

Synthesis and antioxidant, aggregation, and electronic properties of 6-tert-butyl-1,4-benzodioxine substituted phthalocyanines

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Abstract: As a starting material, 7-tert-butyl-dibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile was prepared by the reaction of 4-tert-butylcatechol with 4,5-dichlorophthalonitrile. Metallophthalocyanine complexes (**4–7**) were obtained by cyclotetramerization of 7-tert-butyl-dibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile. All compounds were characterized by elemental analysis and other spectroscopic methods (IR, UV/Vis, and ¹H NMR). Phthalocyanine compounds remained nonaggregated in tetrahydrofuran at the studied concentration ranges. Metallophthalocyanines (**4–7**) were tested for their antioxidant activities. The antioxidant activity processes included evaluation of radical-scavenging activity, chelating activity, and reducing power. These compounds were compared to standard antioxidant ascorbic acid. The electronic data of the new compounds were obtained by computational calculations at the B3LYP/6-31G (d,p) level of theory.

Key words: Phthalocyanines, synthesis, aggregation, antioxidant, electronic properties

1. Introduction

Phthalocyanines have been studied as dyes, in molecular electronics, as liquid crystals, as semiconductor materials, as light-emitting diodes, for nonlinear optical applications, as oxidation catalysts, and for laser dyes, as well as for chemical sensors and for electrochromic displays, etc.^{1–7} Soluble phthalocyanine compounds are preferred for many applications. The solubility can be increased by introducing different kinds of solubility-enhancing substituents such as alkyl, phenoxy, and alkoxy groups at the axial and peripheral positions of the Pc ring.^{8–12} Aggregation is an unfavorable property of phthalocyanine that decreases solubility and brings characterization and purification problems for phthalocyanines. Therefore, peripheral substitution has been performed to achieve nonaggregation of phthalocyanines.^{13,14} Current studies on phthalocyanines have expanded into several application fields such as photolysis of DNA in tumor cells, antibacterial and antioxidant activities, and photosensitizers for photodynamic therapy.^{15–18} A number of phthalocyanine derivatives have been prepared and screened for their antibacterial, antifungal, antioxidant, and antipathogenic activities.^{19,20} Production of antioxidant dyes and material has received considerable attention as a promising approach to combat oxidant and microbes.²¹ Our previous studies described the syntheses, characterization, and antioxidant activity of phthalocyanines bearing different substituents.^{22–24}

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In this paper, we have reported the preparation of some new 6-tert-butyl-1,4-benzodioxine substituted phthalocyanine derivatives and their aggregation behavior and antioxidant activities. The results of computational calculations have also been shown in this article.

