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# Photophysical, photochemical and fluorescence quenching studies of new halogenated phthalocyanine metal complexes

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This study provides an accurate description of the preparation of some new quad-compensatory phthalocyanine complexes of Zn(II) and Cu(II) substituted by 4-(4-bromo-2-formylphenoxy). Several spectroscopic techniques have been employed to characterize phthalocyanine metal complexes including FT-IR, NMR, mass spectrometry, and UV-Visible spectrophotometry. Aggregation studies have been investigated in various DMSO concentrations ranging from $2\times10^{-6}$ M to $10\times10^{-6}$ M. In this research, the bathochromic shift of the Q band of [Zn(Pc)] depends on the solvent type in the following ascending order: (THF< DMF< $CHCl_3$< DMSO and $H_2SO_4$), and for [Cu(Pc)] is (THF< DMSO< DMF< $CHCl_3$ and $H_2SO_4$) respectively. Photophysical properties of the resulting complexes have been evaluated by measuring factors such as absorption and emission. Spectral results show that both complexes **2** and **3** have the potential to be used as sensitizers in photodynamic therapy (PDT) based on their singlet oxygen efficiencies (UD = 0.41, 0.39).

**Keywords**: Metal complexes, Phthalocyanine, Photophysical, Photochemical, PDT

Over the past decade, photodynamic therapy (PDT) has attracted significant scientific interest[1-3]. This type of therapy has interesting aspects such as; being an alternative nonsurgical cancer treatment[4]. Additionally, it has emerged as an effective and promising antibiotic that can overcome typical drug resistance. This treatment method is based on the interaction of a photosensitizing chemical with light to generate singlet oxygen in the cell. Consequently, singlet oxygen targets cancer cells or bacterial cells and destroy them[5-7].

Phthalocyanine (Pcs) is an ideal chemical candidate for PDT because of its outstanding photo-physical and photochemical qualities[1,8,9]. These extraordinary optical characteristics are a result of the 18-electron conjugated system in phthalocyanine. Pcs has been used as a criterion for PDT and various over the-counter medicines and drugs in the clinical development phase[2,5,10-12]. Along with photodynamic therapy, Pcs could be attractive for biological imaging, which is crucial for detecting tumor growth at an early stage when conventional imaging procedures (such as positron emission tomography, X-ray, and magnetic resonance imaging), are not sensitive enough to detect specific lesions[13,14]. Moreover, Pcs have been promoted for use in a wide range of important applications, such as dyes, catalysts[15], solar cells[16], photoconductors[17], neutron capture treatment[18], and imaging with near-infrared[19]. Pcs metallic compounds exhibit excellent optical properties. As expected the metallic cooperation will undoubtedly enhance the optical characteristics of Pcs as well as the time evolution of the excited state[20-23].

