



Synthesis, antioxidant, DNA cleavage and antimicrobial properties of phthalocyanine complexes bearing the poly-hydroxyl groups

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Abstract

(4-((1-((2-(bis(2-hydroxypropyl) amino) ethyl) (2-hydroxypropyl) amino) propan-2-yl) oxy) phthalonitrile) (BHHP) was synthesized from reaction N, N, N', N'- tetrakis (2-hydroxypropyl) ethylene diamine (SM) with 4-nitro phthalonitrile. Zinc, cobalt and copper phthalocyanine complexes were achieved from the reaction of BHHP compound with metal salts. Quantum chemical studies of these phthalocyanines have been computationally supported using density functional theory methods. The antioxidant properties of phthalocyanine compounds were determined with the help of 1, 1-diphenyl-2-picrylhydrazyl radical scavenging ability and chelating ability to iron ions. Compound **6** showed 72.8% inhibition of DPPH free radicals at 200 mg/L concentration and compound **4** showed 71.5% ferrous metal chelating activity at 200 mg/L concentration. The antimicrobial and DNA cleavage activities of compounds were also investigated. All tested phthalocyanine compounds showed excellent nuclease activity at all concentration. Antimicrobial activities of phthalocyanine compounds were detected using broth microdilution method and all test compounds demonstrated perfect antimicrobial activities. According to in vitro studies, copper phthalocyanine compound **6** has the best activity against the *P. aeruginosa* with 8 µg/mL of MIC value.

Keywords Phthalocyanines · Synthesis · Antioxidant · DNA cleavage · Antimicrobial

Introduction

Phthalocyanines (Pcs) which are synthetic analogues of porphyrin compounds have great thermal stability and visible optical properties due to owning an 18- π aromatic macrocycle (Hepokur et al. 2017). These unrivaled specifications enable these materials to be used in many fields, such as

Langmuir–Blodgett films (Roberts et al. 1985), photovoltaic cells (Pia Donzello et al. 2010; Li et al. 2016), fluorescence and chemical sensors (Günsel et al. 2019), semiconductor materials (Kantekin and Bıyıklıoğlu 2008), nonlinear optics (Salan et al. 2009), catalysis (Burkitt et al. 2016), data storage systems (Cabir et al. 2017), photodynamic therapy (PDT) (Ibbotson and Ferguson 2012; Bicalho et al. 2013) photodynamic antimicrobial chemotherapy (PACT) (Sen et al. 2019) and anticancer activity (Hepokur et al. 2017). There are studies in which some Pc compounds show DNA cleavage activity (Özel et al. 2016; Yuan et al. 2016; Ağırtaş et al. 2017). The DNA cleavage could occur with two main pathways oxidative and hydrolytic pathway. Oxidative DNA cleavage by redox-active metal complexes is mediated by the production of ROS through a Fenton-type mechanism. Pc compounds which contain metal ions are good appropriate for implementation as metallonucleases, due to their probability to adjust the redox potential thanks to the choice of proper metal ion (Rao et al. 2008). In particular, scientists have made important progress in the antioxidant and antibacterial activities of these compounds (Yuan et al. 2016; Hande Alici et al. 2018; Aydın et al. 2017). Environmental and toxic effects cannot be ignored in the developing

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technology. It is also necessary for the clean environment that the phthalocyanine compounds synthesized for this purpose show non-toxic and antioxidant-rich properties. Antioxidants are formed from natural or synthetic compounds and decrease the detrimental impacts of free radicals. Researches concentrate on the lighting of the antioxidant qualities of novel Pc compounds (Aydın et al. 2017). Nevertheless, the low solubility of unsubstituted Pc in widespread organic solvents and aqueous media is a potent obstruction (Yuan et al. 2016). The solubility of phthalocyanines can be developed by replacing the inserted metal atom in the interior core and/or by subjoining several functional groups at the phthalocyanine ring (Günsel et al. 2020). Non-aggregated and good solubility phthalocyanines may be a convenient candidate for a good antioxidant and PDT agents (Günsel et al. 2020; Alexere et al. 2017; Saki et al. 2018; Salehi and Karimi 2018). Recently, phthalocyanine compounds are a topic of interest for researchers for their antioxidant and antimicrobial properties. The substituents carried by the new phthalocyanine compounds synthesized in this study are expected to have potentially antioxidant and antimicrobial properties. The non-toxic, antioxidant and antimicrobial properties of phthalocyanines used as photosensors in photodynamic therapy can be seen as a richness for applications. The rich electron structure is the most effective reason for using phthalocyanines as a technological product. In the quantum chemical study, 6-31G and LanL2DZ basis sets of DFT / B3LYP method were run. Here, the LanL2DZ basis set, ab initio third-order (K–Cu), fourth-order (Rb–Ag) and fifth-order (Cs–Au) atoms have been created to replace the innermost nuclear electrons for effective core potentials (ECPs) (Hay and Wadt 1985). Analytical adaptation to potentials is presented for use in multi-center integral evaluation. The basis set of 6-31G (d, p) coincides well with a reasonably experimental correlation (Petersson and Al-Laham 1991).

The synthesis of BHHP and its phthalocyanine complexes is reported herein. In addition, aggregation, DNA cleavage, antioxidant and antimicrobial properties of the compounds were investigated. In addition, DFT/B3LYP's LanL2DZ and 6-31G (d, p) basis sets were used to support the structure of compounds with computational chemistry.

Experimental

Materials

Reference of Armarego was used for chemical purification (Armarego and Chai 2012). For spectral analysis, the structure was characterized by the devices used in our previous study (Cabir et al. 2017).

BHHP (3)

A mixture of SM **1** (1.8182 g, 6.21 mmol) and 4-nitrophthalonitrile **2** (1.0765 g, 6.21 mmol) in 25 mL dry dimethylformamide (DMF) was stirred at the appropriate speed under nitrogen at room temperature. After mixing for the first 15 min, K_2CO_3 (4.27 g, 31 mmol) was added into the mixture over a period of 2 h. Stirring was continued for a further 48 h. After reaction with Thin-layer chromatography (TLC), the product was poured onto water (150 mL) and the precipitate formed was filtered. It was washed with water until neutral and then dried. The compound is soluble in DMSO, DMF, THF, EtOH, MeOH, CH_2Cl_2 , $CHCl_3$, 1, 2-dichloroethane, acetone. Yield: 1.72 g (66%). FT-IR spectrum (cm^{-1}): 3414, 3113, 3078, 2970, 2931, 2831, 2229, 1670, 1597, 1562, 1492, 1411, 1377, 1319, 1292, 1253, 1130, 1091, 1053, 972, 840. ^1H NMR (300 MHz, DMSO- d_6) δ (ppm): 8.00, 7.76, 7.42(m, 3H, Ar-H), 6.86, 6.57(OH, aliphatic), 4.78(CH_3), 3.59(CH_3), 2.50, 2.18(CH_2), 1.75, 1.10(CH_2). MALDI-MS: m/z Calc. 418.53; found 441.89 [M + Na] $^+$.

2, 10, 16, 24 – Tetrakis (1-((2-(bis (2-hydroxypropyl) amino) ethyl) (2-hydroxypropyl) amino) propan-2-yl) oxy) = (BHHP) phthalocyaninato] Zinc (II) (4)

BHHP **3** (0.100 g; 0.24 mmol) and anhydrous $ZnCl_2$ (0.008 g; 0.06 mmol) were powdered in a quartz crucible and heated in a sealed glass tube for 10 min 130 °C. The product formed after cooling to room temperature was several times washed with water, a water–ethanol mixture, ethyl acetate, CH_2Cl_2 , 1,2-dichloroethane, and then filtered. The purity of the product was checked by TLC. The crude product was dissolved in DMF. Insoluble was filtered off. DMF solvent was then removed from the rotary evaporator. The product was collected and dried. This compound is soluble in THF, DMF, and DMSO. Yield: 0.078 g (75%). FT-IR spectrum (cm^{-1}): 3441, 2970, 2935, 2873, 1604, 1481, 1454, 1379, 1319, 1284, 1238, 1118, 1130, 1060, 950, 833, 732, 671. UV–Vis (DMSO) λ_{max} (log ϵ): 684 (5.16), 616(4.61), 352 (4.98). ^1H NMR (300 MHz, DMSO- d_6) δ (ppm): 7.70, 7.31(m, 12H, Ar-H), 6.58 (OH, aliphatic), 3.36 (CH_3), 2.89(CH_3), 2.50(CH_2), 1.02(CH_2). HRMS (ESI); (M + H) calc. for $C_{88}H_{136}N_{16}O_{16}Zn$: 1737.0.

