

Synthesis and spectral and thermal characterization of new metal-free and metallophthalocyanines: investigation of their photophysical, photochemical, and thin film properties

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Abstract: Novel tetrasubstituted metal-free (**2**), zinc (II) (**3**), cobalt (II) (**4**), and copper (II) (**5**) phthalocyanines bearing 2-phenylethanolate groups on the peripheral positions were synthesized by the cyclotramerization reaction of the phthalonitrile derivative **1**. The new compounds were characterized by a combination of IR, ¹H NMR, ¹³C NMR, UV-Vis, elemental analysis, and MS spectra data. The thermal stabilities of the phthalocyanine compounds were determined by thermogravimetric analysis. For metal-free (**2**) and zinc (**3**) phthalocyanines, photochemical (photodegradation and singlet oxygen quantum yields) and photophysical (fluorescence quantum yields and fluorescence lifetimes) properties were analyzed in dimethylsulfoxide (DMSO). The cobalt (**4**) and copper (**5**) phthalocyanines were not evaluated for this purpose because of their paramagnetic behavior. The metal-free (**2**) and zinc (**3**) phthalocyanines' fluorescence quenching behaviors were also investigated. The new phthalocyanine compounds' fluorescence emissions were effectively quenched by 1,4-benzoquinone in DMSO. The thin films of the cobalt phthalocyanine compound (**4**) were grown by electron beam evaporation technique. Crystalline CoPc (**4**) thin films were investigated by X-ray diffraction spectroscopy. Surface morphology of the CoPc (**4**) thin films was characterized by SEM.

Key words: Phthalocyanine, fluorescence, quantum yields, singlet oxygen, photodegradation, thin film

1. Introduction

Phthalocyanines have been the subject of a great deal of wide-ranging research for over 60 years. Phthalocyanines' properties have interesting potential technical applications such as molecular electronics, semiconductor and electrochromic display devices, photovoltaic and solar cells, gas sensors, synthetic metals, liquid crystals, optical disks, photodynamic therapy of cancer, electrophotography, and nonlinear optics.¹⁻⁴ Microwave (MW) irradiation is accelerated by many chemical processes.⁵

Photodynamic therapy (PDT) is of great importance as a combination of a photosensitizing drug and light, used to treat nononcologic diseases. It is used for alternative treatment of malignant tumors. Photosensitizing agents used for the inactivation of several types of cancer cells.⁶

Phthalocyanines in thin film form have recently become very important materials in the field of micro-

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electronics. Thin film applications were used significantly only over the last 2 decades.^{7,8} Phthalocyanine thin films can be used for the fabrication of active elements in electronic devices and also used as gas sensors.⁹ The preparation of thin film techniques has an important role in technological applications. Phthalocyanines can easily be sublimed to form stable and homogeneous thin films because of their thermal and chemical stability.

We have previously described the synthesis and characterization of metal-free and metallophthalocyanine polymers by microwave irradiation.¹⁰ In this paper, we describe the synthesis and characterization of metal-free phthalocyanine (**2**), which was accomplished in DBU and *n*-pentanol in a Schlenk tube under N₂ atmosphere, and metallophthalocyanines **3**, **4**, and **5** by microwave irradiation. In addition, we report on the effects of peripheral substituent on the photochemical and photophysical parameters of the metal-free (**2**) and zinc (**3**) phthalocyanine derivatives. Photochemical (singlet oxygen and photodegradation quantum yields) and photophysical (quantum yields and fluorescence quantum yields) properties were investigated. This work also explores the effects of substituents and the central metal ions (metal-free or zinc) of the phthalocyanine compounds' fluorescence properties and on the quenching of the phthalocyanines by 1,4-benzoquinone (BQ). The thin films of cobalt phthalocyanine compound (**4**) were grown by electron beam evaporation technique.

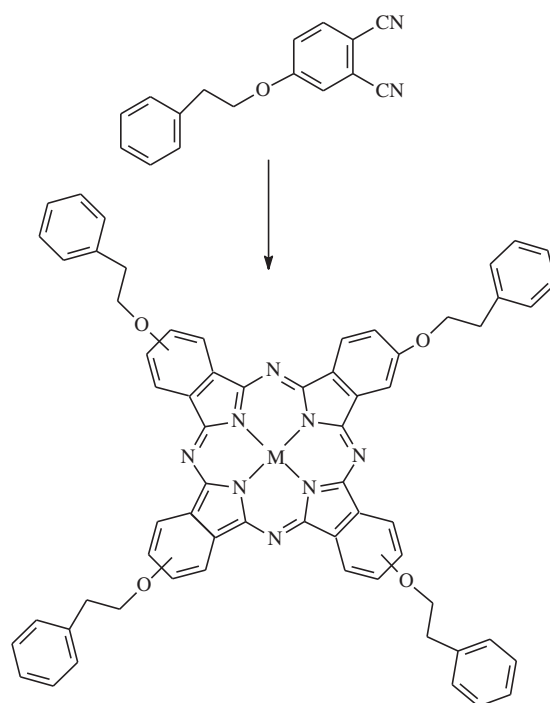
2. Results and discussion

2.1. Synthesis and characterization

The syntheses of new phthalocyanines (**2**, **3**, **4**, and **5**) are shown in Scheme. 4-Phenylethoxyphthalonitrile (**1**) was synthesized by the literature procedure.¹¹

Metal-free phthalocyanine compound (**2**) was synthesized from the corresponding phthalonitrile compound **1** under nitrogen atmosphere in the presence of DBU in dry *n*-pentanol. The IR spectrum of metal-free phthalocyanine (**2**) showed a peak at 3280 cm⁻¹ due to NH vibrations. The disappearance of the C≡N stretching vibration on the IR spectra of phthalonitrile compound **1** suggested the formation of compound phthalocyanine derivative **2**. The ¹H NMR spectra of this compound showed a new signal at $\delta = -5.77$ ppm belonging to the inner core protons in the cavity. The ESI mass spectrum of this compound showed a molecular ion peak at $m/z = 995$ [M]⁺ (Figure 1) consistent with the proposed formula for this structure. The elemental analysis results confirmed the structure of the desired compound (**2**).

Metallophthalocyanines **3**, **4**, and **5** were obtained from the reaction of phthalonitrile derivative **1** with corresponding anhydrous metal salts Zn(CH₃COO)₂ for complex **3**, CoCl₂ for complex **4**, and CuCl₂ for complex **5** in 2-(dimethylamino)ethanol using microwave irradiation. Elemental analysis, ¹H NMR, IR, MS, and UV-Vis spectra confirmed the proposed structures of the metallophthalocyanines. The IR spectra of metal-free and metallophthalocyanines are very similar. The significant difference is the presence of γ (N-H) vibrations of the inner phthalocyanine core protons, which are assigned to a weak band at 3280 cm⁻¹ for metal-free derivatives. This band disappeared in the IR spectra of the metallophthalocyanines. This band is especially beneficial for characterization of metal-free phthalocyanine derivatives. The intense absorption vibrations at 2229 cm⁻¹ corresponding to the C≡N groups for phthalonitrile compound **1** disappeared after their conversion into the metallophthalocyanines **3–5**. The NMR spectra of metallophthalocyanine compounds were similar to those of the precursor phthalonitrile compound **1**. In the ESI mass spectra of **3–5** (Figures 2–4), the molecular ion peaks were observed at $m/z = 1058$ [M]⁺ for complex **3**, $m/z = 1052$ [M]⁺ for complex **4**, and $m/z = 1055$ [M]⁺ for complex **5**, which confirmed the proposed structure. The elemental analyses results of metallophthalocyanine complexes **3–5** confirm the structure of the desired phthalocyanine compounds.