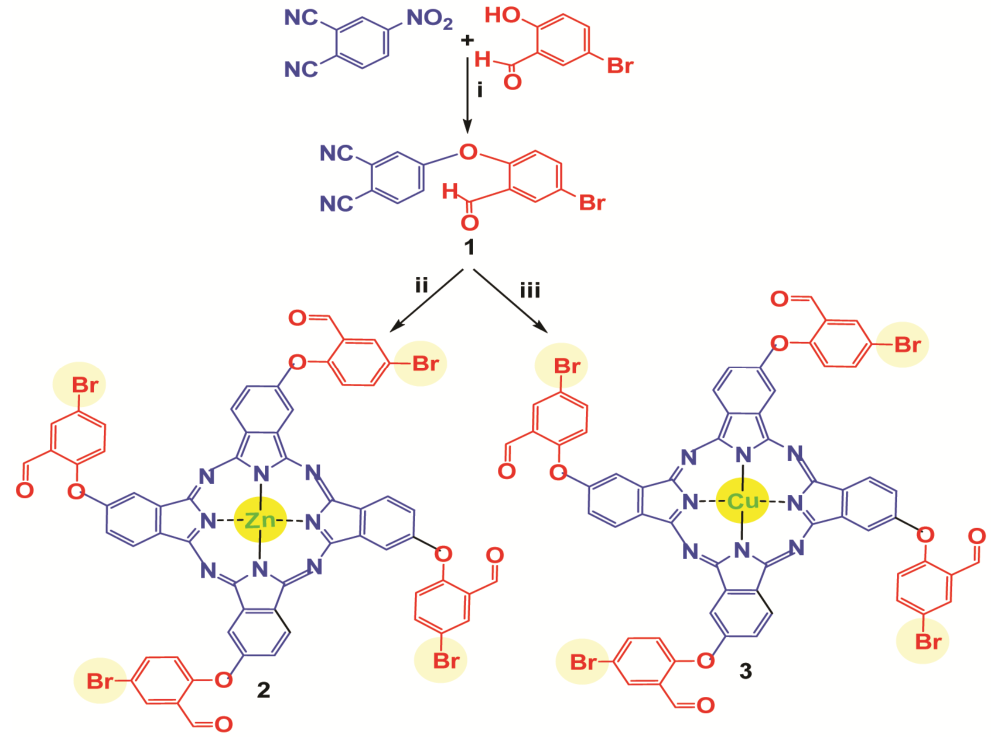
Herein, we report the synthesis of new tetrasubstituted species of zinc and copper phthalocyanines that substituted with 4-(4-Bromo-2-formylphenoxy) groups on the porphyrin skellton. Additionally, their photochemical features and photophysical properties have been investigated. The newly synthesized phthalocyanines metal complexes (2 and 3) showed longer absorption wavelengths, high singlet oxygen quantum yields, and moderate photodegradation quantum yields.

## Experimental Section

All the synthetic reactions were performed in an inert nitrogen atmosphere with anhydrous solvents. All the reagents and solvents were purchased from Sigma Chemical Co. Solvents were dried using molecular sieves (4 Å). 4-Nitrophthalonitrile and 5-bromosalicyladehyde were used as received.

## Synthesis

Scheme 1 showed the synthesis of the phthalonitrile derivative 4-(4-bromo-2-formylphenoxy)phthalonitrile



Scheme 1 — Syntheses of phthalocyanine metal complexes (i) DMF, $K_2CO_3$, 40°C, 72 h, (ii) Pentanol, $ZnCl_2$, DBU, 145°C, 24 h. (iii) Pentanol, $CuCl_2$, DBU, 145°C, 24 h

(**1**) as a precursor for synthesizing Pcs with four (4-bromo-2-formylphenoxy) groups at peripheral sites. The nucleophilic aromatic substitution of 5-bromosalicyladehyde towards 4-nitrophthalonitrile was sped up by the addition of $K_2CO_3$ in anhydrous DMF at (40 °C). After recrystallization with ethanol, pure phthalonitrile derivative (**1**) was collected in a 65% yield. Complexes (**2**) and (**3**) were synthesized using to published methods[24,25] as the 4-bromo-2-formylphenoxy cyclotetramerized for 24 hours, with the required metal salts. N-Pentanol was used as a high-boiling solvent and a small amount of DBU (1,8-Diazabicyclico [5.4.0] undec-7-ene) was added as a catalyst for both reactions. The desired phthalocyanines complexes [Zn(Pc)] **2** and [Cu(Pc)] **3** were prepared in moderate yields of 11% and 13% respectively by cyclotetramerization of the dinitrile compound (**1**) in the presence of $ZnCl_2$ or $CuCl_2$ (Ref. 25). The resulting complexes (**2** and **3**) were purified by filtration and washed several times with hot n-hexane and methanol. Various spectroscopic techniques including FT-IR, NMR, UV-Vis, and MS spectroscopy were utilized to identify the prepared compounds.

**4-(4-Bromo-2-formylphenoxy) phthalonitrile, 1**: Yield 1.30 g (65%). m.p.171°C. FT-IR: 3099 (Ar-H), 2237 (C≡N), 1592 (Ar C=C), 1255 $cm^{-1}$ (Ar-O-Ar); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, 1H), 7.55 (s, 1H), 7.95 (d, 2H), 8.05 (s, 1H), 8.15 (d, 1H), 10.2 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 189.11 (C=O), 161.11 (Ar-C), 155.11 (Ar-C), 139.90 (Ar-C), 136.09 (Ar-C), 132.51 (Ar-C), 129.62 (Ar-C), 124.17 (C-Br), 123.58 (C≡N), 119.11 (Ar-C), 118.37 (Ar-C), 116.80 (Ar-C), 115.22 (Ar-C), 110.11 (Ar-C); MS (MALDI-TOF): m/z = 327 (M +).