2, 10, 16, 24 – Tetrakis (BHHP) phthalocyaninato] Cobalt (II) (5)

In the synthesis of compound **5**, the procedure given for compound **4** was used. Only the metal salt ($CoCl_2$) has been

changed. Yield: 0.085 g (47%). FT-IR spectrum (cm^{-1}): 3400, 2970, 2935, 1612, 1593, 1489, 1450, 1323, 1253, 1207, 1091, 1053, 945, 844, 732, 694. UV-Vis (DMSO) λ_{max} ($\log \epsilon$): 676 (5.12), 334 (5.05). HRMS (ESI); ($M+H$) calc. for $\text{C}_{88}\text{H}_{136}\text{N}_{16}\text{O}_{16}\text{Co}$: 1732.0; found: 1755.0 $[M+Na]^+$.

2, 10, 16, 24 – Tetrakis (BHHP) phthalocyaninato] Copper (II) (6)

In the synthesis of compound **6**, the procedure given for compound **4** was used. Only the metal salt (CuCl_2) has been changed. Yield: 0.04 g (38%). FT-IR spectrum (cm^{-1}): 3429, 2970, 2931, 2873, 1651, 1600, 1481, 1450, 1373, 1284, 1230, 1192, 1126, 1087, 1072, 968, 883, 725, 659. UV-Vis (DMSO) λ_{max} ($\log \epsilon$): 682 (5.18); 616 (4.77); 336 (5.04). HRMS (ESI); ($M+H$) calc. for $\text{C}_{88}\text{H}_{136}\text{N}_{16}\text{O}_{16}\text{Cu}$: 1736.0.

DPPH activity

The method given in the literature was used to investigate this antioxidant parameter of phthalocyanine compounds (Ağırtas et al. 2015). Briefly, 2.0 mL of methanol solution of 0.004% DPPH was added to 500 μL of different concentrations (200–10 mg/L) of Pc compound. Afterwards, these mixtures were incubated for 30 min at room temperature in dark. The absorbance of compounds was measured using UV-VIS spectrophotometer at 517 nm after 30 min incubation. Ascorbic acid and Trolox were used as standard and the same protocol was applied for them. The ability to scavenge DPPH free radical was calculated by the following equation:

$$\% \text{ Inhibition activity} = [A_0 - A_1] / A_0 \times 100$$

A_0 = Control absorbance and A_1 is the absorbance value of the solution containing phthalocyanine compounds and DPPH after 30 min.

Ferrous ion chelating activity

This parameter was examined according to the literature information (Dinis et al. 1994). Briefly, 0.5 mL of the Pc compound solution with various concentrations ranging from 10 to 200 mg/L was mixed to a solution containing 0.025 mL of 2 mM FeCl_2 . After, the reaction was initiated by the addition of 0.1 mL of ferrozine (5 mM). Then, the mixture was vortexed and incubated at room temperature for 10 min. Ferrozine reacted with the bivalent iron to create stable complex species that were soluble in water. The absorbance of the Fe^{2+} -Ferrozine complex was measured at 562 nm spectrophotometrically. EDTA solution was used as a positive control. The chelating activity of the compounds for Fe^{2+} was calculated using the following equation:

$$\text{Chelating activity (\%)} = (A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}} \times 100;$$

where A_{control} is the absorbance of the control reaction, and A_{sample} represents the absorbance obtained in the presence of extracts or EDTA.

DNA cleavage ability

The DNA cleavage activity of Pc compounds was evaluated via their capability to catalyze the transformation of the supercoiled form (Form I) to nicked circular Form (Form II) and linear form (Form III) using agarose gel electrophoresis. pBR322 plasmid DNA molecules and three different concentrations (150 $\mu\text{g/mL}$ and 250 $\mu\text{g/mL}$) Pc compounds were incubated at 37 $^{\circ}\text{C}$ for 30 min. After that, loading dye was added into the reaction solution. These solutions were electrophoresed for 1.5 h at 50 V using 1% agarose gel.

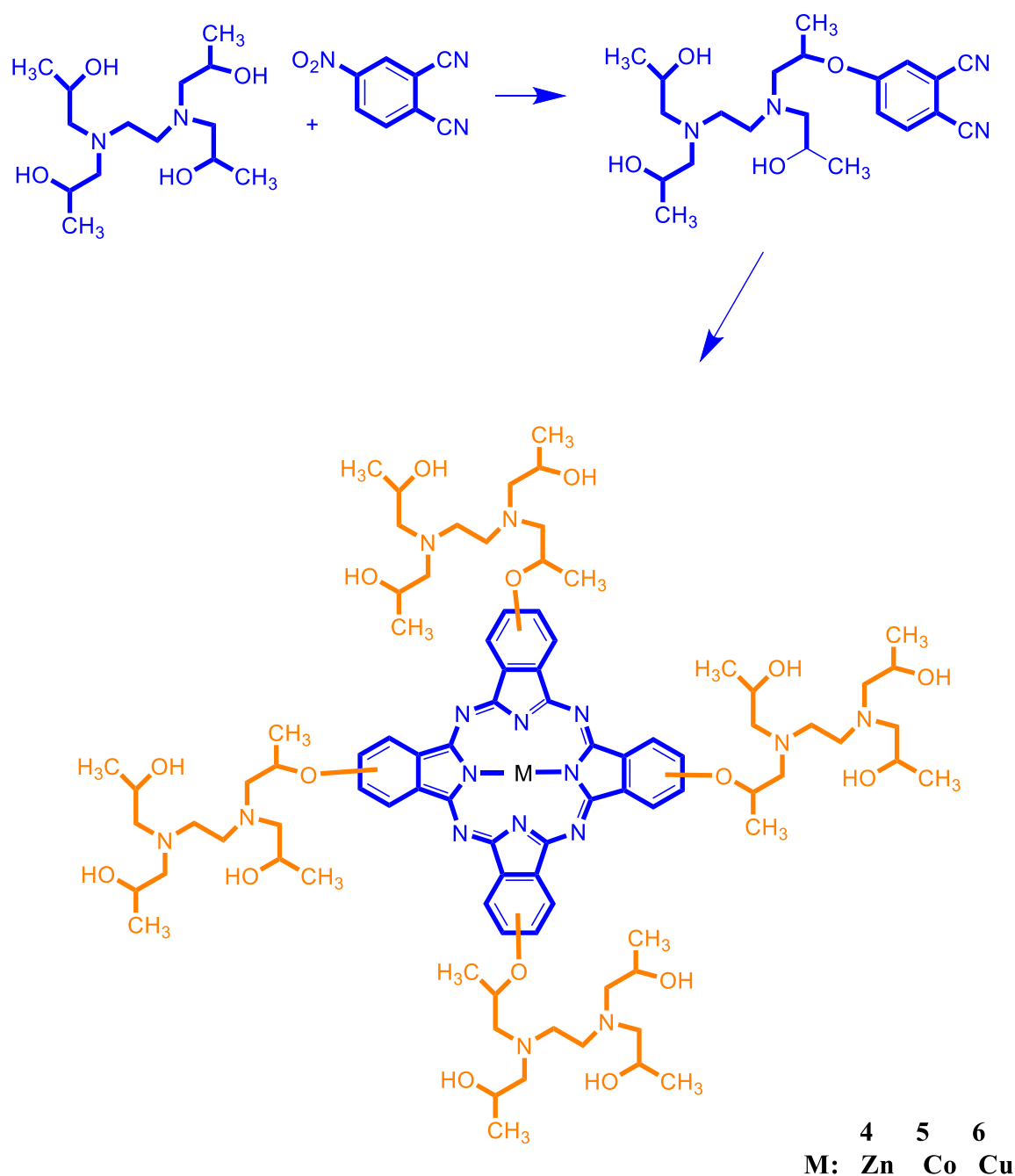
Antimicrobial activity

Antibacterial activities of Pc compounds solutions were detected by broth microdilution method. The microorganisms used to detect of antimicrobial activity of Pc compounds were *Bacillus cereus*, *Escherichia coli* (ATCC 10536), *Staphylococcus aureus* (ATCC 6538), *Enterococcus hirae* (ATCC 10541), *Legionella pneumophila* subsp. *pneumophila* (ATCC 33152), *Pseudomonas aeruginosa* (ATCC 9027), *Candida albicans* and *C. tropicalis*. The microorganisms' growth media were inoculated with $2.9 \cdot 10^8$ CFU/mL. The culture was grown overnight prior to the tests. Twofold serial dilutions of Pc compounds were prepared in 96-well plates. The plates were incubated at 37 ± 2 $^{\circ}\text{C}$ for 1 day. After the incubation, MIC (minimum inhibition concentration) values were detected as the lowest concentration of Pc compounds that inhibited of microorganisms growth.

