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Synthesis, photophysics, and photochemistry of ball-type phthalocyanines

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ABSTRACT

Phthalocyanines (Pcs) have numerous potential applications, including use as photosensitizers for photodynamic cancer therapy. These applications depend on specific photodynamic properties; therefore, new Pc compounds with unique and well characterized properties are in constant demand. In this study, four novel ball-type Pc compounds were synthesized with 1,2-benzenediol as a substituent, including one non-metal complex (H_4Pc_2) and three metal-containing complexes (Mg_2Pc_2, Co_2Pc_2, and Zn_2Pc_2). The structures of the synthesized compounds were characterized using common spectroscopic methods. Quantum yields for fluorescence (Φ_F), triplet state (Φ_T), singlet oxygen (Φ_Δ), and photodegradation (Φ_d) were measured except Co_2Pc_2 in dimethylsulfoxide. All the three compounds exhibited low fluorescence quantum yield, high triplet quantum yield, and good stability in organic solvent, suggesting acceptable photostability. Complexes with H_4Pc_2 and Mg_2Pc_2 demonstrated differences in the Q band in their Uv–Vis spectra. Singlet oxygen quantum yield was 0.35 for Zn_2Pc_2. Fluorescence lifetimes (τ_F) for the complexes ranged from 6.67 to 2.95 ns, while triplet state lifetimes (τ_T) ranged from 50 to 440 μs. This novel group of Pcs possesses properties suitable for photodynamic therapy, particularly ZnPc.

1. Introduction

Since the accidental discovery of phthalocyanine (Pc) in 1907, numerous derivative Pcs have been synthesized, characterized, and applied in fields ranging from dyeing, chemical production, nanoparticle construction, and cancer photodynamic therapy (PDT) [1,2]. This wide applicability is the result of several attractive photophysical and photochemical properties [3,4].

In particular, Pc has attracted considerable interest because of its application as photosensitizers in PDT for cancer treatment [5–21]. Cancer cells can be destroyed by PDT using visible light, molecular oxygen, and a photosensitizer. Currently, Pcs used as photosensitizers are red light-absorbing compounds that produce singlet oxygen under irradiation. However, aggregation of Pc molecules can disrupt these properties. Among new Pcs derivatives [22–26] are the ball-type phthalocyanines [27–46]. Similar to monomer Pcs, the electrical and electrochemical properties of ball-type Pcs can change dramatically depending on the substituent and central metal. However, ball-type Pcs may be prone to aggregation, low yield, poor solubility, and difficulties in synthesis. Thus, relatively few studies have described the synthesis, photophysics, and photochemistry of ball-type Pcs. In this study, the synthesis and properties of ball-type H_2Pc, MgPc, CoPc, and ZnPc complexes bridged by oxygen and containing benzene substituents at peripheral positions are described (Fig. 1).

2. Material and methods

2.1. Materials

Cobalt(II) acetate, magnesium(II) chloride, and zinc(II) acetate were purchased from Sigma–Aldrich, dimethylsulfoxide (DMSO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), dimethylformamide (DMF), methanol, and chloroform from Merck, and 4-nitro phthalonitril from Alfa Aesar. Silica gel for column chromatography and catechol were purchased from Merck. All other reagents were obtained from commercial suppliers. All solvents were used and stored over molecular sieves without further purification.

2.2. Equipment

All equipment used was described in a previous study [47].

2.3. Synthesis

The target precursors were prepared by a nucleophilic aromatic substitution reaction between compound **1** and **2** in DMSO. Ball-type Pc derivatives **4–7** were produced using *n*-pentanol in the presence of DBU at the reflux temperature.

4,4′-(1,2-phenylenebis(oxy))diphthalonitrile (3) [48].