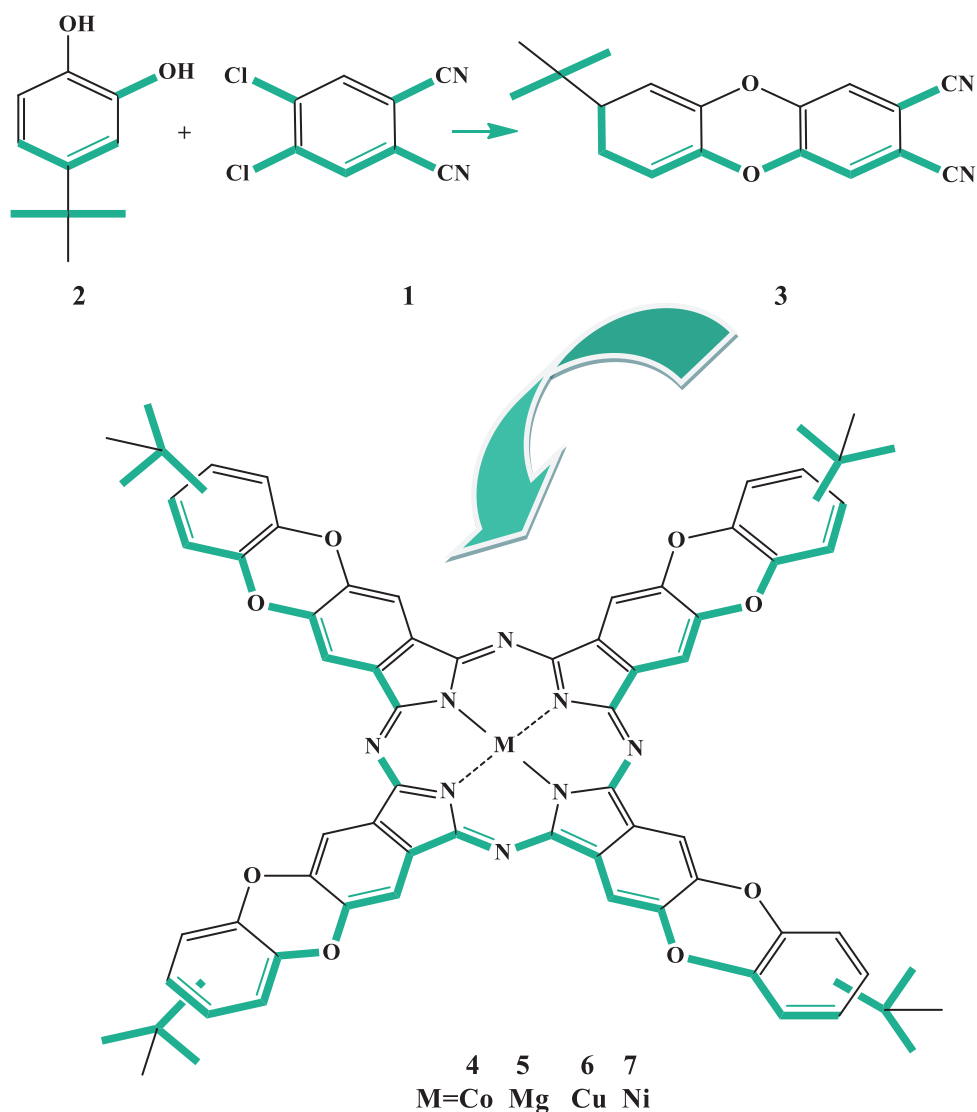
2. Results and discussion

The phthalonitrile and its phthalocyanine complexes were prepared following a slightly modified procedure that was described before.^{23,24} Compounds **4** and **5** were prepared by cyclotetramerization of 7-tert-butyl-dibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile in the presence of DBU, corresponding metal salts, and DMF as solvent with high yields. Dioxin derivatives exhibiting biological and antitumor activity can be found in the literature.²⁵ Compounds **4** and **5** could be prepared by DMF solvent with higher yields. Compounds **6** and **7** were synthesized under the same conditions but without solvent. The main reason for the choice of the dihydrobenzo [b] [1,4] dioxine group as the substituent was the expected contributions to the antioxidant activity and solubility. Solvents such as ethanol, methanol, and tetrahydrofuran were used to purify the products. The purity of phthalocyanine was controlled by thin-layer chromatography. Nonsubstituent phthalocyanine complexes are generally soluble in a limited number of organic solvents. Here the newly synthesized compounds are soluble in organic solvents such as 1,2-dichloroethane, dimethylformamide, tetrahydrofuran, and dimethyl sulfoxide. The new compounds were characterized by several spectroscopic methods including IR, ¹H NMR, UV/Vis spectroscopy, and elemental analysis. The proposed structures of the compounds were confirmed by the results of these analyses. The Scheme gives the synthetic pathway and structure of the compounds.

In the IR spectrum of **3**, the characteristic CN vibration was observed at 2234 cm⁻¹; the aromatic and aliphatic C – H peaks were observed at 3051, 2960, and 2871 cm⁻¹; and C = C and C – O – C vibration peaks were observed at 1566 cm⁻¹ and 1241 cm⁻¹, respectively. After the formation of metallophthalocyanines, the CN stretching frequency peak disappeared in the IR spectra. The C – H stretching vibration of aliphatic methylene groups and Ar – O – Ar vibrations were observed at 2954–2868 and 1237 cm⁻¹ for phthalocyanine **4**, 2955–2868 and 1237 cm⁻¹ for phthalocyanine **5**, 2956–2865 and 1237 cm⁻¹ for phthalocyanine **6**, and 2956 and 1241 cm⁻¹ for phthalocyanine **7**, respectively.

The structures of compounds **3**, **5**, and **7** were confirmed by ¹H NMR spectra. In the ¹H NMR spectrum of compound **3** in DMSO-d₆, aromatic protons appeared at 7.70 and 7.07–6.93 ppm, and aliphatic protons were observed at 1.24 (CH₃) ppm. In the ¹H NMR spectrum of compound **5** in DMSO-d₆, aromatic protons appeared at 7.80 and 7.30–6.91 ppm as a broad band, while the CH₃ aliphatic protons appeared at 1.24 ppm. Integration of the signals in the aromatic region allowed the structure of **5** to be determined. ¹H NMR measurements of compounds **4** and **6** were excluded due to their paramagnetic properties. In the ¹H NMR spectrum of compound **7** in DMSO-d₆, aromatic protons appeared at 7.80 and 7.04–6.98 ppm as a broad band and the CH₃ aliphatic protons appeared at 1.24 ppm.

Figure 1 and Figures 2a–2c show the representative geometry-optimized structure (cobalt phthalocyanine **4**) and the charge distribution in the center of the presented complexes, obtained by natural bond order analysis, respectively.²⁶ The resulting geometries obtained after computations reveal that the complexes indicate square-planar geometry throughout the molecule. The charge distribution depends on the type of the central metal atom. As seen in Figure 2c, the formal charge +2 of the metal atom at the center of the structure decreased to a net charge ranging from +1.391 to +0.964, which is a consequence of charge donation from coordinating nitrogen atoms. The charge distribution maps for **5** (Figure 2a) and **7** (Figure 2b) are also given. The darker blue color for the Mg complex indicates a more positive charge location. All the donor nitrogens were computed



Scheme. Synthetic pathway of compounds 3–7.

to locate negative charges. The coordinating nitrogen atoms are more electron-rich than the connecting nitrogen atoms, which might be a result of the absence of an imino hydrogen atom. The expected -1 formal charge on these atoms decreased absolutely to -0.612 upon coordination to the metal atom.

Moreover, after geometry optimizations, the structures were subjected to time-dependent density functional theory (TD-DFT) calculations with the same basis set (B3LYP/6-31G (d,p)) to compute the electronic spectra of the phthalocyanine compounds. Transition energies and molecular orbital energies and schemes were predicted for singlet state excitations. Molecular orbital energies indicate that transitions from HOMO to LUMO are responsible for the Q band of the experimental spectrum. Calculated UV/Vis spectra and three-dimensional HOMO and LUMO molecular orbital schemes for compounds **5** and **7** are shown in Figures 3 and 4, respectively. The absorption bands for the UV/Vis spectra may slightly differ from the experimental data due to the fact that the computations were performed for isolated molecules, whereas experimental data were obtained for the bulk system (Figure 3).²⁷ The carbon and nitrogen atoms of the central periphery contribute