Results and discussion

The synthesis methods and structures of the BHHP **3** and BHHP substituted metallophthalocyanines **4–6** are shown in Scheme 1. The BHHP (**3**) was obtained through the reaction of SM (**1**) with 4-nitrophthalonitrile (**2**) in dry DMF in the presence of dry K_2CO_3 . Phthalocyanines (**4–6**) were obtained from the reaction of BHHP (**3**) with ZnCl_2 , CoCl_2 , CuCl_2 under N_2 atmosphere. These compounds have a high solubility in organic solvent. The good solubility of phthalocyanine compounds in solvents makes it easy for them to find application in practice. Characterization of newly synthesized compounds was carried out with FT-IR, UV-Vis, ^1H NMR, Mass spectra.

The ^1H NMR spectra of compounds were registered in the DMSO-d_6 . In the ^1H NMR spectra of compound



Scheme 1 The route for the synthesis of compounds **3–6**

3, aromatic, aliphatic proton and aliphatic –OH, –CN signal also appeared this also confirmed the formation of expected products. For compound **3**, aromatic protons appear at 8.00–7.76 and 7.42(Ar–H), and aliphatic protons at 6.86–6.57(OH aliphatic), 4.78, 3.59(CH₃), 2.50–2.18, 1.75–1.35, 1.10 (CH₂) ppm. The ¹H NMR spectra of compound **4** show that aromatic protons appear at 7.70–7.31(Ar–H), and aliphatic protons appear at 6.58(OH), 3.36(CH₃), 2.89, 2.50, 1.02 (CH₂) ppm. In the

¹H NMR spectra of compound **4**, –CN signal also disappeared, this also confirmed the formation of expected products. The phthalocyanine **5** and **6** compounds were not evaluated by NMR spectra due to the paramagnetic Co and Cu metal atoms they contain. The fact that the newly synthesized BHHP **3** showed the expected ion peak at mass spectrum (MALDI-TOF) at *m/z*: 441,898 [M + Na] confirms the predicted structure. ESI ion peaks of Compound **5** was found to be 1755.0 [M + Na].

In the evaluation of FT-IR spectral data of Compound **3**, it is expected to exist in the structure (OH) at 3414 cm^{-1} , (Ar-CH) at 3078 cm^{-1} , (CH_2) and (CH_3) 2970 , 2931 and 2831 cm^{-1} , the presence of peaks (CN) at 2229 cm^{-1} , ($\text{C}=\text{C}$) at 1597 – 1562 cm^{-1} and (Al-O-Ar) at 1253 cm^{-1} confirms the structure. All phthalocyanine compounds, such as BHHP, give vibrations of -OH, CH_3 , CH_2 , functional groups similarly, except the -CN group. After the conversion of BHHP (**3**) to Pc **4–6**, the loss of nitrile (CN) peak vibrations, which is one of the most prominent peaks, appears as an important sign in the synthesis of phthalocyanines and clearly confirms the structure.

Electronic transitions in chemistry of phthalocyanine compounds provide important characteristic information. Spectral peaks, called Q-bands, are essential indicators for phthalocyanine compounds, especially in UV-Vis spectra. These peaks also give information, such as whether metal is attached to the cavity for phthalocyanines. Depending on this result, characteristic Q-band absorption of metallic phthalocyanines with D_{4h} symmetry is observed as a single band. UV-visible spectra measurements for BHHP substituted phthalocyanines were measured in DMSO (Fig. 1S). Q bands for zinc, cobalt and copper phthalocyanine compounds were found to be 684, 676 and 682 nm. Likewise, B bands for zinc, cobalt and copper phthalocyanines are determined as 352, 334 and 336 nm. These Q-band absorptions are considered to belong to from HOMO to LUMO of the Pcs ring (Ağırtas et al. 2014). Figure 1 gives the electronic spectrum of the zinc phthalocyanine compound measured in the 8.40×10^{-6} – $3.90 \times 10^{-6}\text{ mol L}^{-1}$ concentration range. One of the properties investigated for phthalocyanines is aggregation behavior. Determining this feature gives an idea about the role of the compound in photodynamic therapy

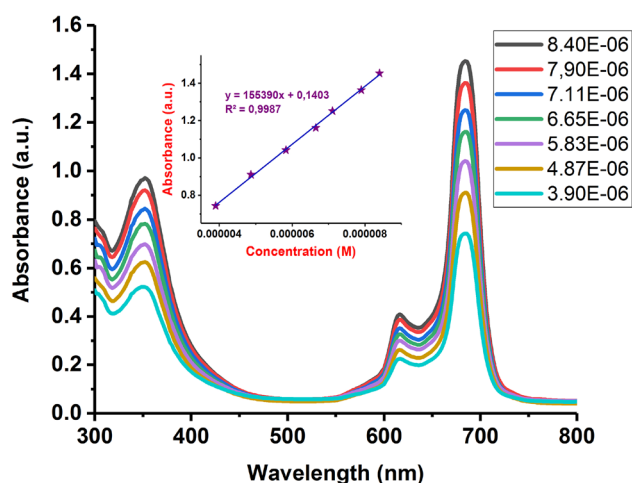


Fig. 1 Compound **4** aggregation study in 8.40×10^{-6} , 7.90×10^{-6} , 7.11×10^{-6} , 6.65×10^{-6} , 5.83×10^{-6} , 4.87×10^{-6} , $3.90 \times 10^{-6}\text{ M}$ concentrations

applications. In this study, as understood from the electronic absorption diagram given in Fig. 1 as an example, it is seen that there is no aggregate in the measurement range of the zinc phthalocyanine compound. Compounds exhibiting this behavior can be seen as a potential advantage for photodynamic therapy applications.

Computational studies

Optimization of complexes containing Zn, Cu and Co atoms was carried out in gas phase with Gaussian 09 program (Frisch MJ et al. 2009). Molecular structures have 257 atoms and around 930 electrons for three complexes. Gaussview 6.0 program was used to build these and visualize the results. DFT method in ground state was used for optimization. In DFT study, B3LYP's LanL2DZ and 6-31G (d, p) basis sets were used. In connection with alpha molecular orbital properties, calculations were performed using excited states for these structures. It is also used to create total surface electron density maps in ground state with these optimizations. Natural bond orbital (NBO) analysis was also performed to investigate the interaction of the orbitals of the compounds. The optimized structures of the Zn-centered Pc in the ground state are given in Fig. 2 at the B3LYP / LanL2DZ basis set for the gas phase. The figure also shows structures with different views of the phthalocyanine core in the investigated molecule.

Quantum chemical studies were carried out to determine the molecular structure, phthalocyanine core compatibility, energy properties, electronic structure of the synthesized compound. With structure optimization, bond length, bond angles, HOMO LUMO energy values were calculated. The distances between the central atom and only some important atoms and some selected angles were evaluated as the result of optimization. N–M distances in 3 compounds were calculated as 1.79 Å, respectively. Compared to metal atoms, Zn has a shorter bond structure than others. When the N–M–N bond angles are evaluated in the calculations, it was found approximately 90° in three compounds. In addition, when dihedral angles are investigated, it proves the phthalocyanine planar structure. It shows that the metal atom is attached to the phthalocyanine center in a stable structure. No deviation from the Pc planarity in the compounds **4–6** was observed. The small structural differences observed in the **5** and **6** molecules investigated by the same method are mostly due to the different nature of metal ions.