Compound	2	3	4	5
M	2H	Zn(II)	Co(II)	Cu(II)

- 2: Schlenk tube, dry n-pentanol, N₂, 160 °C
 3: Microwave, 350 W, 6 min, DMAE, DBU, 175 °C, anhydrous Zn(CH₃COO)₂
 4: Microwave, 350 W, 5 min, DMAE, DBU, 175 °C, anhydrous CoCl₂
 5: Microwave, 350 W, 8 min, DMAE, DBU, 175 °C, anhydrous CuCl₂

Scheme. The syntheses of the metal-free phthalocyanine and metallophthalocyanines.

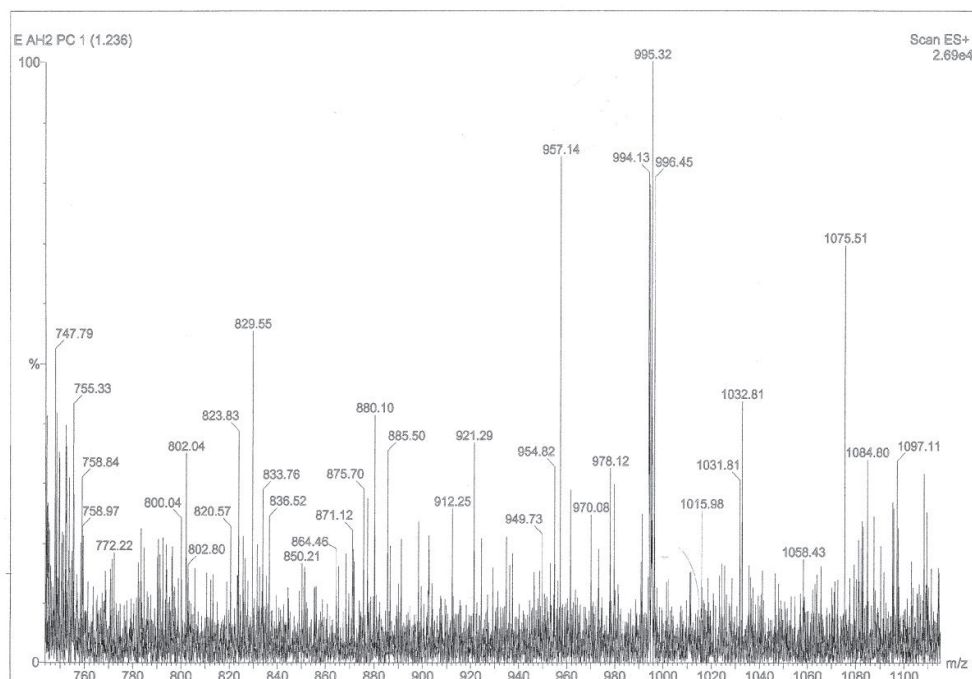


Figure 1. The ESI mass spectrum of metal-free phthalocyanine compound (2).

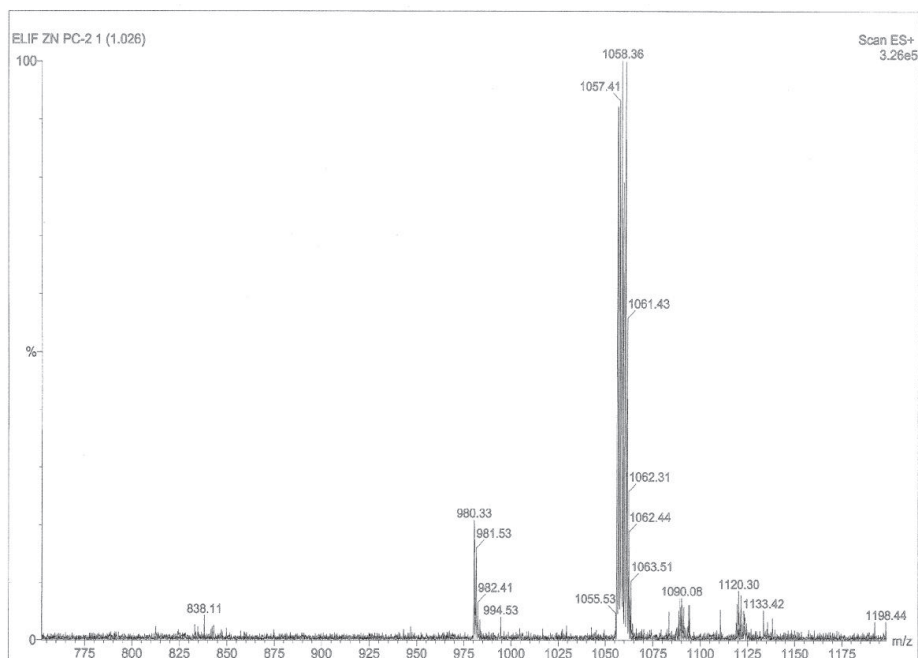


Figure 2. The ESI mass spectrum of ZnPc compound (3).

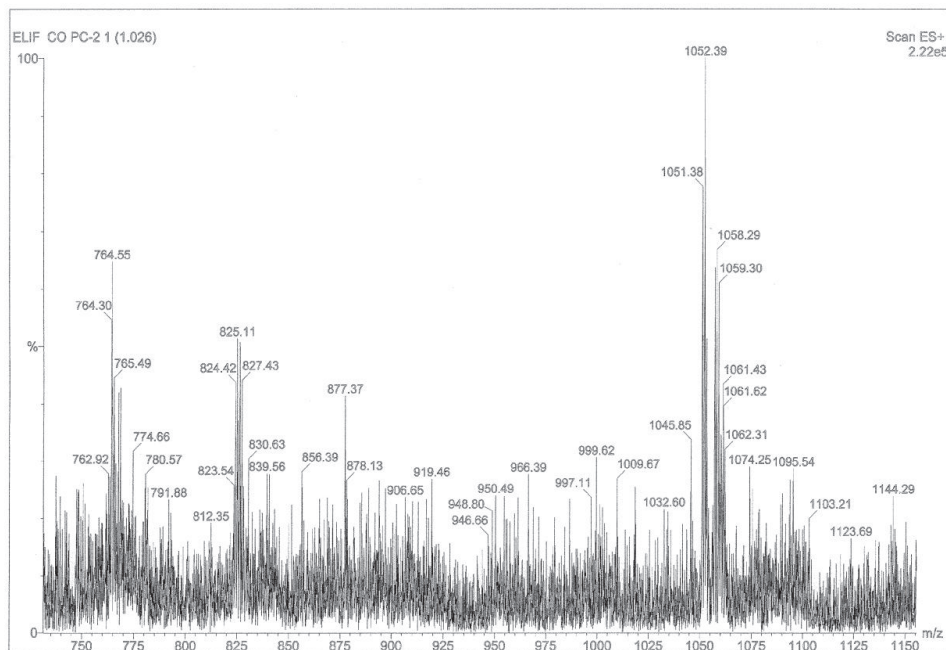


Figure 3. The ESI mass spectrum of CoPc compound (4).