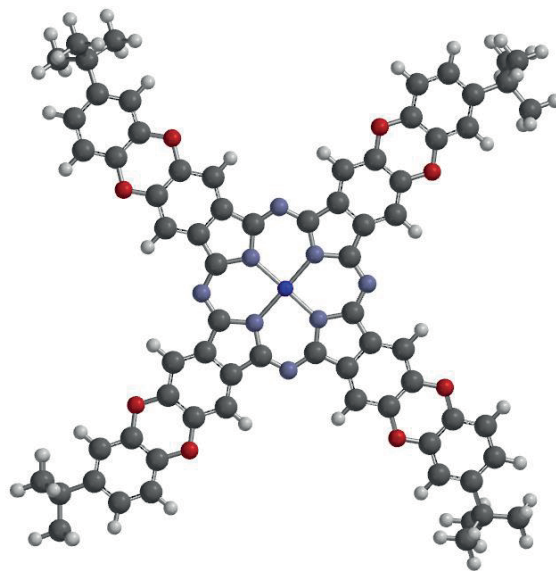


Figure 1. Geometry optimized structure of 4.

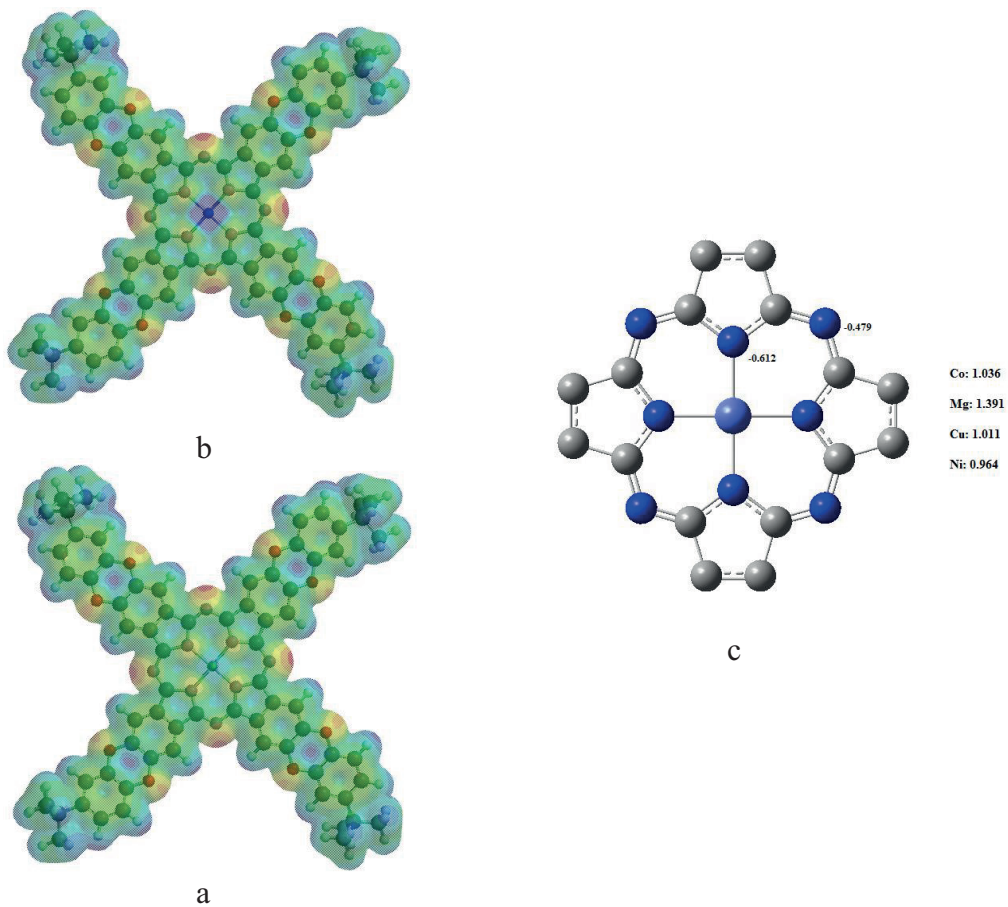


Figure 2. Charge distribution maps for 5 (a) and 7 (b), and charges on Mulliken charge distribution (c).

both HOMO and LUMO of the complexes with little contribution from the outer atoms (Figure 4 for compound 5 and 7).