HOMO and LUMO energies, one of the frontier orbitals, determine molecular activity and electronic properties (Solğun et al. 2020). These global activities are electron affinity and ionization potential, respectively (Gounden et al. 2020). Figure 3 shows the HOMO–LUMO band gap and transition energies calculated for gas-phase phthalocyanine molecules. Molecules frontiers

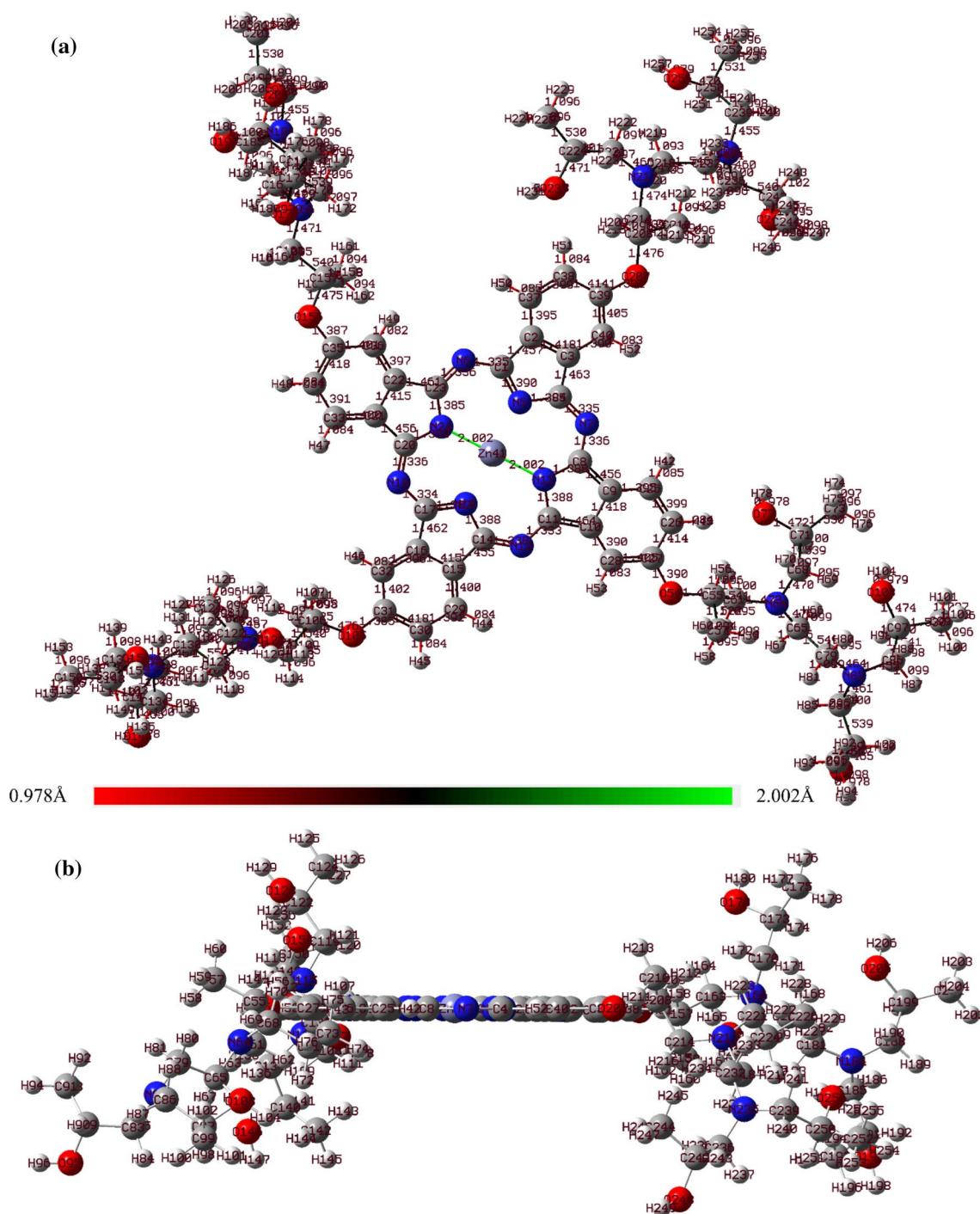


Fig. 2 The optimized structures of the compounds **4** (a) and **6** (b) at DFT/ B3LYP's LanL2DZ and 6-31G (d, p) basis sets

orbitals calculated as for Zn-Pc, EHOMO = − 4.3299 eV—ELUMO = − 2.1666 eV, for Co-Pc, molecule; EHOMO = − 4.5863 eV—ELUMO = − 2.4186 eV and for Cu-Pc, the value of EHOMO = − 4.5082 eV ELUMO = − 2.3946 eV. All HOMO and LUMO energies were calculated at the level of B3LYP / 6-31G (d, p) and LANL2DZ for all systems studied. The low band gaps

obtained here are estimated to be small, the compounds will be effective in electron and hall transport.

In the study of different metal atoms based on the molecular structure investigated, the band gap was found as Zn = 2.1639, Cu = 2.1136 and Co = 2.1677 eV, respectively. Ionization potential ($I = 4.3299$ – 4.5863), electron affinity ($A = 2.1666$ – 2.4186),

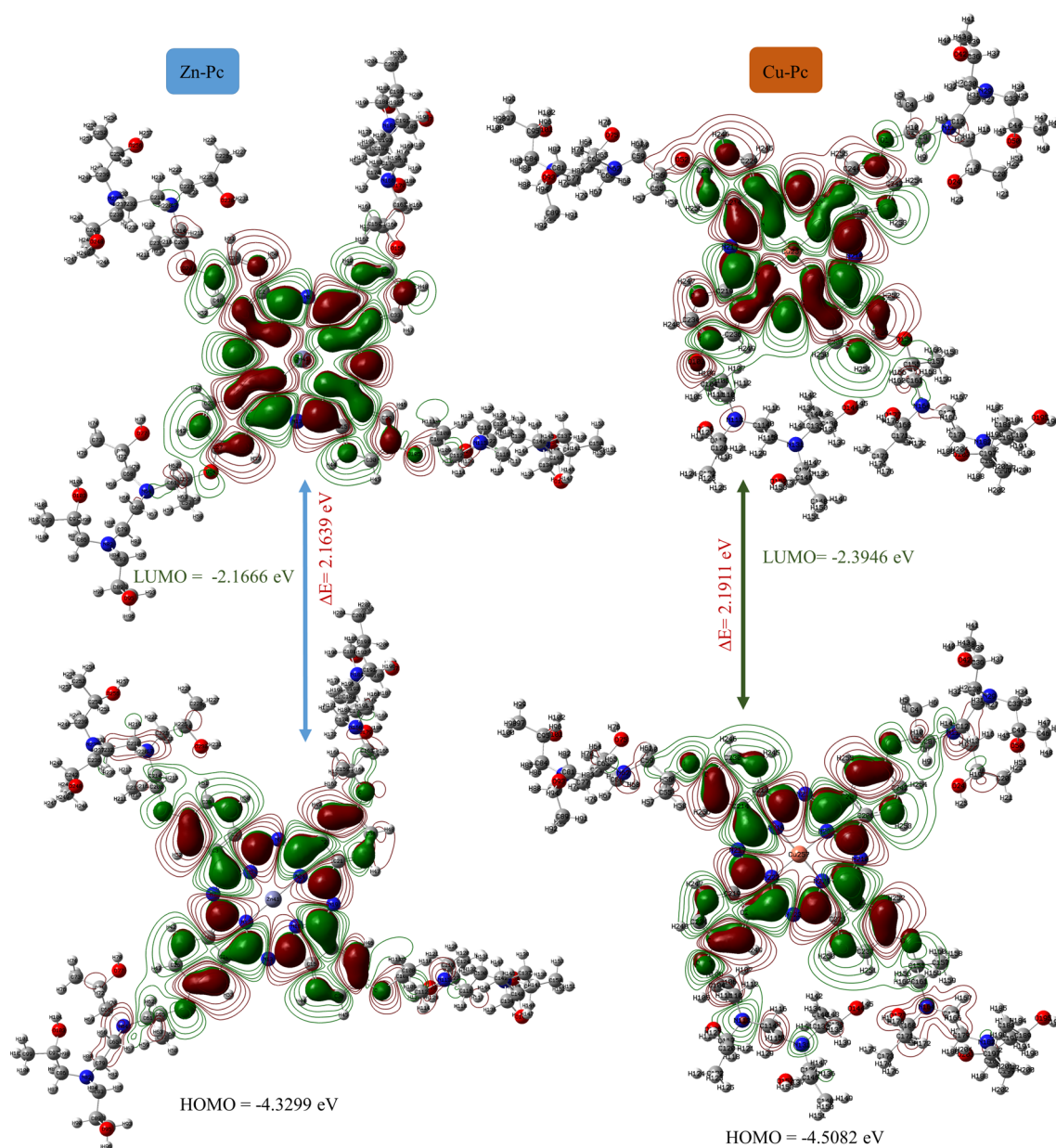


Fig. 3. 4 and 6 compounds HOMO–LUMO energy maps and band gaps

chemical hardness ($\eta = 1.0568$ – 1.08385), chemical softness ($s = 0.5284$ – 0.5419), chemical potential ($\mu = -3.2482$ – -3.5024), electronegativity ($\chi = 1.5833$ – 1.7093) and electrophilicity index ($\omega = 5.7061$ – 6.6886). The electrophilicity values obtained have a good electrophilic property due to the effect of the substituents of the phthalocyanine complexes.