2.2. Thermal characterization

Metallophthalocyanines' thermal behavior was investigated with TG/DTA. The new synthesized phthalocyanines **2–5** were not stable above 636.15 K. The main and initial decomposition temperatures are given in Table 1. The copper phthalocyanine compound (**5**), whose initial decomposition temperature is 692.05 K, is thermally

the most stable compound in Table 1. The initial decomposition temperatures decreased in the order of **5** > **2** > **4** > **3**. Phthalocyanines are known as high thermal stability compounds. This property enables the use of phthalocyanines as technological materials. Showing high thermal stability, compounds **2**, **3**, **4**, and **5** could be used as technological materials. The initial and main decomposition temperatures of substituted phthalocyanines are 473.15–623.15 K and 593.15–723.15 K. Consequently, binding the 2-phenyl methoxy group to the phthalocyanine ring seems to increase thermal stability.

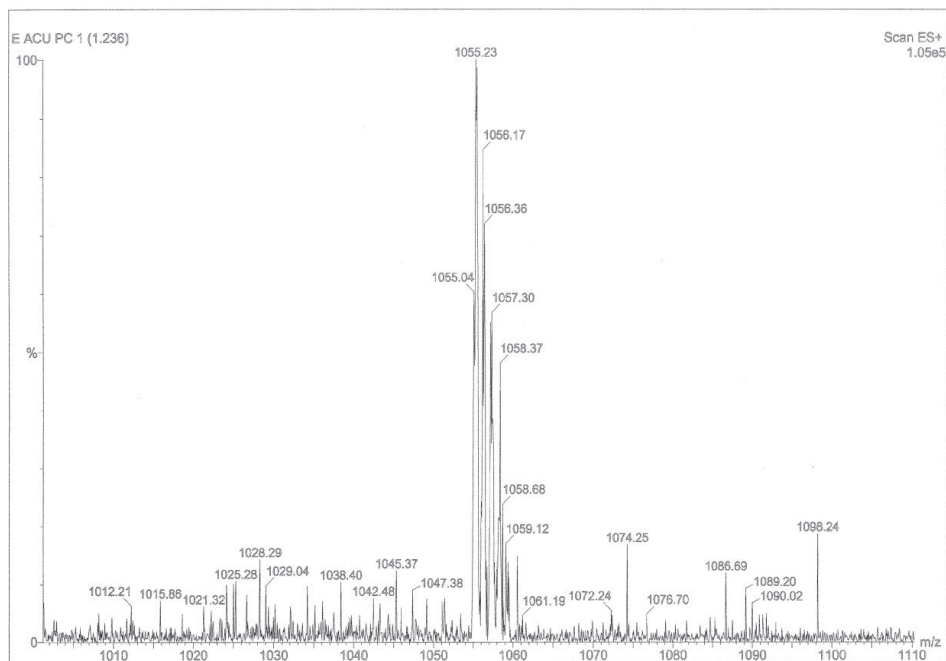


Figure 4. The ESI mass spectrum of CuPc compound (**5**).

Table 1. Thermal properties of the studied phthalocyanines.

Compound	M	Initial decomposition Temperature in K	Main decomposition Temperature in K
2	H ₂	648.05	673.35
3	Zn	636.75	715.55
4	Co	641.65	717.95
5	Cu	692.05	710.75

2.3. UV-Visible absorption spectra

The studied phthalocyanine derivatives **2–5** show typical electron spectra with 2 strong absorption regions, one of them in the UV region at around 240–345 nm (B band) and the other in the visible part of the spectrum at around 670–700 nm (Q band). The studied metal-free (**2**) and metallophthalocyanines (**3–5**) gave typical UV-Vis absorption spectra of phthalocyanines. The electronic absorption spectra of studied phthalocyanine derivatives **2–5** are shown in Figure 5 in chloroform at room temperature. The Q band of the metal-free phthalocyanine (**2**) was observed as 2 split bands at λ_{max} 668 and 705 nm as expected due to D_{2h} symmetry.¹² The metal-free phthalocyanine compound (**2**) showed an intense peak at 341 nm with a shoulder at around 393 nm in the B band region.

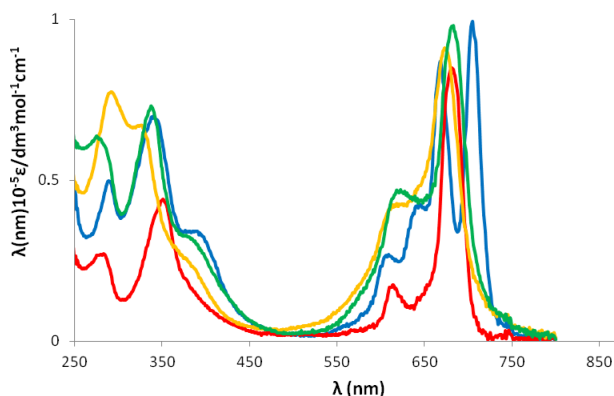


Figure 5. UV-Vis spectra of H₂Pc (—), ZnPc (—), CoPc (—), and CuPc (—) complexes.

The UV-Vis spectra of metallophthalocyanines **3–5** showed intense Q band absorption in chloroform at $\lambda_{\max} = 681$ nm for complex **3**, 675 nm for complex **4**, and 673 nm for complex **5**, with a weaker absorption at 615 nm, 618 nm, and 618 nm for complexes **3**, **4**, and **5** respectively (Figure 5). The single Q bands in metallo derivatives **3–5** are characteristic; metalation, which maintains the planarity of the molecule, increases the symmetry to D_{4h} .¹³ B band absorptions of compounds **3–5** were observed at $\lambda_{\max} = 352$, 292, and 338 nm, respectively, as expected.

The aggregation behavior of new phthalocyanine compounds **2–5** was also studied at different concentrations in DMSO using UV-Vis spectrophotometry. In DMSO, there was a direct correlation between the concentration and the intensity of absorption of the Q band. The phthalocyanine compounds **2–5** had no new bands (normally blue-shifted) because of the aggregated species (see Figure 6 as an example for compound **3**). For these compounds, concentrations ranging from 1.4×10^{-5} to 4×10^{-6} M (in DMSO) complied with the Beer-Lambert law.

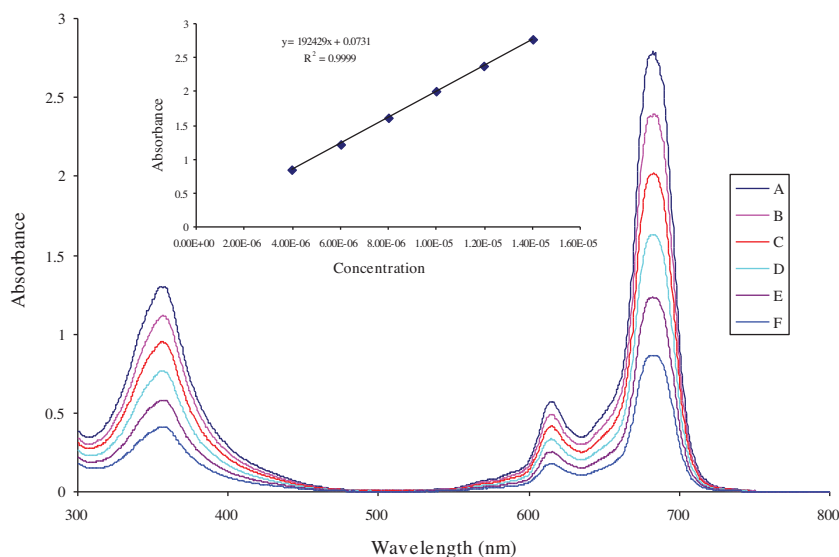


Figure 6. Absorption spectral changes of compound (**3**) in DMSO at different concentrations: 14×10^{-6} (A), 12×10^{-6} (B), 10×10^{-6} (C), 8×10^{-6} (D), 8×10^{-6} (E), 8×10^{-6} (F) M. (Inset: Plot of absorbance versus concentration).