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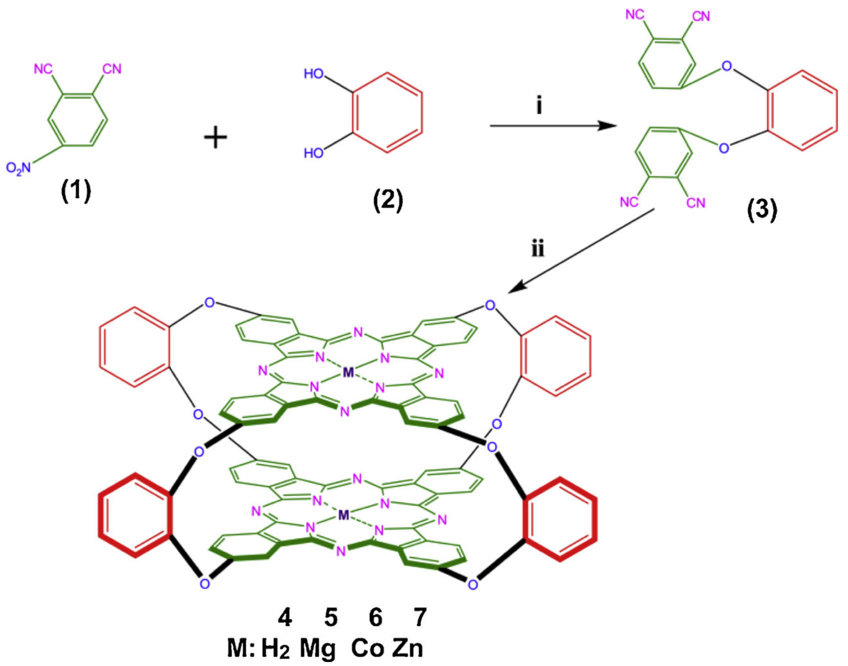

Fig. 1. i: DMSO, 2 days, K_2CO_3 ii: *n*-pentanol, DBU, reflux, overnight, metal salt.

Compound **2** (1.59 g, 14.40 mmoL) was dissolved in anhydrous DMSO (15 mL), and compound **1** (5.00 g, 28.90 mmoL) was added under an Argon atmosphere. Finely ground anhydrous potassium carbonate (7.96 g, 59.00 mmol) was then added and the mixture stirred for 4 h at 70 °C then for 2 days at room temperature. The mixture was poured into water (150 mL), resulting in the formation of a light brown precipitate. The pure product was dried for one week using P_2O_5. Yield was 1.75 g and melting point was 190 °C. The IR (ATR) (υ_{max}/cm^{-1}) results were as follows: 3117/3086/3067 (Ar-CH), 2232 (CN), 1587/1590 (C = C), and 1246 (C-O-C). The ^{1}H NMR (DMSO-d_6) results were as follows: δ, ppm 8.31 (2H, s, Ar–H), 8.04 (2H, d, Ar–H), 7.71 (2H, d, Ar–H), 7.46 (2H, t, Ar–H), and 7.35 (2H, dd, Ar–H). Elemental analysis yielded 72.89% C, 2.65% H, and 15.32% N, consistent with $C_{22}H_{10}N_4O_4$ (C, 72.92%; H, 2.78%; N, 15.46%). Finally, LC–MS yielded *m/z*. $[M+H]^+$: 363.09 and $[M+H_2O]^+$: 380.12.

General Procedure (4–7): A mixture of complex **3** (0.100 g), without metal salt, excess magnesium(II) chloride, zinc(II) acetate, or cobalt(II) acetate (0.050 g), and six to ten drops of DBU in *n*-pentanol was heated within a sealed glass tube for 20 h under argon at reflux temperature. After cooling to room temperature, the blue-green reaction product was washed sequentially with hot methanol, acetone, and hot water. The precipitate was analyzed by silica gel column chromatography with gradients of chloroform, tetrahydrofuran, MeOH, and DMSO. All the complexes were washed with methanol and ethanol. All the complexes (**4–7**) were soluble in THF, DMSO, and DMF, were green in color, and melted above 220 °C. Analytic results are summarized as for compound **3.**

Ball-type H_2Pc (4): (i) Yield 0.023 g. (ii) Uv–Vis (DMSO): λ_{max}/nm: 684, 642, 623, 313. (iii) IR (ATR): ($\mu_{max/}$ cm^{-1}), 2934 (Ar-CH), 1717 (C = O), 1589 (C = C), 1087 (C-O-C). (iv) ^{1}H-NMR (DMSO-d_6): δ, ppm: 7.80–7.10 (44H, Ar-H). (v) Anal. calcd. for $C_{88}H_{44}N_{16}O_8$: C, 72.72%; H, 3.05%; N, 15.42%. Found: C, 72.51%; H, 3.42%; N, 15.85%. (vi) MALDI-TOF-MS: *m/z* calcd. 1453,39, found 1584 $[M+3K+2Li]^+$.