NBO analysis

NBO analysis provides a suitable basis for the evaluation of bonding structures, atomic charges and internal interaction

energies caused by the electronic delocalization effect (Ajayi and Shapi 2020), while architecture of molecular is investigated to lighten transition of charge and conjugative interaction. Transitions of $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ in phthalocyanines centered on Zn, Cu and Co were investigated. The values of high $E^{(2)}$ stabilization energies found by NBO analysis of these compounds give delocalization of π -electrons and stability (Eşme and Sağdıç 2017; Khajehzadeh and Moghadam 2017; Mathammal et al. 2015; Pandey et al. 2017). In this analysis, neutral band orbital energies were calculated using the second-order perturbation theory of the Fock matrix method under the basis sets of DFT/B3LYP/LanL2DZ.

Energy of $E^{(2)}$ on the transition of $\sigma \rightarrow \sigma^*$ is between C8–N12 and C11–N13 for Zn-Pc on natural bond analysis, that is $4.89 \text{ kcal mol}^{-1}$, energy of $E^{(2)}$ on the transition of $\pi \rightarrow \pi^*$ between C4–N7 and C9–C25, that is $36.58 \text{ kcal mol}^{-1}$, energy of $E^{(2)}$ on the transition of $\text{LP}(1) \rightarrow \text{LP}^*(7)$ between N24 and Zn41, that is $29.74 \text{ kcal mol}^{-1}$. Energy of $E^{(2)}$ on the transition of $\sigma \rightarrow \sigma^*$ is between C8–H10 and N11–C15 for Cu-Pc on natural bond analysis, that is $2.89 \text{ kcal mol}^{-1}$, energy of $E^{(2)}$ on the transition of $\pi \rightarrow \pi^*$ between C221–N223 and C224–N228 is $18.89 \text{ kcal mol}^{-1}$, energy of $E^{(2)}$ on the transition of $\text{LP}(1) \rightarrow \text{LP}^*(6)$ between N228 and Cu257 is $29.18 \text{ kcal mol}^{-1}$. Energy of $E^{(2)}$ on the transition of $\sigma \rightarrow \sigma^*$ between C77–H78 and C89–H90 for Co-Pc on natural bond analysis is $17.69 \text{ kcal mol}^{-1}$, energy of $E^{(2)}$ on the transition of $\pi \rightarrow \pi^*$ between C221–N223 and C224–N228 is $20.87 \text{ kcal mol}^{-1}$, energy of $E^{(2)}$ on the transition of $\text{LP}(1) \rightarrow \text{LP}^*(5)$ between N228 and Co257 is $21.78 \text{ kcal mol}^{-1}$.

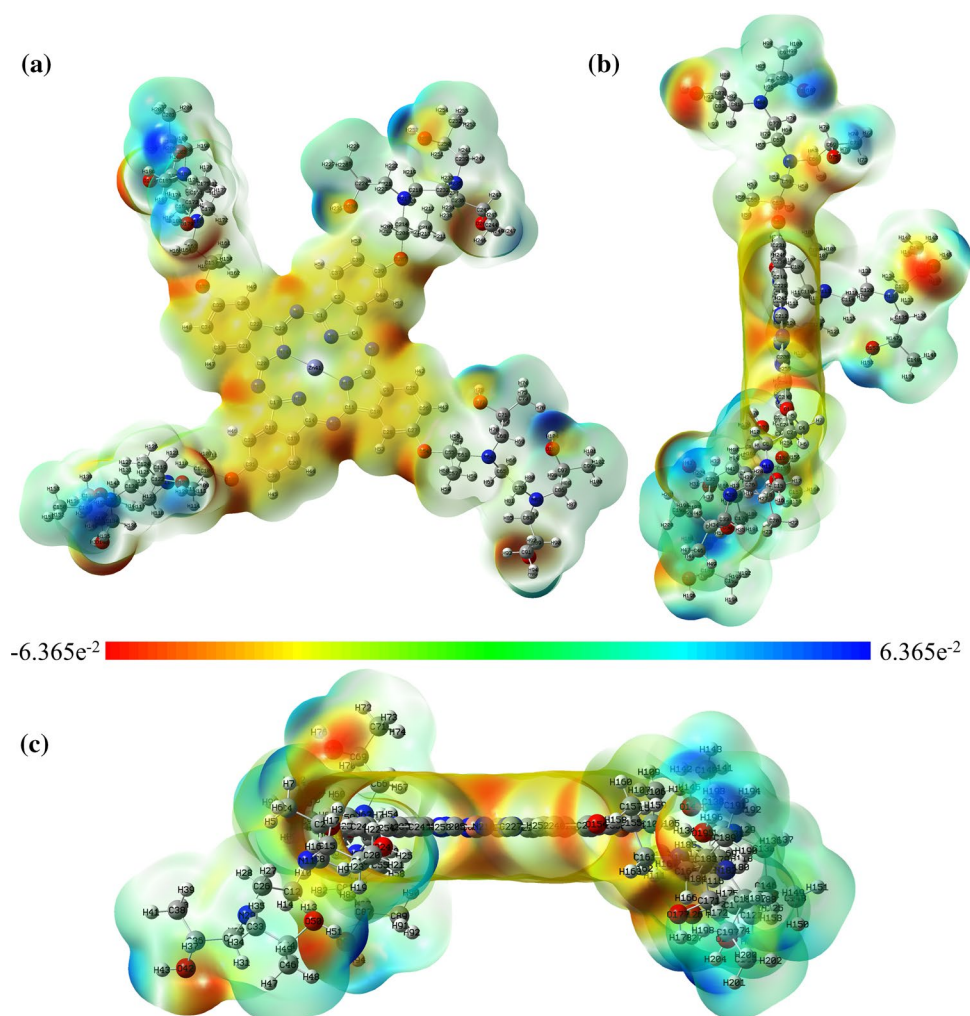
The natural electron configuration of Zn, Cu and Co complex compounds was calculated as Zn41 = $[\text{core}]4s^{(0.43)}3d^{(9.90)}4p^{(0.39)}$, Cu257 = $[\text{core}]4s^{(0.36)}3d^{(9.31)}4p^{(0.38)}4d^{(0.01)}$

and Co257 = $[\text{core}]4s^{(0.10)}3d^{(3.32)}5p^{(0.14)}$. The interaction between electron donors and electron acceptors was found to be intensive in providing conjugation within the molecule. It is also a sign that phthalocyanine molecules have a stable structure.

The dipole moment (μ) was calculated Zn-10.66 D, Co-8.78 D and Cu-12.75 D. Polarizability (α) Zn-833.88 Co-814.17 and Cu-831.21 Å and first hyperpolarizability (β) Zn- 1.11×10^{-34} , Co- 2.19×10^{-34} and Cu- 1.31×10^{-34} esu were calculated. In the results obtained, the compounds can be used as nonlinear optical materials.

The electrostatic potential created by the electrons of a molecule is an important feature in the analysis of molecular activity and determining the behavior it will exhibit in chemical reactions (Vanasundari et al. 2017; Cabir et al. 2019). Molecular electrostatic potential (MEP) plays a descriptive role for information related to hydrogen bonding in reactions alongside electrophilic and nucleophilic attacks (Priya et al. 2019). Electrophilic and nucleophilic reactive sites for Zn, Cu, and Co-Pc are shown in Fig. 4. The red color in the MEP plot represents a negative region indicating electrophilic

Fig. 4 Molecular electrostatic potential maps of compounds **4** (a), **5** (b) and **6** (c)



reactivity, the blue indicates a positive region indicating nucleophilic reactivity. Blue regions in the substituents indicate that -OH groups will interact at a high level.