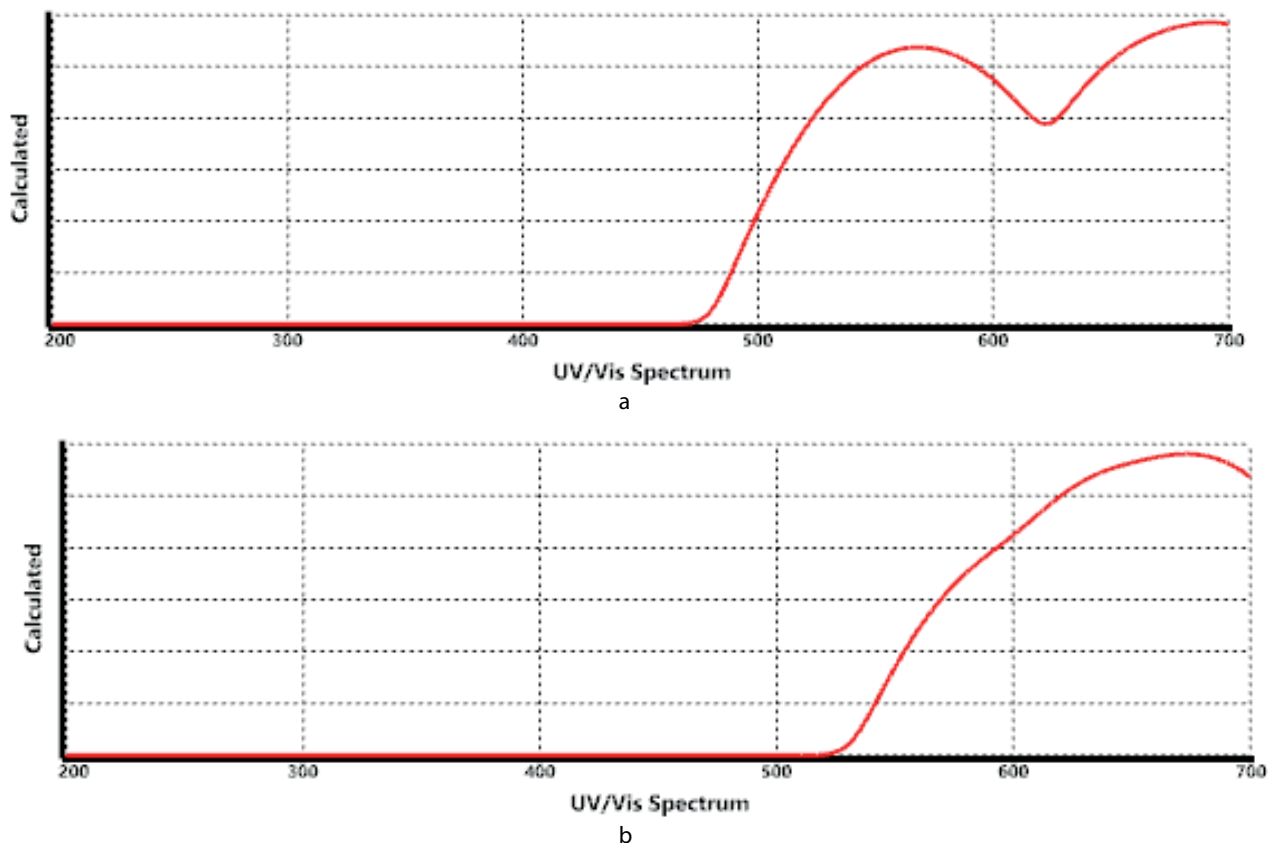


Figure 3. Computed UV/Vis spectra of Mg (5 (a)) and Ni (7 (b)) complexes.

Generally, phthalocyanine aggregation results in a decrease in intensity in the components of the Q bands corresponding to the monomeric species; meanwhile, a new, broader, and blue-shifted band is seen to increase in intensity. The shift to lower wavelengths corresponds to H-type aggregates. The shift to higher wavelengths corresponds to J-type aggregates.²⁸ High aggregation tendency of phthalocyanine compounds due to the interactions between their 18π -electron systems often causes weak solubility or insolubility in many solvents. It also seriously affects their spectroscopic, photophysical, photochemical, and electrochemical properties. Aggregation behavior of phthalocyanines is dependent on some parameters such as concentration, temperature, nature of the substituents, nature of the solvents, and the metal ion types.^{29,30} Electronic absorption spectroscopy has been extensively used to determine the formation of phthalocyanine aggregation. In this study, the aggregation behaviors of 4–7 were investigated at different concentrations in THF. Synthesized metallophthalocyanine compounds 4–7 exhibited quite good solubility in THF. The aggregation behavior of 5 and 6 in THF is shown in Figures 5 and 6, respectively. Phthalocyanine compounds 4–6 did not show aggregation behavior at the studied concentration ranges (for 4: 1.35×10^{-5} to 4.27×10^{-6} M, for 5: 1.38×10^{-4} to 4.39×10^{-5} M, for 6: 1.34×10^{-5} to 4.25×10^{-6} M) in THF. Therefore, these complexes can be used potentially for many applications. Electronic absorptions of phthalocyanine compounds 4–6 in THF are displayed in Figure 7.