**Tetra-(4-bromo-2-formylphenoxy)phthalocyaninatozinc(II), 2**: Yield 0.3 g (11%). m.p.300°C. FT-IR: 3074 (Ar-H), 1230 $cm^{-1}$ (Ar-O-Ar); UV-Vis (DMSO): $\lambda_{max}$/nm = 681; $^1$H NMR (CDCl3): δ 10.09 (s, 4H), 8.17 (d, 4H), 8.03 (s, 4H), 7.95 (d, 8H), 7.56 (s, 4H), 7.26 (d, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 188.39 (4C=O), 160.76 (Ar 4C), 154.89 (Ar 4C), 139.38 (Ar 4C), 136.75 (Ar 4C), 135.99 (Ar 4C), 132.97 (Ar 4C), 129.23 (4C-Br), 124.32 (Ar 8C), 118.80 (4C-N), 117.23 (Ar 4C), 116.20 (Ar 4C), 115.70 (Ar 4C), 109.72 (Ar 4C).

**Tetra-(4-bromo-2-formylphenoxy) phthalocyaninatocopper(II), 3**: Yield 0.3 g (11%). m.p(300°C. FT-IR: 3062 (Ar-H), 1234 $cm^{-1}$ (Ar-O-Ar); UV-Vis (DMSO): $\lambda_{max}$/nm = 678; $^1$H NMR ($CDCl_3$): δ 10.09

(s, 4H), 8.14 (d, 4H), 8.06 (s, 4H), 7.92 (d, 8H), 7.66 (s, 4H), 7.32 (d, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 188.48 (4C=O), 160.80 (Ar 4C), 154.89 (Ar-4C), 139.42 (Ar-4C), 136.78 (Ar-4C), 133.02 (Ar-4C), 129.65 (Ar-4C), 124.37 (4C-Br), 123.70 (Ar-8C), 118.83 (4C-N), 117.23 (Ar-4C), 116.25 (Ar-4C), 115.75 (Ar-4C), 109.71 (Ar-4C).

## Results and Discussion

### Chemical characterization

As described in Scheme 1, the new halogenated Pcs (**2** and **3**) were synthesized using two different reactions steps. The newly synthesized zinc and copper phthalocyanine complexes (**2** and **3**) are highly soluble in common organic solvents such as DMSO, DMF, THF, and $CHCl_3$ (see Fig. 1 and Fig. 2).

The chemical techniques employed to identify the synthesized macromolecules are described in detail below.

### FT-IR spectroscopy

The IR spectra of compound (**1**) in Fig. S1 showed the presence of the Ar-O-Ar stretching at 1255 cm$^{-1}$ and the absence of the $NO_2$ band which usually appears at 1350 cm$^{-1}$ confirming the successful synthesis of compound (**1**). Additionally, sharp C≡N vibrations of dinitrile groups appeared at 2237 cm$^{-1}$ and the aromatic C–H peaks occurred at 3099 cm$^{-1}$. The C-Br stretching vibrations were observed at 831 cm$^{-1}$. The absence of the C≡N band in the FT-IR spectra (Figs. S2 and S3) of complexes (**2** and **3**) confirms the cyclotetramerization of Pcs. The aromatic C–H peaks occurred at 3074 cm$^{-1}$ for **2** and 2927 cm$^{-1}$ for **3**. Furthermore, the aromatic C–O–C vibrations were observed at 1230 cm$^{-1}$ for **2** and 1234 cm$^{-1}$ for **3**. Additionally, the bearing of azomethine groups showed up sharp bands caused by –C=N stretching frequency and these characteristic Schiff base stretching band appeared at 1608 cm$^{-1}$ for complexes **2** and **3** respectively. The C-Br stretching vibrations were observed at 821 cm$^{-1}$ for both **2** and **3** complexes. These IR vibrations are in agreement with previously reported Pcs complexes[2,3,5].