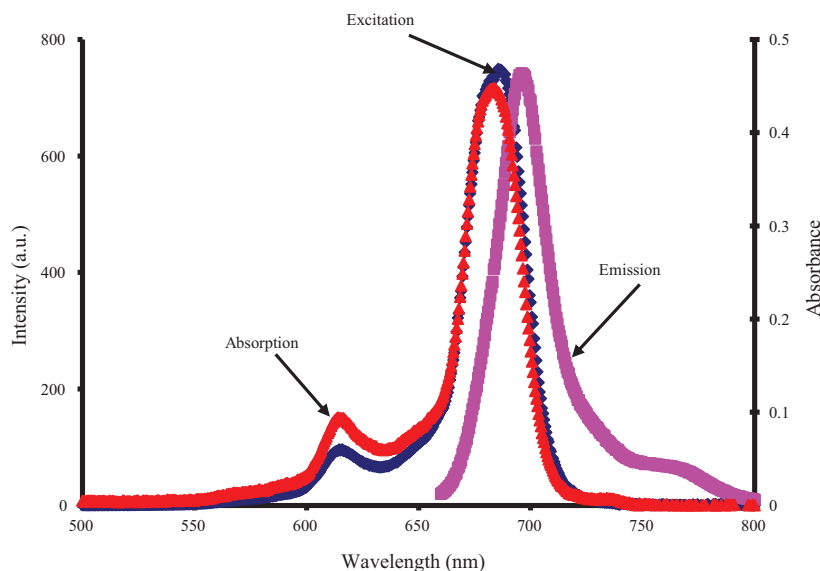


Figure 7. Absorption, fluorescence, emission and excitation spectra for compound **3** in DMSO. Excitation wavelength = 650 nm.

2.4. Fluorescence spectra

The fluorescence behavior of metal-free (**2**) and zinc (**3**) phthalocyanines was studied in DMSO. Figure 7 shows the absorption, fluorescence excitation, and emission spectra of complex **3** in DMSO. The forms of the absorption spectra were similar to those of the excitation spectra for the zinc (**3**) and metal-free (**2**) phthalocyanine compounds. For phthalocyanine derivatives (**2** and **3**), it is suggested that the nuclear configurations of the ground and excited states are similar and not affected by excitation.

Fluorescence excitation and emission peaks for compounds **2** and **3** are listed in Table 2. Fluorescence emission peaks were observed at 715 nm for compound **2** and 696 nm for compound **3** in DMSO. While the observed Stokes shift of the substituted zinc phthalocyanine complex (**3**) is higher, the shift of the metal-free (**2**) phthalocyanine compound is lower than that of unsubstituted ZnPc (Table 2). The cobalt (**4**) and copper (**5**) phthalocyanine compounds did not show fluorescence in DMSO due to paramagnetic behavior of central Co(II) and Cu(II) metals in the phthalocyanine cavity.

Table 2. Absorption, excitation, and emission spectral data for unsubstituted and substituted metal-free (**2**) and zinc(II) (**3**) phthalocyanines in DMSO.

Compound	Q band λ_{\max} , (nm)	$\log \varepsilon$	Excitation λ_{Ex} , (nm)	Emission λ_{Em} , (nm)	Stokes shift Δ_{Stokes} , (nm)
2	673, 705	4.14, 4.12	674, 706	715	9
3	683	5.28	686	696	13
ZnPc ^a	672	5.14	672	682	10

^aData from ref.³⁰

2.5. Fluorescence quantum yields and lifetimes

The metal-free (**2**) and zinc (**3**) phthalocyanine compounds' fluorescence quantum yields (Φ_F) are characteristic for Pc compounds in DMSO. While the Φ_F value of the substituted zinc phthalocyanine compound **3** is higher

than unsubstituted ZnPc (**Std-ZnPc**), the Φ_F value of metal-free phthalocyanine compound (**2**) is similar to the experimental error. The substituted zinc phthalocyanine complex (**3**) shows a higher Φ_F value than the metal-free phthalocyanine compound in DMSO (Table 3).

Table 3. Photophysical and photochemical parameters of unsubstituted and substituted metal-free (**2**) and zinc(II) (**3**) phthalocyanines in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	$^a k_F$ (s^{-1}) ($\times 10^8$)	Φ_d	Φ_Δ
2	0.19	8.75	46.06	0.21	1.48×10^{-3}	0.29
3	0.23	1.47	6.40	1.56	1.58×10^{-5}	0.75
ZnPc ^b	0.18	1.22	6.80	1.47	2.61×10^{-5}	0.67

^a k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.

^b Data from ref.³⁰

The τ_F values of novel phthalocyanine compounds **2** and **3** are higher than those of unsubstituted ZnPc (**Std-ZnPc**). A low τ_F value is obtained for the zinc phthalocyanine complex (**3**) as compared to the metal-free (**2**) phthalocyanine compound.

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 3. While the τ_0 value of the studied metal-free phthalocyanine compound (**2**) is higher, the τ_0 value of the studied zinc(II) phthalocyanine compound (**3**) is lower than that of **Std-ZnPc** in DMSO. The substituted metal-free phthalocyanine compound (**2**) showed higher τ_0 values when compared to substituted zinc phthalocyanine complex (**3**) in DMSO. The rate constant for fluorescence (k_F) of studied metal-free phthalocyanine compound (**2**) is lower than those of both **Std-ZnPc** and studied zinc phthalocyanine complex (**3**) in DMSO.

2.6. Singlet oxygen quantum yields

An ideal photosensitizer must effectively produce singlet oxygen for damaging tumor cells during PDT. Energy transfer occurs between the ground state of molecular oxygen and the triplet state of a photosensitizer (such as phthalocyanine) and leads to the production of singlet oxygen. The singlet oxygen quantum yield (Φ_Δ) is used to quantify generating singlet oxygen value and this parameter is important for photosensitizers in PDT applications. In this study, the metal-free (**2**) and zinc (**3**) phthalocyanine compounds' singlet oxygen quantum yields (Φ_Δ) were determined by using DPBF as a quencher. The UV-Vis spectrum of compound **3** in Figure 8 showed that the DPBF absorption disappeared. Five factors are responsible for the magnitude of the determined quantum yield of singlet oxygen. These are ability of substituents, triplet excited state energy, triplet excited state lifetime, solvents, and the efficiency of the energy that is transferred between the ground state and the triplet excited state of oxygen. The Q band intensity of phthalocyanine compounds **2** and **3** did not change during the Φ_Δ determination. This shows that phthalocyanine compounds **2** and **3** did not decompose.