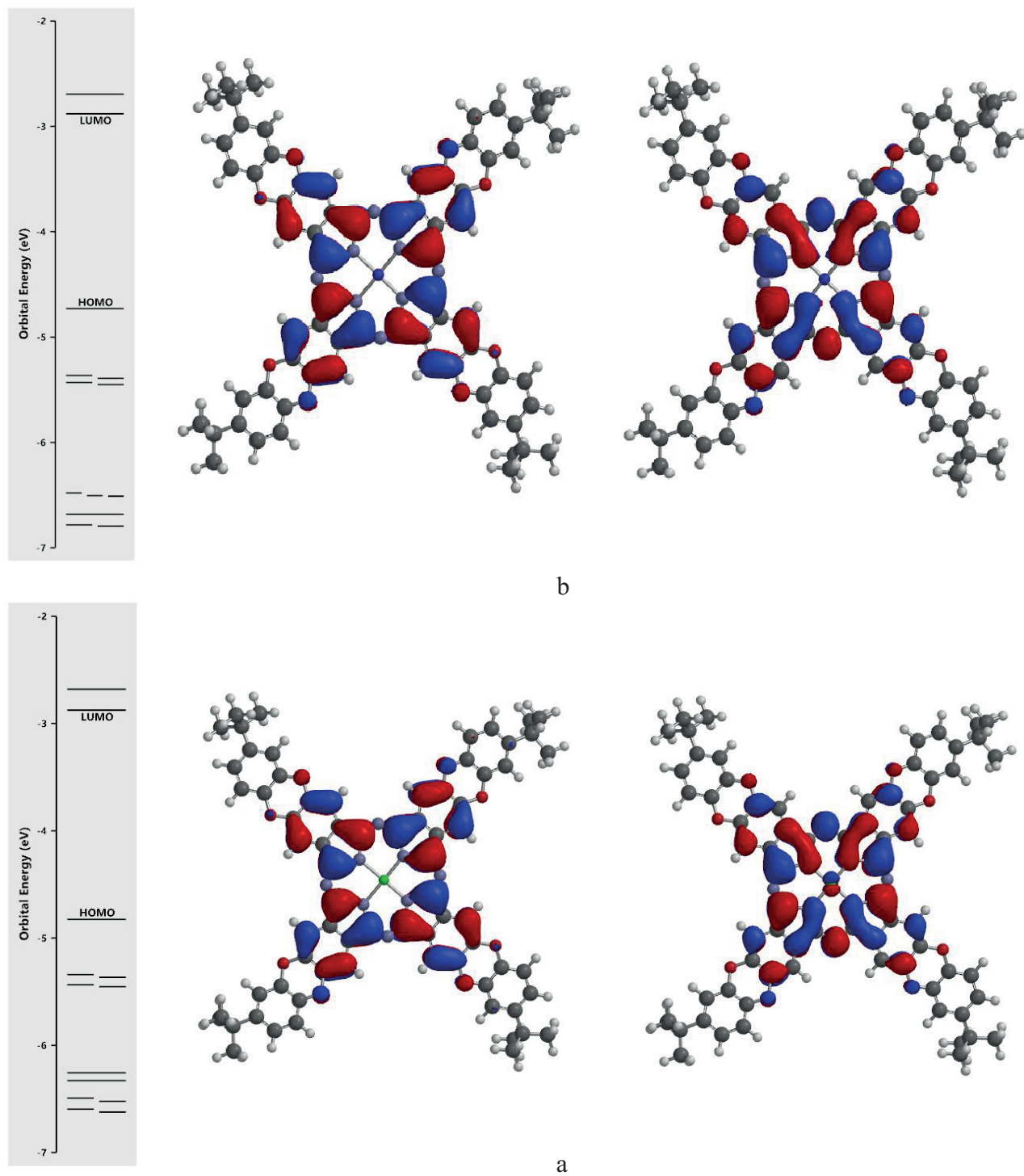


Figure 4. Frontier molecular orbital schemes and molecular orbital energy levels of Mg (5 (a)) and Ni (7 (b)) phthalocyanines.

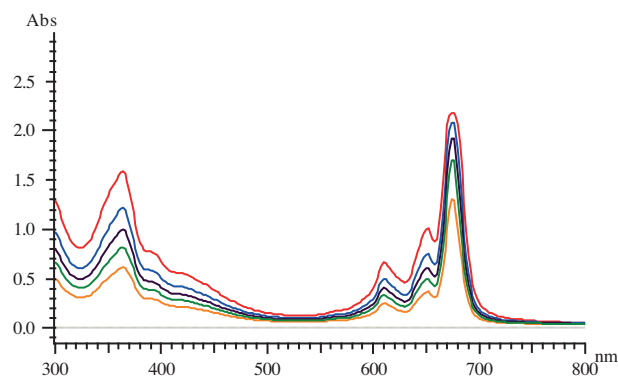


Figure 5. The aggregation behavior of compound 5 in THF.

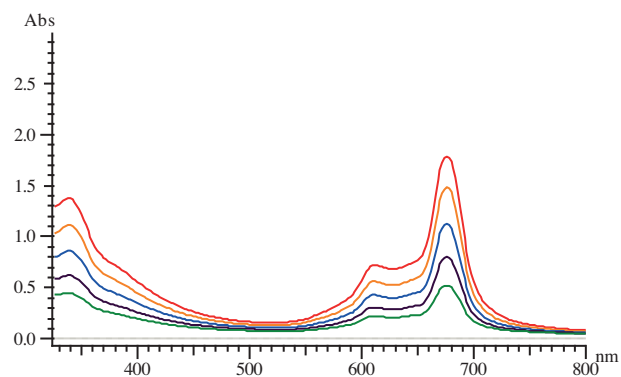


Figure 6. The aggregation behavior of compound 6 in THF.

It is well known that free radicals are major factors in biological damage.³¹ DPPH radical-scavenging test systems are generally used to determine the ability of phthalonitrile and its phthalocyanine complexes to scavenge free radicals generated from DPPH reagent.³¹ As can be seen in Figure 8, the tested phthalonitrile and its phthalocyanine complexes showed dose-dependent free radical-scavenging (DPPH) activities. The DPPH radical-scavenging activities of **3**, **4**, **5**, **6**, and **7** were found to be 20.7%, 13.4%, 11.3%, 20.4%, and 11.1% at a concentration of 25 mg/L, respectively. The data obtained here correlate well with the literature data of the previous phthalocyanine studies.²⁸ The DPPH scavenging activity of compound **3** (20.7%) is almost the same as that of phthalocyanine **6** (20.4%). The maximum free radical-scavenging activity was determined as 59.06% with **3** at a concentration of 100 mg/L. Ascorbic acid and Trolox were used as positive standards.

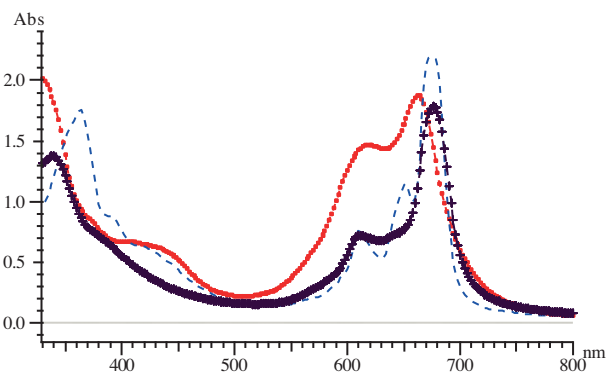


Figure 7. Electronic absorptions of phthalocyanine compounds 4 (red), 5 (blue), and 6 (black) in the THF.