Ball-type MgPc (5): (i) Yield 0.018 g. (ii) Uv–Vis (DMSO): λ_{max}/nm: 701, 670, 637, 616 329. (iii) IR (ATR): ($\mu_{max/}$ cm^{-1}) 3093/3053/2957 (Ar-CH), 1717 (C = O), 1620 (C = C), 1271 (C-O-C). (iv) ^{1}H NMR (DMSO-d_6): δ, ppm: 7.75–7.15 (40H, Ar-H). (v) Anal. calcd. for $C_{88}H_{40}N_{16}O_8Mg_2$: C, 70.56; H, 2.69; N, 14.96. Found: C, 70.41; H, 2.43; N, 15.02%. (vi) MALDI-TOF-MS: *m/z* calcd. 1497.97, found 1527 $[M+Na+Li]^+$.

Ball-type CoPc (6): (i) Yield 0.031 g. (ii) Uv–Vis (DMSO): λ_{max}/nm: 672, 606, 318. (iii) IR (ATR): ($\mu_{max/}$ cm^{-1}) 3065 (Ar-CH), 1714 (C = O), 1611 (C = C), 1261 (C-O-C). (v) Anal. calcd. for $C_{88}H_{40}N_{16}O_8Co_2$: C, 67.44; H, 2.57; N, 14.30. Found: C, 67.31; H, 3.05; N, 14.95%. (vi) MALDI-TOF-MS: *m/z* calcd. 1567.23, found 1567.32 $[M]^+$, 1585 $[M+H_2O]^+$.

Ball-type ZnPc (7): (i) Yield 0.025 g. (ii) Uv–Vis (DMSO): λ_{max}/nm: 681, 631, 611, 337. (iii) IR (ATR): ($\mu_{max/}$ cm^{-1}) 3100 (Ar-CH), 1217(C = O), 1618 (C = C), 1276 (C-O-C). (iv) ^{1}H NMR (DMSO-d_6): δ, ppm: 7.80–7.10 (40H, Ar-H). (v) Anal. calcd. for $C_{88}H_{40}N_{16}O_8Zn_2$: C, 66.89; H, 2.55; N, 14.18%. Found: C, 66.55; H, 2.50; N, 13.65%. (vi) MALDI-TOF-MS: *m/z* calcd. 1580.18, found 1588 $[M+8H]^+$, 1591 $[M+Li+4H]^+$.

2.4. *Photophysical and photochemical studies*

The fluorescence quantum yield (Φ_F), fluorescence lifetime (τ_F), triplet quantum yield (Φ_T), triplet quantum lifetime (τ_T), singlet oxygen quantum yield ($\Phi_{\Delta)}$, and efficiency of singlet oxygen formation (S_Δ) for complexes **4**, **5**, and **7** as well as the photodegradation quantum yield (Φ_d) for complexes **4**, **5**, **6**, and **7** were measured using standard methodologies [47].

3. Results and discussion

3.1. *Synthesis and characterization*

Phthalonitriles are the most popular choice of starting compound due to high yields of desired Pc complexes [49]. The preparation of ball-type Pcs was performed by ipso substitution of 4-nitrophthalonitrile with the corresponding bridging ligand having a diol functionality, followed by a typical cyclotetramerization reaction procedure. The complexes of compound **3** investigated in this study were H_2Pc (**4**), MgPc (**5**), CoPc (**6**), and ZnPc (**7**). Complexes **4–7** were purified by silica gel column chromatography using $CHCl_3$, THF, MeOH, and DMSO as mobile phases, respectively. The structures and purity of these H_2, Mg, Zn, and Co Pc derivatives were confirmed by Uv–Vis, ^{1}H NMR, IR, mass spectroscopy, and elemental analyses.