For **Std-ZnPc** complex, the value of Φ_Δ is lower than for new zinc phthalocyanine compound (**3**) but higher than for new metal-free (**2**) phthalocyanine in DMSO (Table 3). When we compare the Φ_Δ values of new phthalocyanine compounds **2** and **3** we see that zinc phthalocyanine compound (**3**) is higher. Generally, zinc phthalocyanine compounds possess high triplet yields and they can generate high amounts of singlet oxygen due to the d^{10} configuration of the central Zn^{2+} ion, which make them valuable photosensitizers for PDT applications.

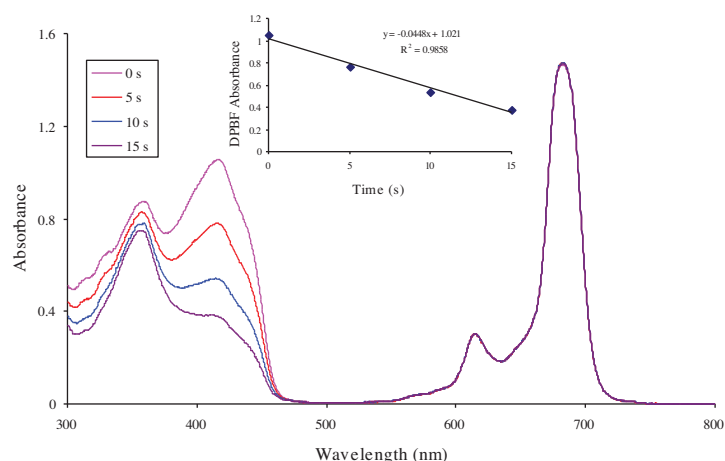


Figure 8. Absorption changes during the determination of singlet oxygen quantum yield. This determination was for compound **3** in DMSO at a concentration of 1×10^{-5} M. (Inset: Plot of DPBF absorbance versus time).

2.7. Photodegradation study

The compounds' photodegradation properties showed their stability. This is very important for reactions of photocatalytic chemistry applications (such as photosensitization). Photodegradation generally depends on concentration, the structure of the molecule, light intensity, and solvent.¹⁴

The metal-free (**2**) and zinc (**3**) phthalocyanine compounds' spectral changes observed during light irradiation are shown in Figure 9. Photodegradation was not associated with phototransformation for metal-free (**2**) and zinc (**3**) phthalocyanine compounds. This is because the shape of the absorption spectra did not change with collapse of the spectra.

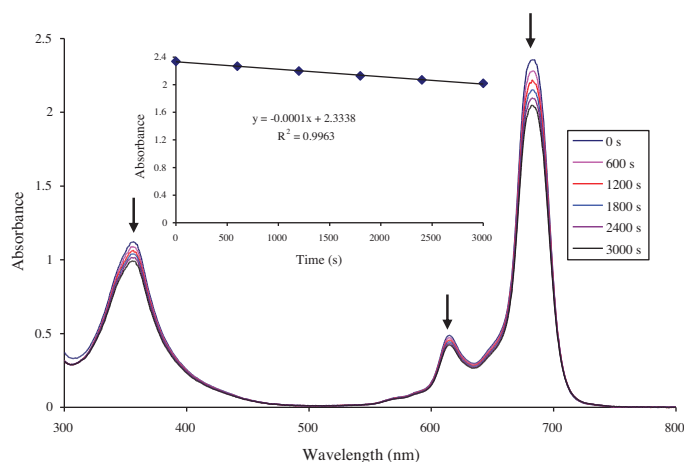


Figure 9. Absorption changes during the photodegradation studies of compound **3** in DMSO under light irradiation showing the disappearance of the Q-band at 10 -min intervals. (Inset: Plot of absorbance versus time).

The photodegradation quantum yield (Φ_d) values of zinc (**3**) and metal-free (**2**) phthalocyanine compounds are shown in Table 3. While the Φ_d value of zinc (**3**) phthalocyanine complex is lower than that of unsubstituted zinc phthalocyanine complex, the Φ_d value of the metal-free (**2**) compound is higher than that of

unsubstituted zinc phthalocyanine complex in DMSO. The metal-free phthalocyanine compound (**2**) is approximately 100 times less stable to degradation compared to zinc phthalocyanine complex (**3**) (Table 3) because the Φ_d value of the metal free phthalocyanine compound (**2**) is 100 times higher than that of zinc phthalocyanine complex (**3**).

2.8. Fluorescence quenching studies by 1,4-benzoquinone (BQ)

Phthalocyanine compounds may also be used as photosynthetic mimickers. An essential requirement for an effective photosynthetic mimicker is the ability to undergo excited state charge transfer with ease; for example, phthalocyanine–quinone systems have proved to be favored candidates for understanding the energy transfer process.¹⁵

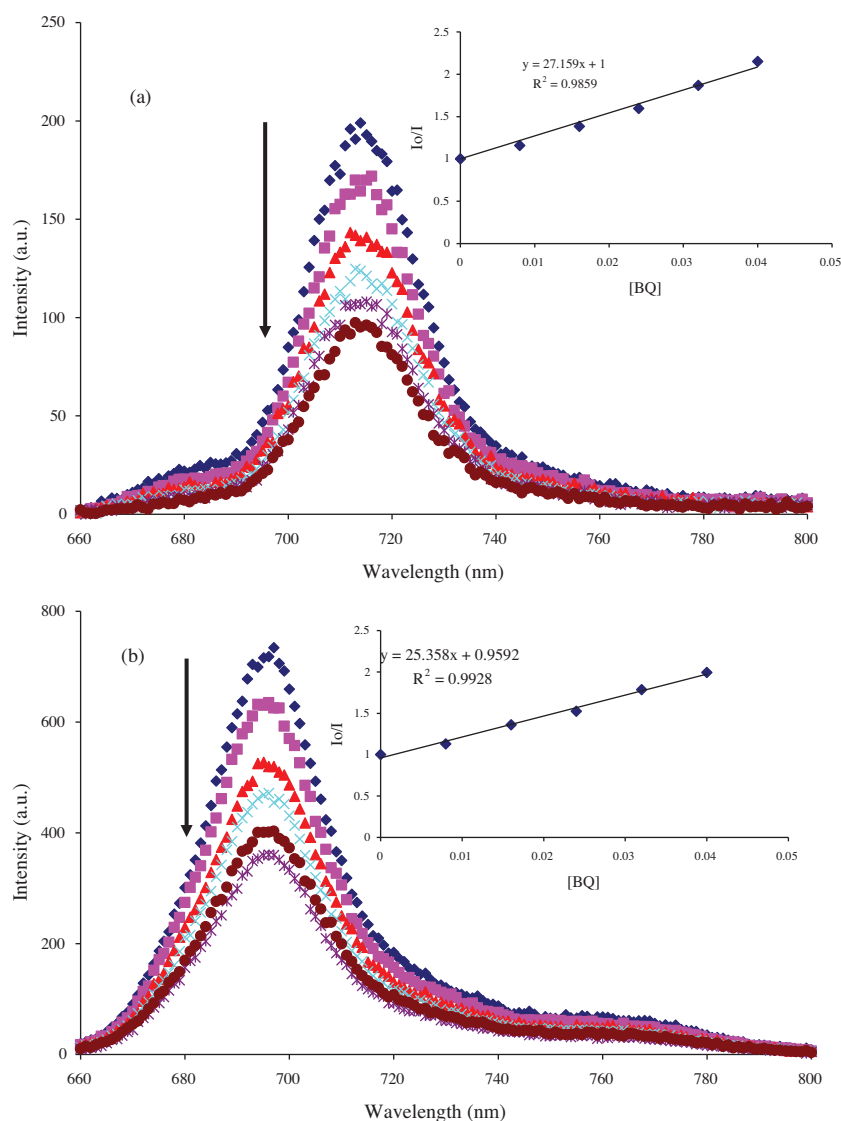


Figure 10. Fluorescence emission spectral changes of: (A) for compound **2** and (B) for compound **3** (1.00×10^{-5} M) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M. (Inset: Stern–Volmer plots for BQ quenching of **2** and **3** in DMSO).