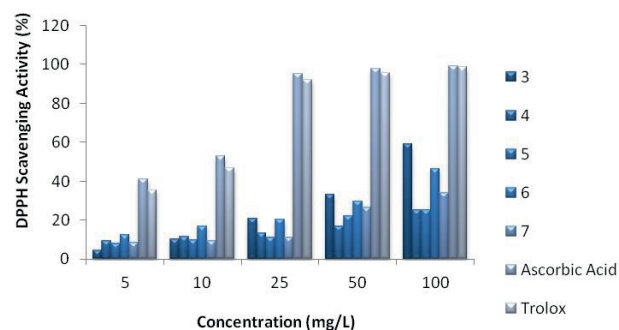


Figure 8. DPPH scavenging activity of different concentrations of compounds and standards.

Iron, which causes hydroxyl radical generations, can stimulate lipid peroxidation by Haber–Weiss and Fenton-type reactions in biological systems. The metal ions both possess catalytic activity and correlate with the incidence of arthritis and cancer.³² The ferrous ion-chelating activities of the tested phthalonitrile and its phthalocyanine complexes are presented in Figure 9. It was observed that chelating activities of the tested phthalonitrile and its phthalocyanine complexes increased when the concentration increased. At a concentration of 50 mg/L, the ferrous ion-chelating activities of the tested phthalonitrile and its phthalocyanine complexes were found to be in the following order: **5** > **3** > **4** > **7** > **6**. The highest chelating activity was found as

76.8% with **3** at a concentration of 100 mg/L in all studied test samples. EDTA was used as a standard and showed 100% chelating activity at a concentration of 50 mg/L.

In this study, the color of the solutions of tested phthalonitrile and its phthalocyanine complexes changed from yellow to various shades of green and blue depending upon the reducing power of these antioxidants.³³ The presence of an antioxidant substance induces the reduction of the Fe^{3+} /ferricyanide complex to the ferrous form. The results showed that the maximum reducing powers of **3**, **4**, **5**, **6**, **7**, and α -tocopherol were 0.109, 0.106, 0.089, 0.098, and 0.495, respectively, at a concentration of 100 mg/L (Figure 10).

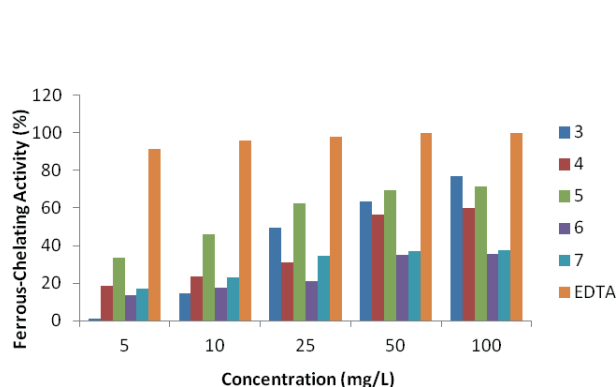


Figure 9. Metal chelating activity of different concentrations of compounds and EDTA.

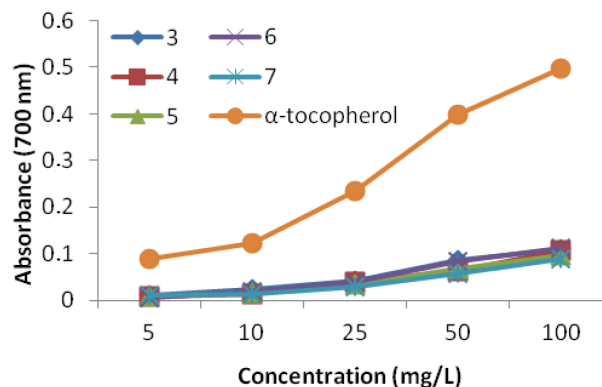


Figure 10. Reducing power of different concentrations of compounds and α -tocopherol.

In this study, we have designed, synthesized, and characterized metallophthalocyanine derivatives (Co, Mg, Cu, Ni) soluble in organic solvents, derived from 7-tert-butylidibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile. These complexes were not aggregated in a wide concentration range in THF. In addition, the antioxidant activities of the phthalonitrile and its phthalocyanine complexes were determined. The main characteristic of an antioxidant is its ability to trap free radicals. Antioxidant compounds scavenge free radicals such as peroxide, hydroperoxide, or lipid peroxyl and thus inhibit the oxidative mechanisms that lead to degenerative diseases. The phthalonitrile and its phthalocyanine complexes provided remarkable antioxidant activities. Compound **3** showed good chelating activity at a concentration of 100 mg/L and from that point of view it might be used as a standard after the toxicological test systems. Computational calculations at the level of (B3LYP/6-31G (d,p)) were performed to obtain structural and electronic properties of the novel complexes.

3. Experimental

3.1. Synthesis

2,2-Diphenyl-1-picrylhydrazyl (DPPH), ferrous chloride, 3-(2-pyridyl)-5,6-bis(4-phenyl-sulfonic acid)-1,2,4-triazine (ferrozine), ascorbic acid, Trolox, and dimethylformamide (DMF) were obtained from Sigma-Aldrich GmbH (Steinheim, Germany). CoCl_2 , MgCl_2 , CuCl_2 , NiCl_2 , K_2CO_3 , CHCl_3 , THF, DMSO, and DBU were purchased from Merck (Darmstadt, Germany). The solvents were purified according to standard procedure³⁴ and stored over molecular sieves (4 Å). All reactions were carried out under dry nitrogen atmosphere. Melting points were measured on an electrothermal apparatus. Electronic spectra were recorded on a Hitachi U-2900 spectrophotometer. Routine IR spectra were recorded on a Thermo Scientific FTIR (ATR sampling accessory)

spectrophotometer. ^1H NMR spectra were recorded on a Bruker 300 MHz spectrometer with tetramethylsilane as the internal standard.