The IR spectrum of **3** exhibited a vibrational peak at 2232 cm^{-1}, indicating the presence CN. A diagnostic feature of **4–7** formation from **3** was the disappearance of this sharp CN vibrational peak. Otherwise, the IR spectra of complexes **4–7** resembled that of compound **3.** Complexes **4–7** showed Ar-O-Ar peaks at 1246, 1254, 1271, 1261, and 1276 cm^{-1}, respectively.

The ^{1}H NMR spectra of complexes **3–5** and **7** recorded in DMSO were also similar, although **4, 5,** and **7** demonstrated more intricate spectral patterns as they are mixed isomers. The ^{1}H NMR spectrum of complex **6** (CoPc) could not be obtained due to the presence of a paramagnetic metal. The aromatic protons of **3** appeared at 8.31, 8.04, 7.71, 7.46, and 7.35 ppm and integration yielded the expected total of 10 protons. The ^{1}H NMR spectra of complexes **4, 5,** and **7** exhibited aromatic protons between 7.80 and 7.10 ppm, and integration yielded totals of 44, 40, and 40 for protons, respectively (Please see Fig. S1 in supplementary data).

Elemental analysis results were also consistent with the proposed structures for compounds **3–7,** yielding percentage carbon, hydrogen, and nitrogene values within acceptable range for Pc complexes.

These purified Pc complexes **4–7** were further characterized using mass spectroscopy. For their expected mass values, in the positive ion and negative ion MALDI-MS spectra, the protonated, deprotonated, molecular ion peak, and fragment ions as adducted Li, Na, K, H_2O were observed [50]. This indicates that leaving groups are available for these complexes under MALDI matrix conditions and under laser energy (Please see Fig. S2 in supplementary data). The MALDI spectra confirmed further that the complexes were synthesized successfully and separated efficiently.

The absorption spectra of monomeric metal phthalocyanines (MPcs) are characterized by intense electron absorption between 600–750 nm and the less intense broad band at ˜350 nm is the B band [51]. For metal-free Pcs, Q band splitting is indicative of D_{2h} symmetry while the symmetry of MPcs is generally D_{4h}. The absorption spectra of Pcs are sensitive to the central metal, solvent, substitution pattern, and aggregation [52–55]. Altered absorption features can also indicate the presence of additional electronic levels in aggregates. The specific molecular arrangement of Pcs in aggregates can result in broadening and splitting of the main absorption Q band, with loss vibrational component resolution and both a hypsochromic or bathochromic shift [56,57].

Complexes **4–7** exhibited Q band absorptions at 684, 670/701, 672, and 681 nm in DMSO, respectively (Fig. 2, Table 1). The Uv–Vis spectra of these ball-type Pcs resemble those of other Pcs but with several interesting differences. All showed unique spectral behavior in DMSO, with a very broad band extending from 550 nm to 720 nm. The broad vibrational band around 611–642 nm observed in the spectra of **4–7** has been reported to indicate aggregation of Pc complexes, including ball-type complexes. In addition, complex **5** showed low symmetry. The unexpected differences in Q band shape among complexes, particularly the split in complex **5** not observed in the others, suggest differences in symmetry [58,59].

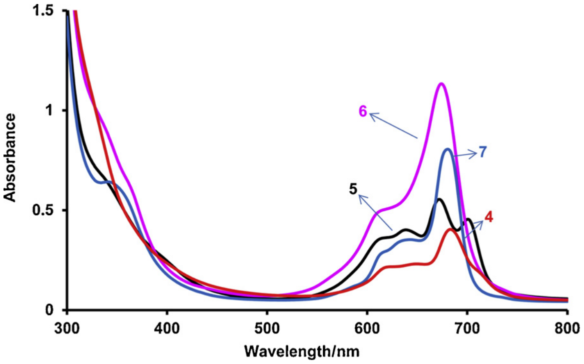

Fig. 2. Uv–Vis absorption spectra for compounds **4–7** in DMSO.