The zinc (**3**) and metal-free (**2**) phthalocyanine compounds' fluorescence quenching by BQ (in DMSO) was found to obey Stern–Volmer kinetics (Figure 10). The Stern–Volmer plots of phthalocyanine compounds **2** and **3** gave straight lines, depicting diffusion-controlled quenching mechanisms. It is known that quinones have large relevance to electron transfer processes because of their electron affinities.¹⁶ The phthalocyanine compounds' excited singlet state energy is less than the quinones' lowest excited state energy.¹⁷ The phthalocyanine compounds were reduced easily, but transfer of energy from BQ to the excited phthalocyanine molecule did not occur. Therefore, fluorescence quenching of phthalocyanine compounds deals with transferring electrons from BQ excited state to the phthalocyanine.¹⁸ The BQ quenching of zinc (**3**) and metal-free (**2**) phthalocyanine compounds' k_q (bimolecular quenching constant) and K_{SV} values are listed in Table 4. The K_{SV} values of the substituted phthalocyanine compounds **2** and **3** are lower than those of unsubstituted zinc phthalocyanine complex. When comparing the substituted complexes, compound **2** showed higher K_{SV} values than compound **3** in DMSO. The substitution of the phthalocyanine framework with 2-phenylethanolate groups seems to decrease the K_{SV} values of phthalocyanine compounds. The bimolecular quenching constant (k_q) values of the studied phthalocyanine compounds (**2** and **3**) are also lower than for the unsubstituted zinc phthalocyanine complex in DMSO; thus substitution with 2-phenylethanolate groups seems to decrease the k_q values of the complexes. The k_q values of phthalocyanine compounds **2** and **3** were close to the diffusion-controlled limits, $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.¹⁹

Table 4. Fluorescence quenching data for unsubstituted and substituted metal-free (**2**) and zinc(II) (**3**) phthalocyanines in DMSO.

Compound	K_{SV} (M^{-1})	$k_q/10^{10}(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
2	27.16	0.31
3	25.36	1.72
ZnPc ^a	31.90	2.61

^a Data from ref.³⁰

2.9. SEM analysis of CoPc (**4**) thin films

Figures 11 and 12 show SEM micrographs of CoPc (**4**) thin films sintered at various temperatures such as 150 and 270 °C. When the films were carefully analyzed, the matrix phase looked homogeneous but some particles seen on the surface belong to materials splashed onto the surface of the thin film. Additionally, the film surfaces are almost homogeneous and the particle size of the deposition is below the micron level. Therefore, it can be said that the CoPc (**4**) deposition was performed successfully. The nanoparticles are almost spherical.

A small region on the surface of the film was observed to be aggregated (Figure 13), but these aggregations are thought to be ineffective on the whole film structure and also these aggregations are caused by splash melting because of the rise in probe current at the beginning of the heating of the target material.

It is observed from X-ray analysis curves taken after transformation into a thin film (before the sintering process) that the structure has an amorphous character and does not have a peak representing crystallization.

Two diffraction patterns that are about 2θ 21° and about 38° belonging to phthalocyanine substance were observed in the X-ray diffraction pattern (Figures 14 and 15) after the sintering process. Accordingly, it is understood that the films obtained turned into a crystallized structure following thermal processing. It is known that the larger peak observed at about 42.6 is the base peak.

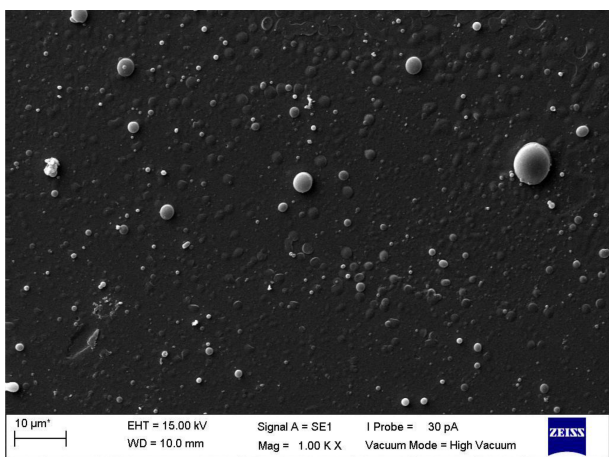


Figure 11. SEM micrographs of CoPc (4) thin film sintered at 150 °C.

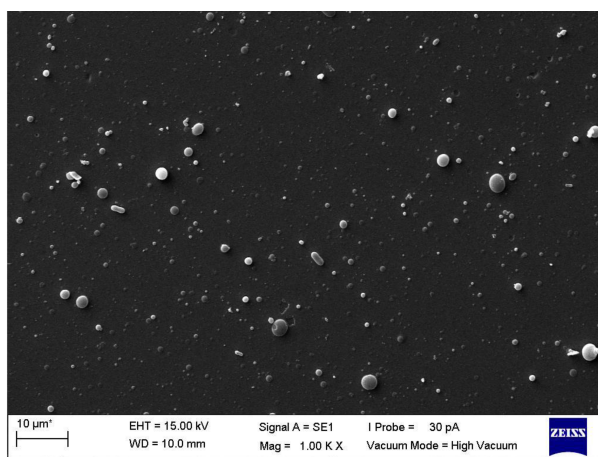


Figure 12. SEM micrographs of CoPc (4) thin film sintered at 270 °C.

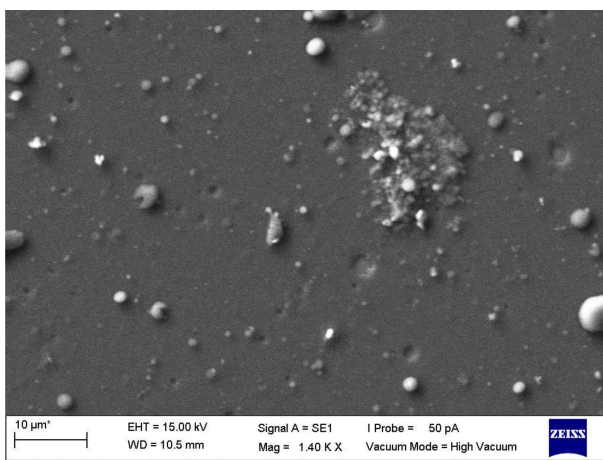


Figure 13. SEM micrographs of CoPc (4) thin film; particle aggregation can be observed.

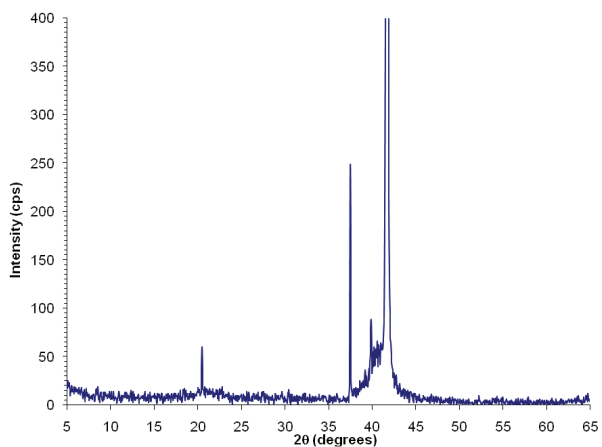


Figure 14. X-ray diffractogram of CoPc (4) thin film sintered at 150 °C.