DPPH radical scavenging activity

Keeping of humans towards oxidative damage and improvement of prophylactics for cancer and another helpless diseases are prominent directions in biochemistry and medicine over the world. Antioxidants play a big role in protecting the biological system by creating resistance against diseases. For this reason, antioxidant substances are widely used in different fields of medicine and industry (Korotkova et al. 2003). Therefore, the synthesis of novel antioxidant substances is important. This approach is based on the elimination of the DPPH radical in the presence of antioxidant compounds capable of delivering hydrogen atoms or electrons. It results in the purple color of the DPPH radical turning yellow. The strength of the antioxidants tested is proportional to the degree of color change and this discoloration is detected spectrophotometrically (Hande Alici et al. 2018). In the study, the DPPH radical scavenging activities of metallophthalocyanines (**4–6**) and standards (Ascorbic acid and Trolox) against DPPH were experimented and the DPPH free-radical scavenging efficiency results are indicated in Fig. 5. The phthalocyanine compounds investigated in this study showed a reasonable level of DPPH radical scavenging activity. The scavenging capability of the compounds at 100 mg/L on the DPPH radical scavenging is in the following order of Trolox > Ascorbic acid > **6** > **4** > **5** and is found to be 99.69%, 98.82, 59.69%, 54.24% and 51.62, respectively, at the same concentration. When the concentration increased from 50 mg/L to 200 mg/L, DPPH radical scavenging activity for compound **6**, compound **4**, compound **5** was found to increase from 51.2%, 46.8%, 42.2% to 72.8%, 69.7%, 67%, respectively. As seen in Fig. 5, the DPPH activity of the phthalocyanine compounds was dose-dependent

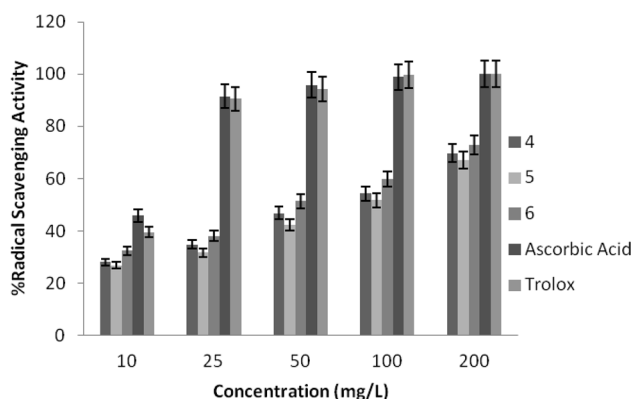


Fig. 5 Free-radical scavenging activity of the compounds on DPPH radicals

activity. The compound with the best free-radical scavenging capacity at all concentrations was observed by compound **6**, the highest activity value was determined as 72.8% at 200 mg/L concentration. Results of the study indicated better activities with previous studies (Saki et al. 2018). These phthalocyanines, which have DPPH free-radical sweeping capability, are expected to provide positive contributions to human health if preferred in textile, structure and plastic dyeing. The performance tests required for photodynamic therapy can be safely used as a sensor agent, if appropriate (Saki et al. 2018).

Ferrous chelating activity

Ferrozine is used as a parameter to determine the metal chelating activity of its compounds. This method reveals whether the investigated compounds have the ability to chelate transition metal ions. Ferrozine, a powerful ferrous iron chelating compound, quantitatively formation complex with Fe^{2+} . If other chelating agents are existing in the medium, the formation of the complex is disturbed, so the color density is decreased (Saki et al. 2018). Phthalocyanine compounds were experienced for their Fe^{2+} chelating ability at various concentrations, and this activity was compared with the chelating capability of the EDTA. Iron-containing ion-chelating activities were found to increase with increasing concentration of the compounds studied. When the concentration increased from 50 mg/L to 100 mg/L, iron-chelating activities for compound **4**, compound **6**, compound **5** were found to increase from 51.3%, 30.1%, 27.0% to 60.7%, 41.7%, 34.6%, respectively. The maximum chelating activity was found as 71.5% for compound compound **4** at the concentration of 200 mg/L. The iron-chelating activities of the compounds at 200 mg/L were in the following descending order of EDTA > compound **4** > compound **6** > compound **5** and were found to be 100%, 71.5%, 56.6% and 54.28%, respectively, at the same concentration (Fig. 6). Özel et al.

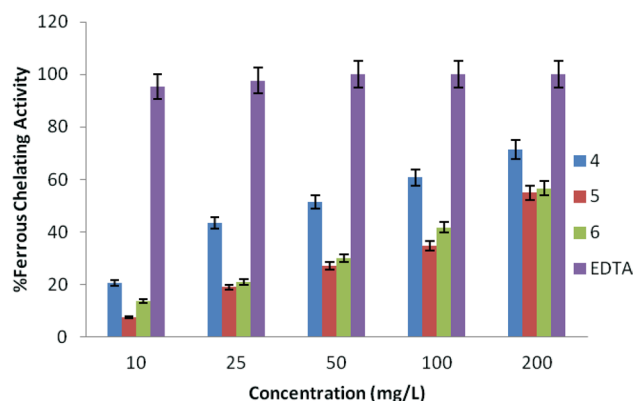


Fig. 6 Metal chelating activity of compounds

demonstrated the highest chelating activity of phthalocyanine compounds as 36.8% at 100 mg/L concentration [13]. Our results showed better chelating activities than their findings.

DNA cleavage activity

The DNA cleavage activities of synthesized compounds (4–6) were performed using agarose gel electrophoresis. The supercoiled pBR322 plasmid DNA was incubated with different concentrations of the compounds. It is well known that the metal compounds induce random breaks to one of the double-chain DNA molecule. As a result of which, the supercoiled form opens to form an open circular after one nick and later to a linear form if two nicks on supplementary chain are within a short distance (Jin et al. 2014). Ultimately, the DNA degraded into small parts of various size which were not determined in our study. As a result, all compounds demonstrated significant cleavage effects because linear form was lost and it was fully cut into little parts. Smear images were seen in Lane 4, 5 and 7 as nucleotide residue. The DNA cleavage activities of the phthalocyanine compounds examined here are compatible with the studies in the literature (Jin et al. 2014). Also, these results indicated that Pc compounds can be suitable for nuclease activity antimicrobial and anticancer application after further toxicological test systems (Fig. 7).

Antimicrobial activity

In this study, metallophthalocyanines were tested against 3 Gr-negative (*Legionella pneumophila* subsp. *pneumophila*, *Pseudomonas aeruginosa*, *Escherichia coli*), 3 Gr-positive (*Bacillus cereus*, *Enterococcus hirae*, *Staphylococcus aureus*) bacteria and 2 fungi (*Candida albicans*,

C. tropicalis) were used using MIC method. The results are presented in Table 1. According to the results obtained from the study, compound 6 showed better antimicrobial activity than other metallophthalocyanine compounds (compound 5 and compound 4). The MIC values for compound 6 were determined as 16 µg/mL, 16 µg/mL, 16 µg/mL, 64 µg/mL, 8 µg/mL, 64 µg/mL, 32 µg/mL, 64 µg/mL against *E. hirae*, *S. aureus*, *B. cereus*, *E. coli*, *P. aeruginosa*, *L. pneumophila* subsp. *Pneumophila*, *C. albicans* and *C. tropicalis*, respectively. Also, when evaluated in terms of microorganism, *P. aeruginosa* was the most affected species from the compounds. The MIC values for *P. aeruginosa* were determined as 8 µg/mL, 16 µg/mL, 32 µg/mL, against compound 6, compound 5 and compound 4, respectively. According to results, this study can contribute to novel antimicrobial drug development based on the compound.

These phthalocyanine compounds, whose antioxidant and antibacterial properties are examined, have industrial coloring properties. The developing technology of the world has naturally reached dimensions that threaten the environment and human health. It is desirable that the phthalocyanine compounds of technological importance have non-toxic and antioxidant properties, both harmless to the environment and harmless to human beings. Reasonable antioxidant and antibacterial effects show that these compounds can also be used in the coloring of textile products. It can be preferred as safe compounds instead of dyes that have toxic effects. The fact that the data obtained from the study parameters are reasonable indicates that the compounds are safe in the health sector or other areas needed.