### NMR spectroscopy

In the $^1$H NMR spectra of compound (**1**) in Fig. S4 the aromatic protons (CN-Ar-H) were identified as singlet, doublet, and doublet, respectively at (δ 8.03, 7.25, and 7.55) ppm. The (Br-Ar-H) aromatic protons were found at (δ 8.15 and 7.93) ppm as singlet and doublet for two protons. A singlet peak at δ 10.09 ppm was assigned to the aldehyde proton (O=C-H).

The $^{13}$C NMR spectra (Fig. S7) of compound (**1**) showed five characteristic peaks. The aromatic carbons (C-Ar) were appeared between 161.1 ppm and 111.2 ppm. While, the (C-Br) and (C-CN) carbons were found to be at 124.3 and 123.2 ppm, respectively. The carbonyl carbon (C=O) was detected at 188.7 ppm.

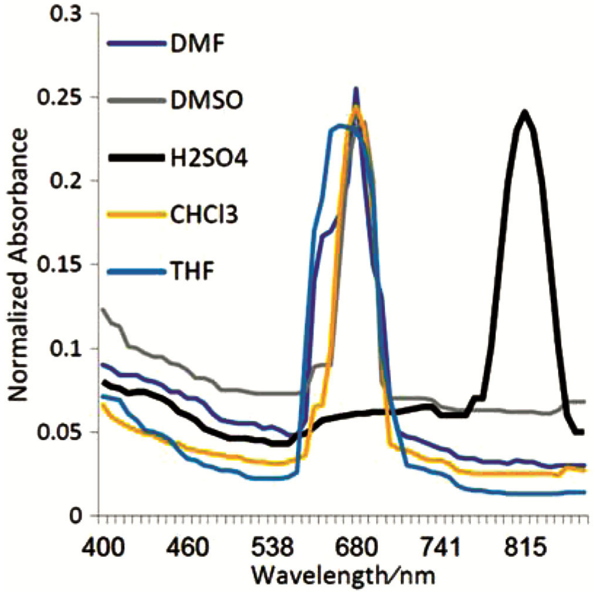


Fig. 1 — Electronic spectra of **2** in various solvents at ($8 \times 10^{-6}$ M) concentration

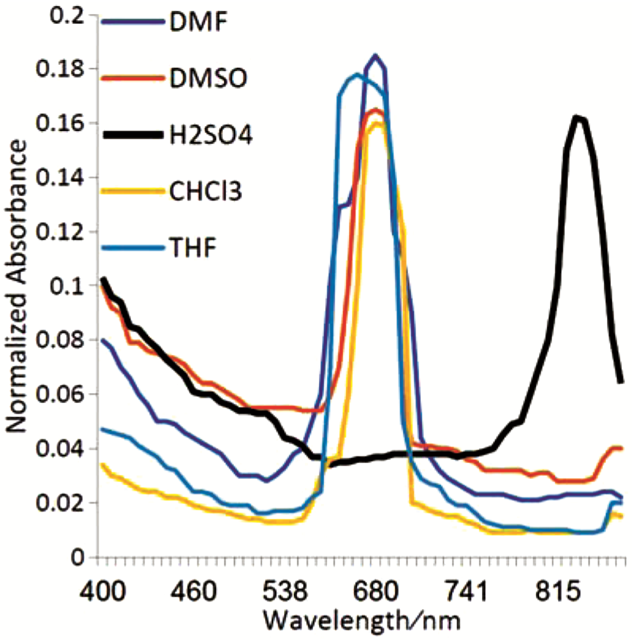


Fig. 2 — Electronic spectra of **3** in various solvents at ($8 \times 10^{-6}$ M) concentration

In the $^1$H NMR spectra in Figs. (S5 and S6) of the Zn(II) and Cu(II) complexes (**2** and **3**) were approximately identical. The proton signals of the aromatic were observed at a region ranging from 7.25 to 8.16 ppm. A singlet peak at δ 10.09 and 10.10 ppm assigned to the aldehyde protons (O=C-H) were also observed. The imine protons belonging to the phthalocyanine rings of the synthesized complexes were observed at the expected regions in the $^1$H NMR spectrum.