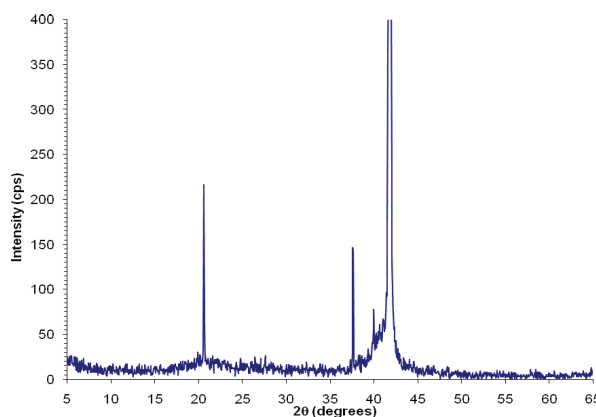


Figure 15. X-ray diffractogram of CoPc (4) thin film sintered at 270 °C.

3. Experimental

3.1. Materials

Dry nitrogen atmosphere was used in all reactions by standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego.²⁰ 1,3-Diphenylisobenzofuran (DPBF), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,4-benzoquinone (BQ) were purchased from Fluka. 4-Phenylethoxyphthalonitrile (**1**) were prepared according to the literature procedure.¹¹

3.2. Equipment

A PerkinElmer 1600 FTIR spectrophotometer (potassium bromide pellets) was used for the IR spectra and a Varian Mercury 200 MHz spectrometer (in CDCl₃) for the ¹H and ¹³C NMR spectra. Chemical shifts are reported (δ) relative to Me₄Si as internal standard. Varian 711 and VG Zapspec spectrometers were used for mass spectra (ESI). A LECO elemental analyzer (CHNS O932) and a Unicam 929 AA spectrophotometer were used for elemental analyses. Unicam UV2-100 and Shimadzu 2001 spectrophotometers (using 1-cm pathlength cuvettes at room temperature) were used for UV-Vis spectra. UV-Visible absorption spectra of the thin films were measured by a PerkinElmer Lambda 35 UV/Vis spectrometer. A Seiko II Exstar 6000 thermal analyzer was used to record DTA curves under nitrogen atmosphere with a heating rate of 20 °C min⁻¹ in the temperature range 30–900 °C using platinum crucibles. A domestic microwave oven was used for the synthesis of metallo phthalocyanines. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter using 1-cm pathlength cuvettes at room temperature. Photo-irradiations were done using a General Electric quartz line lamp (300 W) for metal-free (**2**) and zinc (**3**) phthalocyanine derivatives. To filter off infrared and ultraviolet radiations, a water filter and a Schott (600 nm glass cut off) filter were used respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. A PowerMax 5100 (Moletron Detector Inc.) were used to measure the light intensities.

3.3. Photophysical parameters

3.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1):^{21,22}

$$\Phi_F = \Phi_F(Std) \cdot \frac{F \cdot A_{Std} \cdot n^2}{F_{Std} \cdot A \cdot n_{Std}^2}, \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**2** and **3**) and the standard, respectively. A and A_{Std} are the relative absorbance of the samples (**2** and **3**) and standard at the excitation wavelength, respectively. n and n_{std} are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.20$)²³ was employed as the standard in DMSO.

Natural radiative (τ_0) lifetimes were determined using Photochem CAD program using the Strickler–Berg equation.²⁴ The fluorescence lifetimes (τ_F) were evaluated using Eq. (2):

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (2)$$

3.4. Photochemical parameters

3.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_{Δ}) determinations were described in the literature.^{25–27}

Eq. (3) was employed for the calculation of Φ_{Δ} values:

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{R.I_{abs}^{Std}}{R^{Std}.I_{abs}} \quad (3)$$

3.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determination was described in the literature.²⁵

Φ_d values were determined using Eq. (4):

$$\Phi_d = \frac{(C_0 - C_t).V.NA}{I_{abs}.S.t} \quad (4)$$

3.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching by 1,4-benzoquinone (BQ) determination was described in the literature.²⁸

BQ values were determined using Eq. (5):

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \quad (5)$$

K_{SV} is the Stern–Volmer constant, which is the product of the bimolecular quenching constant (k_q) and the τ_F . K_{SV} is expressed in Eq. (6):

$$K_{SV} = k_q \cdot \tau_F \quad (6)$$

3.5. Synthesis

3.5.1. Metal-free phthalocyanine (2)

4-Phenylethoxyphthalonitrile (**1**) (0.3 g, 1.2 mmol), DBU (3 drops), and dry *n*-pentanol (5 mL) were added to a Schlenk tube and then the mixture was heated and stirred at 160 °C for 24 h under N₂. Then the reaction mixture was cooled at 30 °C and precipitated by adding ethanol. The solid product was filtered and washed with ethanol (30 mL). The green solid product was purified by column chromatography on silica gel with chloroform/methanol (8:1) as eluent. Yield: 0.85 g (28%). Anal. Calcd (%) for C₆₄H₅₀N₈O₄: C: 77.24; H: 5.06; N: 11.26. Found: C: 77.51; H: 5.18; N: 11.39. IR (KBr pellets), ν_{max} (cm⁻¹): 3280 (N-H), 3021 (Ar-H), 2922–2868 (Aliph. C-H), 1603, 1465, 1321, 1236, 1096, 1010, 821, 747, 697. ¹H NMR (CDCl₃), (δ : ppm): 7.61–6.33 (m, 32H, Ar-H), 3.97 (m, 8H, Ar-O-CH₂), 3.09 (m, 8H, CH₂), –5.77 (br s, 2H, N-H). ¹³C NMR (CDCl₃), (δ : ppm): 159.37, 138.71, 138.65, 136.51, 129.49, 129.47, 129.21, 128.91, 128.59, 127.37, 127.01, 126.87, 122.00, 117.38, 68.59, 36.12. UV-Vis [(chloroform) $\lambda_{max}/nm10^{-5}\epsilon$ (mol⁻¹ cm⁻¹): 705 (4.99), 668 (4.94), 642 (4.62), 606 (4.42), 393 (4.52), 341 (4.84). MS (ES⁺), (*m/z*): 995 [M]⁺.

3.5.2. General procedure for metallo phthalocyanine complex synthesis

4-Phenylethoxyphthalonitrile (**1**) (0.3 g, 1.2 mmol), anhydrous metal salts (0.3 mmol), 2-(dimethylamino) ethanol (2.5 mL), and DBU were irradiated in a microwave oven at 175 °C, 350 W for 6 min. After cooling to

room temperature, the reaction mixture was refluxed with ethanol (35 mL) to precipitate the product, which was filtered off and dried in vacuo over P_2O_5 . The obtained green solid product was purified with column chromatography on silica gel with chloroform/methanol (8:1) as eluent. $Zn(CH_3COO)_2$ (0.055 g, 0.3 mmol), $CoCl_2$ (0.039 g, 0.3 mmol), and $CuCl_2$ (0.040 mg, 0.3 mmol).