3.2. 7-Tert-butyldibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile (3)

A mixture of 4-tert-butylcatechol **2** (0.83 g, 5 mmol) and 4,5-dichlorophthalonitrile **1** (0.98 g, 5 mmol) in 30 mL of DMF was stirred at room temperature under nitrogen atmosphere. After stirring for 15 min, K_2CO_3 (5.2 g, 36 mmol) was added to the mixture over a period of 2 h. After stirring the reaction mixture for a further 24 h at 80 °C, the reaction mixture was poured into water (150 mL) and stirred. The precipitate was filtered, washed with water, and dried in vacuum. Yield: 1.33 g (91%). Compound is soluble in dimethyl sulfoxide, methanol, benzene, acetone, toluene, dichloromethane, chloroform, tetrahydrofuran, and 1,2-dichloroethane. Mp: 209–210 °C. Anal. calculated for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$: C 74.47; H 4.86; N 9.65 %. Found C 74.58; H 4.77; N 9.49 %. ^1H NMR (d_6 -DMSO, 300 MHz, δ ppm): 7.70 (s, 2H, Ar – H); 7.07–6.93 (m, 3H, Ar – H); 1.24 (s, 9H, CH_3). IR spectrum (cm^{-1}): 3051 (Ar – H), 2960 (CH_3), 2871, 2234 (CN), 1566 (C = C), 1494, 1429, 1241 (Ar – O – Ar), 1123, 899, 814, 710.

3.3. [Tetrakis 6-(tert-butyl)-2,3-dihydrobenzo [b] [1,4] dioxine) phthalocyaninato] cobalt(II) (4)

A mixture of 7-tert-butyldibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile **3** (0.124 g, 0.43 mmol) and CoCl_2 (0.020 g) was dissolved in DMF (2.5 mL) under nitrogen in the presence of DBU (0.05 mL). Then the mixture was heated for 24 h under nitrogen atmosphere at 153 °C. After cooling to room temperature, the crude product was precipitated by adding water. The precipitate was filtered and washed with cold and hot ethanol and methanol several times. The product was dissolved in THF to remove impurities. Then the THF was evaporated to dryness to obtain the final product. This procedure was repeated several times. The purity of the final product was controlled by thin-layer chromatography. The product is soluble in 1,2-dichloroethane, dimethylformamide, tetrahydrofuran, and dimethyl sulfoxide. Yield: 0.041 g (32%). Calc. for $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Co}$: C, 70.87; H, 4.63; N, 9.18 %. Found: C, 70.79; H, 4.70; N, 9.22 %. UV/Vis (THF) λ max ($\log \epsilon$): 662 (5.27), 620 (5.16), 314 (5.28). IR spectrum (cm^{-1}): 3064 (Ar – H), 2954 (CH_3), 2868, 1587 (C = C), 1512 (C = C), 1495, 1463, 1288, 1237 (Ar – O – Ar), 1089, 934, 810, 750.

3.4. [Tetrakis 6-(tert-butyl)-2,3-dihydrobenzo [b] [1,4] dioxine) phthalocyaninato] magnesium(II) (5)

A mixture of 7-tert-butyldibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile **3** (0.124 g, 0.43 mmol) and MgCl_2 (0.020 g) was dissolved in DMF (2.5 mL) under nitrogen in the presence of DBU (0.05 mL). Then the mixture was heated for 48 h under nitrogen atmosphere at 153 °C. After cooling to room temperature, the crude product was precipitated by adding water. The precipitate was filtered and washed with cold and hot ethanol and methanol several times. The product was dissolved in THF to remove impurities. Then the THF was evaporated to dryness to obtain the final product. This procedure was repeated several times. The purity of the final product was controlled by thin-layer chromatography. The product is soluble in 1,2-dichloroethane, dimethylformamide, tetrahydrofuran, and dimethyl sulfoxide. Yield: 0.032 g (25%). Calc. for $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Mg}$: C, 72.94; H, 4.76; N, 9.45 %. Found: C, 72.88; H, 4.80; N, 9.48. ^1H NMR (DMSO- d_6 , 300 MHz, δ ppm): 7.80 (s, 8H, Ar – H); 7.30 – 6.91 (m, 12H, Ar – H); 1.24 (s, 36H, CH_3). UV/Vis (THF) λ max ($\log \epsilon$): 674 (5.34), 610 (4.88), 364

(5.24). IR spectrum (cm^{-1}): 3068 (Ar – H), 2955 (CH_3), 2868, 1587 (C = C), 1512 (C = C), 1495, 1465, 1286, 1237 (Ar – O – Ar), 1089, 934, 810.

3.5. [Tetrakis 6-(tert-butyl)-2,3-dihydrobenzo [b] [1,4] dioxine) phthalocyaninato] copper(II) (6)

A mixture of 7-tert-butyldibenzo [b,e] [1,4] dioxine-2,3-dicarbonitrile **3** (0.100 g, 0.35 mmol) and CuCl_2 (0.020 g) was powdered in a quartz crucible and heated in a sealed glass tube for 5 min under nitrogen at 270 °C. The mixture was cooled to room temperature. After washing with cold and hot ethanol and methanol several times, the product was filtered. The product was dissolved in THF to remove impurities. Then the THF was evaporated to dryness to obtain the final product. This procedure was repeated several times. The purity of the final product was controlled by thin-layer chromatography. The product is soluble in dimethylformamide, tetrahydrofuran, dimethyl sulfoxide, and dichloroethane. Yield: 0.014 g (13%). Calc. for $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Cu}$: C, 70.60; H, 4.61; N, 9.15 %. Found: C, 70.66; H, 4.57; N, 9.20 %. UV/Vis (THF) λ max (log ϵ): 676 (5.17), 612 (4.75), 340 (5.05) IR spectrum (cm^{-1}): 3062 (Ar – H), 2956 (CH_3), 2865, 1588 (C = C), 1512 (C = C), 1495, 1462, 1286, 1237 (Ar – O – Ar), 1090, 935, 810.