In the $^{13}$C NMR spectra in Figs. (S8 and S9) of the Zn(II) and Cu(II) complexes (**2** and **3**) also approximately similar. The three characteristic peaks (C-Ar, C-Br and C=O) were detected at the expected regions in the $^{13}$C NMR spectra.

## Mass spectra

The mass spectra in Fig. S10 of compound (**1**) showed the molecular ion peak at m/z = 327 [M+]. Another characteristic peak at m/z = 301.90 was attributed to compound (**1**) after losing one CN group. The intense peak at m/z = 200.10 was related to the compound (**1**) after the phthalonitrile fragment was eliminated. An interesting peak with moderate intensity at m/z = 154.90 related to the bromobenzene fragment that remained.

## UV-Spectroscopy

The electronic absorption spectra (Fig. 3) of the complexes (**2** and **3**) show peaks at 681 and 678 nm respectively. These absorptions exhibits a single intense Q band in DMSO which arises from the π-π* transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)[26].

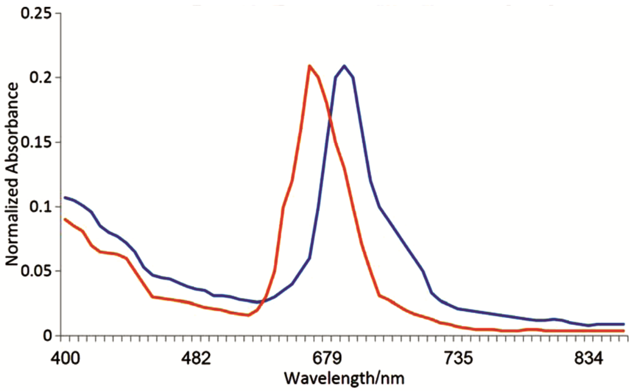


Fig. 3 — UV–Vis spectra of phthalocyanines in a DMSO solution for complexes (**2** and **3**) ($1\times10^{-5}$ M) are displayed in blue and red respectively

## Aggregation studies

Aggregation has a significant impact on the bioavailability, optical and photodynamic therapy characteristics, singlet oxygen production efficiencies and *in vivo* dispersion in highly delocalized π-electron systems[26]. However, non-aggregated phthalocyanines with bulky group substitutions have a strong solubility, which is crucial for purification and characterization. Several factors, including concentration, temperature, can influence the aggregation behavior of Pcs, substituent character, locations, and solvent type[27-30]. The aggregation behavior of complexes **2** and **3** was investigated by UV-Vis absorption at varied concentrations of DMSO (Fig. 4 and Fig. 5).

To determine the aggregation effect of the peripheral halogen substituted phthalocyanine. Fig. 4 and Fig. 5 showed complexes **2** and **3** followed the Lambert-Beer law at concentrations ranging from (2-$10\times10^{-6}$) M in DMSO. This confirmed the non-aggregation nature of these complexes. As the material concentration increases, aggregation causes a corresponding rise in the Q band's density, but no