Conclusions

The new phthalocyanine compounds with BHHO substituents were originally synthesized and characterized. They are more soluble in organic solvents no substituted phthalocyanines according to. Theoretical calculations contribute to

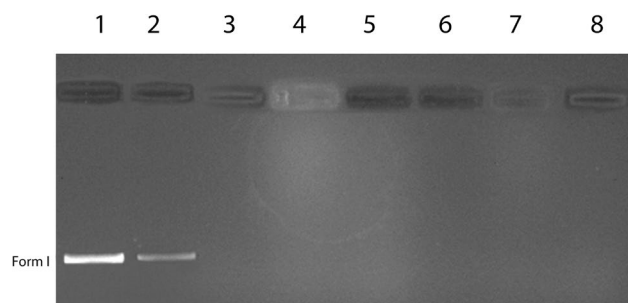


Fig. 7 DNA cleavage activities of phthalocyanine compounds. Lane 1, pBR 322 DNA; Lane 2, pBR 322 DNA + DMSO; Lane 3, pBR 322 DNA + 250 µg/mL of compound 6; Lane 4, pBR 322 DNA + 150 µg/mL of compound 6; Lane 5, pBR 322 DNA + 250 µg/mL of compound 5; Lane 6, pBR 322 DNA + 150 µg/mL of compound 5; Lane 7 pBR 322 DNA + 250 µg/mL of compound 4; Lane 8, pBR 322 DNA + 150 µg/mL of compound 4

Table 1 MIC values (µg/mL) of the test compounds

Microorganisms	MIC values (µg/mL)		
	4	5	6
<i>E. hirae</i>	256	32	16
<i>S. aureus</i>	64	16	16
<i>B. cereus</i>	64	64	16
<i>E. coli</i>	128	64	64
<i>P. aeruginosa</i>	32	16	8
<i>L. pneumophila</i> subsp. <i>pneumophila</i>	256	256	64
<i>C. albicans</i>	128	32	32
<i>C. tropicalis</i>	64	64	64

synthesis as a supportive. The calculated dipole moments show that the phthalocyanine compounds have non-linear optical properties. HOMO–LUMO energy values show that have the ability of phthalocyanine compounds to be a potential compound for inorganic semiconductor materials. The antioxidant activity of phthalocyanine compounds was determined using ferrous chelating activity and DPPH free-radical scavenging methods. Copper phthalocyanine showed the best DPPH activity at all concentrations. The maximum chelating activity was achieved with zinc phthalocyanine compound. All metallophthalocyanine compounds showed good DNA cleavage activity, and for this reason, they can be suitable agents for cleavage of DNA. Eventually antimicrobial activities of phthalocyanine compounds were detected using broth microdilution method. According to the results of the study, particularly Copper phthalocyanine had remarkable antibacterial activity for *P. aeruginosa*. Consequently, this study can contribute to novel drug progression on based the Pc compound. Besides, after further studies, the Pc compound can be evaluated as novel therapeutical agent for the microorganisms.

References

- Ağırtaş M, Güven M, Gumus S, Özdemir S, Dündar A (2014) Metallo and metal free phthalocyanines bearing (4-(1(4-phenoxyphenyl)-1-phenylethyl)phenol substituents: Synthesis, characterization, aggregation behavior, electronic, antioxidant and antibacterial properties. *Synth Met* 195:177–184. <https://doi.org/10.1016/j.synthmet.2014.06.004>
- Ağırtaş MS, Karataş C, Özdemir S (2015) Synthesis of some metallophthalocyanines with dimethyl 5-(phenoxy)-isophthalate substituents and evaluation of their antioxidant-antibacterial activities. *Spectrochim Acta Part A* 135:20–24. <https://doi.org/10.1016/j.saa.2014.06.139>
- Ağırtaş MS, Öndeş MY, Özdemir S, Okumuş V (2017) DNA cleavage properties and synthesis of metallophthalocyanines with 5-methyl-[1, 2, 4] triazolo [1, 5-a] pyrimidin-7-oxy substituents. *Inorg Nano Metal Chem* 47:1097–1102. <https://doi.org/10.1080/24701556.2017.1284086>
- Ajayi TJ, Shapi M (2020) Solvent-free mechanochemical synthesis, hirshfeld surface analysis, crystal structure, spectroscopic characterization and NBO analysis of Bis(ammonium) Bis((4-methoxyphenyl) phosphonodithioato)-nickel (II) dihydrate with DFT studies. *J Mol Struct* 1202:127254. <https://doi.org/10.1016/j.molstruc.2019.127254>
- Alexere SMI, Sliem MA, El-Balshy RM, Amin RM, Harith MA (2017) Exploiting biosynthetic gold nanoparticles for improving the aqueous solubility of metal-free phthalocyanine as biocompatible PDT agent. *Mater Sci Eng C* 76:727–734. <https://doi.org/10.1016/j.msec.2017.03.129>
- Armarego WLF, Chai CLL (2012) Purification of laboratory chemicals, Butterworth-Heinemann Oxford
- Aydın M, Alici EH, Bilgiçli AT, Yarasir MN, Arabaci G (2017) Synthesis, characterization, aggregation, fluorescence and antioxidant properties of bearing (4-(methylthio)phenylthio) tetra substituted phthalocyanines. *Inorg Chim Acta* 464:1–10. <https://doi.org/10.1016/j.ica.2017.04.038>
- Bicalho LS, Longo JPF, Cavalcanti CEO, Simioni AR, Bocca AL, de Almeida Santos MDFM, Tedesco AC, Azevedo RB (2013) Photodynamic therapy leads to complete remission of tongue tumors and inhibits metastases to regional lymph nodes. *J Biomed Nanotechnol* 9:811–818. <https://doi.org/10.1166/jbn.2013.1589>
- Burkitt R, Whiffen TR, Yu EH (2016) Iron phthalocyanine and MnOx composite catalysts for microbial fuel cell applications. *Appl Catal B Environ* 181:279–288. <https://doi.org/10.1016/j.apcatb.2015.07.010>
- Cabir B, Ağırtaş MS, Duygulu E, Yuksel F (2017) Synthesis of some metallophthalocyanines bearing 9-phenyl-9H-fluoren-9-yl) oxy functional groups and investigation of their photophysical properties. *J Mol Struct* 1142:194–199. <https://doi.org/10.1016/j.molstruc.2017.04.060>
- Cabir B, Yildiko U, Ağırtaş MS (2019) Synthesis, DFT analysis, and electronic properties of new phthalocyanines bearing ETAEO substituents on peripheral position. *J Coord Chem* 72:2997–3011. <https://doi.org/10.1080/00958972.2019.1680832>
- Cabir B, Yildiko U, Ağırtaş MS, Horoz S (2020) Computational DFT calculations, photovoltaic properties and synthesis of (2R, 3S)-2, 3, 4-trihydroxybutoxy substituted phthalocyanines. *Inorg Nano Metal Chem*. <https://doi.org/10.1080/24701556.2020.1725051>
- Dinis TCP, Madeira VMC, Almeida LM (1994) Action of phenolic derivatives (Acetaminophen, Salicylate, and 5-Aminosalicylate) as inhibitors of membrane lipid peroxidation and as peroxyl radical scavengers. *Arch Biochem Biophys* 315:161–169. <https://doi.org/10.1006/abbi.1994.1485>
- Eşme A, Sağdıç SG (2017) Spectroscopic (FT–IR, FT–Raman, UV–Vis) analysis, conformational, HOMO–LUMO, NBO and NLO calculations on monomeric and dimeric structures of 4-pyridazinecarboxylic acid by HF and DFT methods. *J Mol Struct* 1147:322–334. <https://doi.org/10.1016/j.molstruc.2017.06.110>
- Frisch MJTG, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji HCM, Li X, Hratchian HP, Izmaylov AF, Bloino JZG, Sonnenberg JL, Hada M, Ehara M, Toyota K., Fukuda RHJ, Ishida M, Nakajima T, Honda Y, Kitao, ONH, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro FBM, Heyd JJ, Brothers E, Kudin KN, Staroverov VN., Kobayashi RNJ, Raghavachari K, Rendell A, Burant JC, Iyengar SSTJ, Cossi M, Rega N, Millam MJ, Klene M, Knox JECJ, Bakken V, Adamo C, Jaramillo J, Gomperts RSR, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JWMM, Morokuma K, Zakrzewski VG, Voth, GASP, Dannenberg JJ, Dapprich S, Daniels AD, Farkas ÖFJ, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision D.01. Gaussian, Inc., Wallingford CT
- Gounden D, Nombona N, van Zyl WE (2020) Recent advances in phthalocyanines for chemical sensor, non-linear optics (NLO) and energy storage applications. *Coord Chem Rev* 420:213359. <https://doi.org/10.1016/j.ccr.2020.213359>
- Günsel A, Kırbaç E, Tüzün B, Erdoğan A, Bilgiçli AT, Yarasir MN (2019) Selective chemosensor phthalocyanines for Pd²⁺ ions; synthesis, characterization, quantum chemical calculation, photochemical and photophysical properties. *J Mol Struct* 1180:127–138. <https://doi.org/10.1016/j.molstruc.2018.11.094>
- Günsel A, Kobyaoglu A, Bilgiçli AT, Tüzün B, Tosun B, Arabaci G, Yarasir MN (2020) Novel biologically active metallophthalocyanines as promising antioxidant-antibacterial agents: synthesis, characterization and computational properties. *J Mol Struct* 1200:127127. <https://doi.org/10.1016/j.molstruc.2019.127127>
- Hande Alici E, Günsel A, Akin M, Bilgiçli AT, Arabaci G, Nilüfer Yarasir M (2018) Synthesis, characterization, antioxidant and antibacterial properties of non-peripherally and peripherally tetra-substituted phthalocyanines. *J Coord Chem* 71:3077–3089. <https://doi.org/10.1080/00958972.2018.1511778>