3.6. [Tetrakis 6-(tert-butyl)-2,3-dihydrobenzo [b] [1,4] dioxine) phthalocyaninato] nickel(II) (7)

A mixture of 7-tert-butyldibenzo [b,e] [1, 4] dioxine-2,3-dicarbonitrile **3** (0.100 g, 0.35 mmol) and NiCl_2 (0.017 g) was powdered in a quartz crucible and heated in a sealed glass tube for 5 min under nitrogen at 270 °C. The mixture was cooled to room temperature. After washing with cold and hot ethanol and methanol several times, the product was filtered. The product was dissolved in THF to remove impurities. Then the THF was evaporated to dryness to obtain the final product. This procedure was repeated several times. The purity of the final product was controlled by thin-layer chromatography. The product is soluble in dimethylformamide, tetrahydrofuran, dimethyl sulfoxide, and dichloroethane. Yield: 0.0132 g (12%). Calc. for $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Ni}$: C, 70.89; H, 4.63; N, 9.19 %. Found: C, 70.86; H, 4.59; N, 9.21 %. ^1H NMR (DMSO-d_6 , 300 MHz, δ ppm): 7.80 (s, 8H, Ar – H); 7.04–6.98 (m, 12H, Ar – H); 1.24 (s, 36H, CH_3). UV/Vis (THF) λ max (log ϵ): 672 (5.18), 620 (4.80), 316(5.05). IR spectrum (cm^{-1}): 3050 (Ar – CH), 2956 (CH_3), 1589 (C = C), 1564 (C = C), 1492, 1241 (Ar – O – Ar), 1201, 1170, 1123, 1094, 830.

3.7. 2,2-Diphenyl-1-picrylhydrazyl radical-scavenging activity

DPPH free radical-scavenging activity of the compounds was tested by measuring the change in the absorbance of DPPH at 517 nm by spectrophotometer.²⁹ The stock solutions of all test compounds and DPPH were prepared in methanol and DMF, respectively. Different concentrations (10–100 mg/L) of 400 μL of test compounds were added to 1600 μL of methanol solution of DPPH. The mixture was then shaken vigorously and left to stand for 30 min in the dark at room temperature. The control contained 1600 μL of DPPH solution and 400 μL of methanol. The absorbance was measured at 517 nm against a blank, which consisted of only 2 mL of DMF, by a spectrophotometer. Inhibition of the free radical DPPH in percentage (I %) was calculated according to following formula:

$$I\% = (A_{control} - A_{sample})/A_{control} \times 100$$

Here, $A_{control}$ is the absorbance of the control reaction (containing all reagents except the test compound), and A_{sample} is the absorbance of the test compound. Tests were carried out in triplicate.

3.8. Metal chelating activity

The ferrous chelating activity of the test compounds was studied as reported in the literature.²⁴ DMF solution of compounds (1.0 mL) was added to 3.7 mL of deionized water and the mixture was then reacted with FeCl₂ (2 mM, 0.1 mL) and ferrozine (5 mM, 0.2 mL) for 10 min. Finally, the absorbance was measured at 562 nm against a blank solution by spectrophotometer. The ferrous chelating activity of the test compounds was calculated as follows:

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

Here, A_{control} is the absorbance of the control reaction (containing only FeCl₂ and Ferrozine), and A_{sample} is the absorbance of the compounds/reference. EDTA was used as a positive control.

3.9. Reducing power

The reducing power of the test compounds was examined using the method of Oyaizu.³⁵ Different concentrations of test compounds (1.25 mL, 5–100 mg/L) were added to 1.25 mL of 200 mM sodium phosphate buffer (pH 6.6) and 1.25 mL of 1% potassium ferricyanide. The mixture was incubated at 50 °C for 20 min. After 20 min, 1.25 mL of 10% trichloroacetic acid (w/v) was added and the mixture was centrifuged at 1000 rpm for 8 min. Supernatant solution (5 mL) was mixed with 1.25 mL of deionized water and 0.25 mL of 0.1% of ferric chloride. The absorbance was measured spectrophotometrically at 700 nm. α -Tocopherol was used as a standard.

3.10. Computational method

Three-dimensional structures of the compounds were obtained upon geometry optimization using density functional theory at the B3LYP/6-31 G (d,p) level with no symmetry restrictions. All computational calculations were performed using the Gaussian 09 package program.³⁶ The vibrational analysis for each metal phthalocyanine complex did not yield any imaginary frequencies, which indicates that the structure of each molecule stands at least at a local minimum on the potential energy surface. The normal mode analysis was performed for $3N - 6$ vibrational degrees of freedom, N being the number of atoms in the structure of the phthalocyanine compounds.

The TD-DFT calculations were done to obtain the vertical excitation energies, oscillator strengths (f), and excited state compositions in terms of excitations between the occupied and virtual orbitals for metal complexes.^{37,38} In this study, the TD-DFT method with the same basis set was applied to obtain absorption wavelengths and the oscillation strength (f) within the visible to near-UV region.

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