jpeg)

Fig. 9. Fluorescence emission spectra of ZnPc (3) and GaPc (4) in THF during the titration with  $Pd^{2+}$ ions.

![](_page_36_Figure_1.jpeg)

**Fig. 10**. Fluorescence emission spectra of ZnPc (3) and GaPc (4) towards metal ion mixture  $[Ag^+, Cd^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}]$  in the presence and absence of Pd<sup>2+</sup> ions

![](_page_37_Figure_1.jpeg)

Fig. 11. Representations of complexes in which the ligand is formed by different metal atoms

![](_page_37_Figure_3.jpeg)

Fig. 12. The optimized structures, HOMO, LUMO and electrostatic potential structures of ligand using DFT/B3LYP/6-31++G(d,p).

# Selective Chemosensor Phthalocyanines for Pd<sup>2+</sup> ions; Synthesis, Characterization, Quantum Chemical Calculation, Photochemical and Photophysical properties

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- ✓ The synthesis of novel-type phthlocyanines bearing "(4-bromophenyl)methanethiol" as functional groups at peripheral positions.
- ✓ Selective chemosensor for  $Pd^{2+}$  ions.
- ✓ The investigation of photophysical and photochemical parameters
- $\checkmark$  The analysis of frontier molecular orbitals