3.5.3. Zinc(II) phthalocyanine (3) complex

It was synthesized by a general procedure for metallophthalocyanine with $Zn(CH_3COO)_2$ (0.055 g, 0.3 mmol). Yield: 0.127 g (40%). Anal. Calcd (%) for $C_{64}H_{48}N_8O_4Zn$: C: 72.62; H: 4.57; N: 10.59. Found: C: 72.90; H: 4.78; N: 10.42. IR (KBr pellets), ν_{max}/cm^{-1} : 3024 (Ar-H), 2920–2862 (Aliph. C-H), 1606, 1489, 1454, 1382, 1338, 1277, 1236, 1120, 1093, 1047, 949, 823, 744, 698. 1H NMR ($CDCl_3$), (δ : ppm): 7.13–5.78 (m, 32H, Ar-H), 3.36 (m, 8H, Ar-O- CH_2), 2.72 (m, 8H, CH_2). ^{13}C NMR ($CDCl_3$), (δ : ppm): 154.69, 145.88, 137.90, 133.96, 133.92, 131.58, 124.74, 124.12, 124.08, 122.09, 117.82, 112.32, 99.64, 99.27, 64.04, 31.43. UV-Vis [(chloroform) $\lambda_{max}/nm10^{-5}\epsilon(mol^{-1} cm^{-1})$]: 681 (4.93), 615 (4.23), 352 (4.64). MS (ES^+), (m/z): 1058[M] $^+$.

3.5.4. Cobalt(II) phthalocyanine (4) complex

It was synthesized by a general procedure for metallophthalocyanine with $CoCl_2$ (0.039 g, 0.3 mmol). Yield: 0.132 g (42%). Anal. Calcd (%) for $C_{64}H_{48}N_8O_4Co$: C: 73.07; H: 4.60; N: 10.65. Found: C: 73.29; H: 4.77; N: 10.78. IR (KBr pellets), ν_{max}/cm^{-1} : 3021 (Ar-H), 2920–2851 (Aliph. C-H), 1608, 1523, 1483, 1464, 1384, 1343, 1238, 1124, 1095, 1064, 958, 821, 751, 698. UV-Vis [(chloroform) $\lambda_{max}/nm10^{-5}\epsilon(mol^{-1} cm^{-1})$]: 675 (4.96), 618 (4.63), 327 (4.83), 292 (4.88). MS (ES^+), (m/z): 1052[M] $^+$.

3.5.5. Copper(II) phthalocyanine (5) complex

It was synthesized by a general procedure for metallophthalocyanine with $CuCl_2$ (0.040 mg, 0.3 mmol). Yield: 0.124 g (39%). Anal. Calcd (%) for $C_{64}H_{48}N_8O_4Cu$: C: 72.75; H: 4.58; N: 10.60. Found: C: 72.91; H: 4.83; N: 10.78. IR (KBr pellets), ν_{max}/cm^{-1} : 3021 (Ar-H), 2923–2851 (Aliph. C-H), 1606, 1463, 1383, 1342, 1236, 1119, 1094, 1057, 746, 697. UV-Vis [(chloroform) $\lambda_{max}/nm10^{-5}\epsilon(mol^{-1} cm^{-1})$]: 673 (4.99), 618 (4.67), 385 (4.49), 338 (4.86). MS (ES^+), (m/z): 1055[M] $^+$.

3.6. Thin film production

The thin film of cobalt phthalocyanine (4) on MgO substrates was produced using an electron beam evaporation system in a high vacuum state. First, some amount of cobalt phthalocyanine (4) was compacted to diameter 13 mm and this tablet was put into the sample holder of the system. The distance between sample and substrate was about 7 cm for all production and MgO substrates of size 5 mm \times 5 mm were used during the film deposition. In the first step, 10 substrates were put into the holder and cobalt phthalocyanine (4) thin films were deposited on the MgO substrate for 5 min using a very low probe current. During the deposition process substrates were rotated at very slow speed in order to have a homogeneous film structure. At the end of the process, dark green films were produced successfully.

After the deposition process, all films were sintered at different temperatures such as 150 and 270 °C. For this process the films were put in a quartz tube and sealed up to 10^{-3} mbar; then the quartz tube was put into a programmable tube furnace and a 2 h sintering time was chosen in order to get a homogeneous crystalline structure.

The structural properties of films as deposited and sintered at various temperatures under vacuum were determined by X-ray diffractometer (Rigaku D-max III).

Physical vapor deposition (PVD) is known as a micro-electro-mechanical systems (MEMS) process. Electron beam evaporation (e-beam evaporation) is the large part of this process. Deposition processes are used to release a material from a source and transfer that material to a substrate, forming a thin film or coating.

Electron beam physical vapor deposition (EBPVD) is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. Atoms return to the gaseous phase with the electron beam method. Then it turns into solid form, everything in the vacuum chamber (within line of sight) with a thin layer of the anode material.

This process has potential industrial applications for thermal barrier coatings and wear resistance in the aerospace and tool industries and for hard coatings for cutting, and optical and electronic films for the semiconductor industry because of the very high deposition rate.²⁹

4. Conclusion

In this research, 4 new highly soluble tetrakis-2-phenylethanolate substituted metal-free (**2**), zinc (**3**), cobalt (**4**), and copper (**5**) phthalocyanines were synthesized. IR, UV-Vis, ¹H and ¹³C NMR, mass spectroscopy, and elemental analysis were used to characterize the new compounds. The metal-free (**2**) and zinc (**3**) phthalocyanine compounds' photophysical and photochemical properties (comparison of the central metal effect) were investigated in DMSO. All the compounds show excellent solubility in most solvents such as DMF, chloroform, DMSO, and toluene. The metallophthalocyanines **3–5** exhibit single narrow Q bands and the metal-free complex (**2**) shows a splitting Q band in the UV-Vis spectra. Therefore, it promotes the formation of phthalocyanine complexes. The metal-free (**2**) and zinc (**3**) phthalocyanine compounds' fluorescence behavior was studied in DMSO. The phthalocyanine compounds' fluorescence quantum yields are typical for Pcs. In DMSO, the Φ_{Δ} values of the studied phthalocyanine compounds ranged from 0.29 (for compound **2**) to 0.75 (for compound **3**), giving an indication of the potential of the compounds as photosensitizers (especially compound **3**) in photocatalytic applications such as PDT. The substituted metal-free (**2**) phthalocyanine compound showed approximately 100 times less stability than the substituted zinc (**3**) phthalocyanine complex. The fluorescence quenching behavior of the substituted metal-free (**2**) and zinc (**3**) phthalocyanine compounds was studied by BQ in DMSO. The studied phthalocyanine compounds **2** and **3** showed lower K_{sv} and k_q values when compared to the unsubstituted zinc phthalocyanine complex.

The CoPc thin films were prepared on MgO substrates by electron-beam evaporation system in high vacuum state. At the end of the process, dark green films were produced successfully. After the deposition process, the surface morphology was characterized by scanning electron microscopy. When the films were carefully analyzed, the matrix phase appeared homogeneous but some particles seen on the surface belonged to materials splashed onto the surface of the thin film. The structural properties of films as deposited and sintered at various temperatures under vacuum were determined by X-ray diffractometer. Two diffraction patterns, which are about 2θ 21° and about 38° belonging to a phthalocyanine substance, were observed in the X-ray diffraction pattern after the sintering process.

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