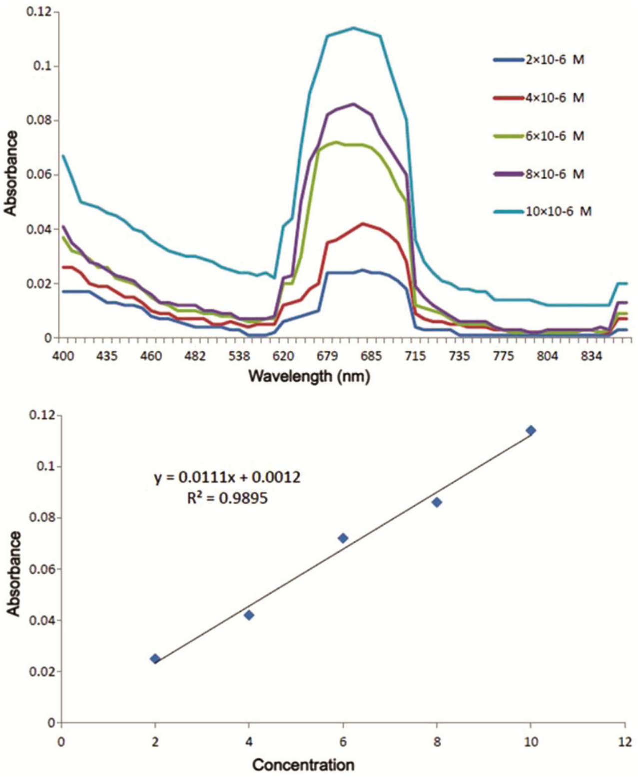


Fig. 4 — Absorbance changes of [ZnPc] complex **2** in DMSO at different concentrations: $10\times10^{-6}$M (A), $8\times10^{-6}$ M (B), $6\times10^{-6}$ M (C), $4\times10^{-6}$ M (D), $2\times10^{-6}$ M (E). (Inset: Plot of absorbance *vs*. concentration)

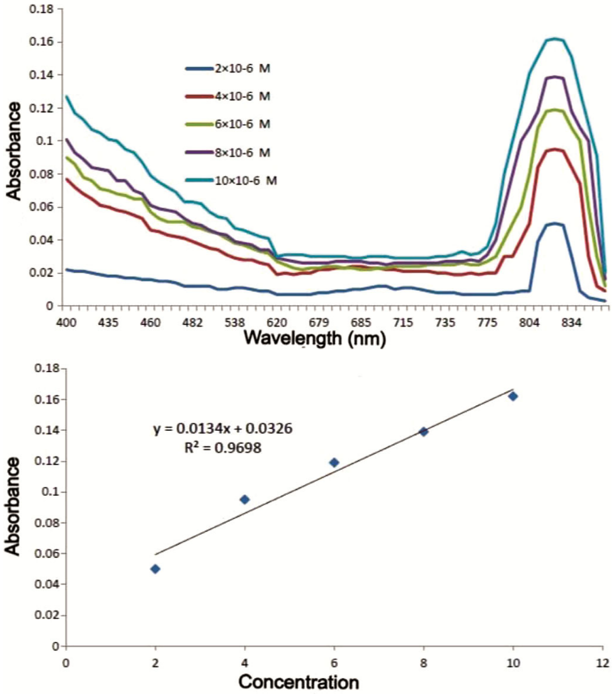


Fig. 5 — Absorbance changes of [CuPc] complex **3** in DMSO at different concentrations: 10×10$^{-6}$M (A), 8×10$^{-6}$ M (B), 6×10$^{-6}$ M (C), 4×10$^{-6}$ M (D), 2×10$^{-6}$ M (E). (Inset: Plot of absorbance *vs*. concentration)

additional band is discernible[31]. Additionally, complexes (**2**) and (**3**) electronic absorption in a variety of solvents, including DMF, DMSO, $H_2SO_4$, $CHCl_3$, and THF, was investigated (Fig. 1 and Fig. 2). In this research, the bathochromic shift of Q band depending on the solvent type for [ZnPc] was in the following ascending order (THF< DMF< $CHCl_3$< DMSO and $H_2SO_4$), and for [CuPc] was (THF< DMSO< DMF< $CHCl_3$ and $H_2SO_4$) respectively. Complexes (**2** and **3**) did not show any evidence of aggregation in different concentrations owing to the substituent effect (5-bromosalicyladehyde at the peripheral positions). As the concentration of the complexes increases, the absorption intensity enhances, and no new band was formed due to aggregation. Since the aggregation of Pcs can block ROS production. Additionally, non-aggregated Pcs are of great importance in terms of PDT yields[32].

## Photophysical and photochemical studies

The fluorescence quenching, photochemical and photophysical properties of the newly synthesized Pcs (**2** and **3**) were examined using the methods as previously reported[33]. Full details are provided in the 'Supplementary Information' section.