- Hay PJ, Wadt WR (1985) Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J Chem Physics* 82:299–310. <https://doi.org/10.1063/1.448975>
- Hepokur C, Günsel A, Yarasir MN, Bilgiçli AT, Tüzün B, Tüzün G, Yaylim İ (2017) Novel type ketone-substituted metallophthalocyanines: synthesis, spectral, structural, computational and anticancer studies. *RSC Adv* 7:56296–56305. <https://doi.org/10.1039/C7RA10517G>
- Ibbotson SH, Ferguson J (2012) Ambulatory photodynamic therapy using low irradiance inorganic light-emitting diodes for the treatment of non-melanoma skin cancer: an open study. *Photodermatol Photoimmunol Photomed* 28:235–239. <https://doi.org/10.1111/j.1600-0781.2012.00681.x>
- Jin Q-M, Lu Y, Jin J-L, Guo H, Lin G-W, Wang Y, Lu T (2014) Synthesis, characterization, DNA binding ability and cytotoxicity of the novel platinum(II), copper(II), cobalt(II) and nickel(II) complexes with 3-(1H-benzo[d]imidazol-2-yl)- β -carboline. *Inorg Chim Acta* 421:91–99. <https://doi.org/10.1016/j.ica.2014.05.036>
- Kantekin H, Büyüklüoğlu Z (2008) Synthesis and characterization of new polymeric phthalocyanines substituted with pyridine through methyleneoxy bridges by microwave irradiation. *Dyes Pigm* 77:432–436. <https://doi.org/10.1016/j.dyepig.2007.07.004>
- Khajehzadeh M, Moghadam M (2017) Molecular structure, FT IR, NMR, UV, NBO and HOMO–LUMO of 1-(3-(dimethylamino)propyl)-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile by DFT/B3LYP and PBE/PBE methods with LanL2DZ and 6–311++G(d,2p) basis sets. *Spectrochim Acta Part A* 180:51–66. <https://doi.org/10.1016/j.saa.2017.02.055>
- Korotkova E, Karbainov YA, Voronova O (2003) Investigation of antioxidant and catalytic properties of some biologically active substances by voltammetry. *Anal Bioanal Chem* 375:465–468. <https://doi.org/10.1007/s00216-002-1687-y>
- Li N, Sun Z, Liu R, Xu L, Xu K, Song XM (2016) Enhanced power conversion efficiency in phthalocyanine-sensitized solar cells by modifying TiO₂ photoanode with polyoxometalate. *Sol Energy Mater Sol Cells* 157:853–860. <https://doi.org/10.1016/j.solmat.2016.08.005>
- Mathammal R, Monisha NR, Yasaswini S, Krishnakumar V (2015) Molecular structure, vibrational analysis (FT-IR, FT-Raman), NMR, UV, NBO and HOMO–LUMO analysis of N, N-Diphenyl Formamide based on DFT calculations. *Spectrochim Acta Part A* 139:521–532. <https://doi.org/10.1016/j.saa.2014.11.057>
- Özel A, Barut B, Demirbaş Ü, Büyüklüoğlu Z (2016) Investigation of DNA binding, DNA photocleavage, topoisomerase I inhibition and antioxidant activities of water soluble titanium(IV) phthalocyanine compounds. *J Photochem Photobiol B* 157:32–38. <https://doi.org/10.1016/j.jphotobiol.2016.02.005>
- Pandey M, Muthu S, Nanje Gowda NM (2017) Quantum mechanical and spectroscopic (FT-IR, FT-Raman, 1H, 13C NMR, UV-Vis) studies, NBO, NLO, HOMO, LUMO and Fukui function analysis of 5-Methoxy-1H-benzo[d]imidazole-2(3H)-thione by DFT studies. *J Mol Struct* 1130:511–521. <https://doi.org/10.1016/j.molstruc.2016.10.064>
- Petersson GA, Al-Laham MA (1991) A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms. *J Chem Phys* 94:6081–6090. <https://doi.org/10.1063/1.460447>
- Pia Donzello M, Viola E, Tomachinskaya LA, Ercolani C, Corsini M, Zanello P, Stuzhin PA (2010) Synthesis and properties of styryl-substituted tetrapyrrolineporphyrins [St8PyzPzM], M = 2NaI, MgII(H₂O) and ZnII. *J Porphyr Phthalocya* 14:793–803. <https://doi.org/10.1142/S1088424610002677>
- Priya MK, Revathi BK, Renuka V, Sathya S, Asirvatham PS (2019) Molecular structure, spectroscopic (FT-IR, FT-Raman, 13C and 1H NMR) analysis, HOMO-LUMO energies, Mulliken, MEP and thermal properties of new chalcone derivative by DFT calculation. *Mater Today Proc* 8:37–46. <https://doi.org/10.1016/j.matpr.2019.02.078>
- Rao R, Patra AK, Chetana PR (2008) Synthesis, structure, DNA binding and oxidative cleavage activity of ternary (l-leucine/isoleucine) copper(II) complexes of heterocyclic bases. *Polyhedron* 27:1343–1352. <https://doi.org/10.1016/j.poly.2007.12.026>
- Roberts GG, Petty MC, Baker S, Fowler MT, Thomas NJ (1985) Electronic devices incorporating stable phthalocyanine Langmuir-Blodgett films. *Thin Solid Films* 132:113–123. [https://doi.org/10.1016/0040-6090\(85\)90463-8](https://doi.org/10.1016/0040-6090(85)90463-8)
- Saki N, Akin M, Atsay A, Pekbelgin Karaoglu HR, Kocak MB (2018) Synthesis and characterization of novel quaternized 2, 3-(diethylmethylamino)phenoxy tetrasubstituted Indium and Gallium phthalocyanines and comparison of their antimicrobial and antioxidant properties with different phthalocyanines. *Inorg Chem Commun* 95:122–129. <https://doi.org/10.1016/j.inoche.2018.07.010>
- Salan Ü, Kobayashi N, Bekaroğlu Ö (2009) Effect of peripheral substitution on the electronic absorption and magnetic circular dichroism (MCD) spectra of metal-free azo-coupled bisphthalocyanine. *Tetrahedron Lett* 50:6775–6778. <https://doi.org/10.1016/j.tetlet.2009.09.108>
- Salehi MH, Karimi AR (2018) Novel octa-substituted metal (II) phthalocyanines bearing 2,6-di-tertbutylphenol groups: synthesis, characterization, electronic properties, aggregation behavior and their antioxidant activities as stabilizer for polypropylene and high density polyethylene. *Polym Degrad Stab* 151:105–113. <https://doi.org/10.1016/j.polymdegradstab.2018.03.005>
- Sen P, Sindelo A, Mafukidze DM, Nyokong T (2019) Synthesis and photophysical properties of novel axially di-substituted silicon (IV) phthalocyanines and their photodynamic antimicrobial chemotherapy (PACT) activity against *Staphylococcus aureus*. *Synth Met* 258:116203. <https://doi.org/10.1016/j.synthmet.2019.116203>
- Solğun DG, Keskin Yıldırım MSÜ, Ağırtaş MS (2020) DFT analysis and electronic properties, and synthesis of tetra (9-phenyl-9H-xanthene-9-yl) oxy peripheral-substituted zinc phthalocyanine. *Chem Pap*. <https://doi.org/10.1007/s11696-020-01087-4>
- Vanasundari K, Balachandran V, Kavimani M, Narayana B (2017) Spectroscopic investigation, vibrational assignments, Fukui functions, HOMO-LUMO, MEP and molecular docking evaluation of 4-[(3, 4-dichlorophenyl) amino] 2-methylidene 4-oxo butanoic acid by DFT method. *J Mol Struct* 1147:136–147. <https://doi.org/10.1016/j.molstruc.2017.06.096>
- Yuan L, Gui L, Wang Y, Zhang Q, Zhou L, Wei S (2016) Photophysical and photochemical studies of a novel amphiphilic zinc phthalocyanine and its interaction with calf thymus DNA. *Spectrochim Acta Part A Mol Biomol Spectrosc* 158:1–8. <https://doi.org/10.1016/j.saa.2016.01.011>

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