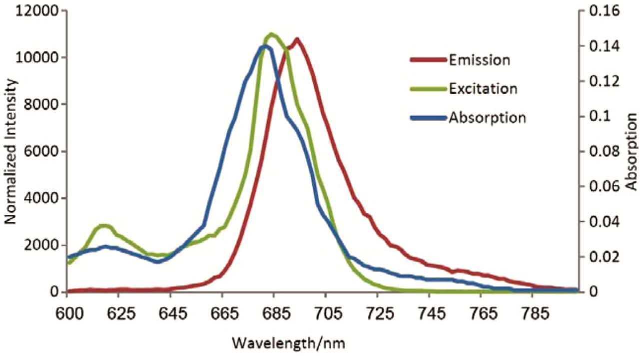


Fig. 6 — Absorption (681), excitation (683), and emission (693) spectra of complex **2** in DMSO

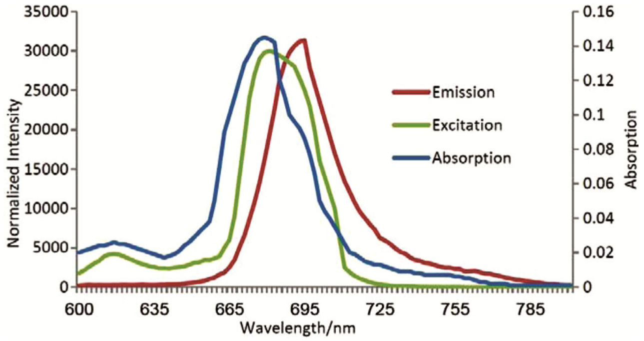


Fig. 7 — Absorption (679), excitation (681), and emission (695) spectra of complex **3** in DMSO

## Fluorescence spectra and quantum yields ($\Phi_F$)

The absorption, emission, and excitation spectra of complexes **2** and **3** are displayed in Fig. 6 and Fig. 7. The fluorescent quantum yields of (Pcs **2**, **3**) were calculated in a DMSO solution. Fluorescence emission was detected at 693 nm and 695 nm for **2** and **3**, respectively. The similar wavelengths in the absorption and excitation spectra of Pcs (**2**, **3**) indicate that the nuclear configurations of the ground and excited states remain unchanged and unaffected by the excitation wavelength. Due to aggregation preventing full phthalocyanines emission in water, fluorescence quantum yields were assessed in DMSO (Ref. 32).

## Singlet oxygen quantum yields ($\Phi\Delta$)

The efficacy of the complexes for photocatalytic applications such as PDT depends on photo-induced oxidative reactions, which are crucial and necessary. Singlet oxygen is a highly reactive, lethal oxidative species involved in these activities. Measurements of singlet oxygen production in DMSO were performed to determine if the produced complexes were suitable

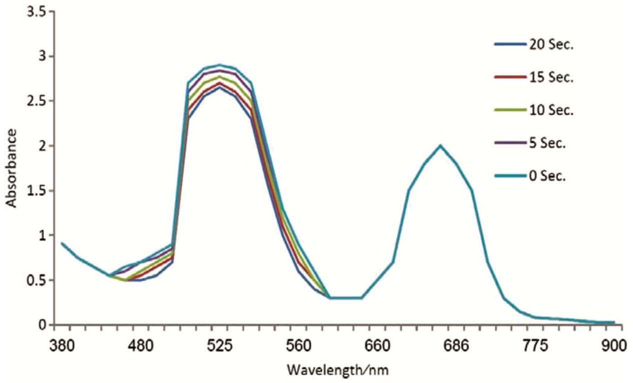


Fig. 8 — A typical spectrum used to measure the complex **2** singlet oxygen quantum yield in DMSO

for PDT study. The spectrum variations of the DPBF absorption band are displayed in Fig. 8. The complexes did not degrade during the observations, as indicated by the spectral data, which showed no variations in the intensity of the Q bands[33].

## Conclusion

In this research, novel peripherally tetrasubstituted zinc and copper phthalocyanines bearing the (4-bromo-2-formylphenoxy) group were synthesized and characterized. The spectroscopic characteristics of the phthalocyanines (Pcs) were studied in various organic solvents. According to the Lambert-Beer Law, none of the Pcs in DMSO exhibited any aggregation species at any of the concentrations. To determine if the complexes are suitable for photodynamic therapy (PDT), their photophysicochemical characteristics were examined.

## Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

## Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

## Acknowledgments

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