The presence of two sharp peaks at 670 nm and 701 nm in the spectrum of **5** suggests partial demetallation. Complex **5** also demonstrated a blue-shift of the Q band relative to complex **4**. Complex **4** exhibited only one Q band (at 684 nm), while both complexes showed two vibrational bands at around 623 and 642 nm and a shoulder at around 718 nm. Complex **7** also exhibited two vibration bands, at 611 nm and 631 nm. Complex **5** exhibited broad peaks at 606 nm and at 672 nm. Typical of ball-type phthalocyanines, the intensities of the B bands were high relative to the Q band for all the complexes, which may be due to intramolecular interactions between the Pc rings. The aromatic groups and the distance between the two Pc units of ball-type molecules substantially influence the degree of interaction between the rings. It can be seen from the electron absorption spectrum of complexes **4–7** that the Q band is broad. In addition, the Q band maximum wavelength positions of all the complexes were shifted roughly 2 nm longer at low concentrations. Thus, broadening of the Q band can be attributed to intramolecular interactions.

3.2. *Fluorescence spectra, lifetime (τ_F) and quantum yields (Φ_F)*

The fluorescence emission from MPcs is usually short lived, on the order of 10^{-8} s. MPc fluorescence properties such as intensity and quantum yield are influenced by multiple factors including aggregation, solvent properties, concentration (due to quenching), the nature of the central metal atom, substituent type (particularly halogenation), and photo-induced energy transfer [10]. Fluorescence is reduced substantially in the presence of paramagnetic metals and metals of high atomic number (due to the heavy atom effect). These types of compounds encourage intersystem crossing (ISC), a spin-forbidden process that occurs as a consequence of spin-orbit coupling. As a result of the lower energy of emitted photons, Pc fluorescence emission spectra are red-shifted relative to the absorption spectra (Fig. 3). This difference in spectral position is known as the Stokes shift. Minimal re-arrangement of the atomic coordinates during photoexcitation results in smaller Stokes shifts [60]. In general, the shapes of excitation spectra are similar to the corresponding absorption spectra; however, conformational re-organization during excitation may alter the shape of emission spectra.

The absorption, fluorescence excitation, and emission spectra of complex **7** in DMSO are shown in Fig. 3a-b, and the band features of all the complexes are summarized in Table 1 together with fluorescence lifetime data (Please see Fig. S3 in supplementary data for the other complexes). Complex **4** exhibited peak fluorescence emission at 698 nm, complex **5** at 694 nm, and complex **7** at 692 nm. Emission maxima were blue-shifted owing to the atom size. All the complexes showed similar fluorescence behavior, including the same Q band maxima in absorption and excitation spectra. However, absorption and emission spectra were broadened compared to emission spectra due to molecular aggregation. The spectra of complexes **4** and **5** were much broader than that of **7**, suggesting more extensive aggregation. The proximity of the Q band absorption peak to the Q band excitation maximum for all the complexes suggests that the nuclear configurations of the ground and excited states are similar and not altered during excitation. In contrast to monomeric metal-free Pcs [30,32], the emission spectrum of complex **4** was not split and was broader. This may explain which metal-free Pcs are known to fluoresce with only a main peak assigned as the 0–0 transition of the fluorescence, similar to complex **5** [26]. The emission peak of complex **4** was narrower since aggregates are not known to fluoresce. The Stoke's shifts of complexes **4**, **5**, and **7** were 14, 24, 11 nm, respectively, typical for MPc complexes [30–33].

The fluorescence quantum yield Φ_F values were also typical of MPc complexes (in DMSO, 0.033 for **4**, 0.084 for **5**, and 0.058 for **7**). The Φ_F values are typically lower for ball-type Pc derivatives than for other derivatives, as the ball-type structure may encourage ISC to the triplet

Table 1
Summary of Uv–Vis absorption (Q band), emission and excitation spectral data, photophysical properties, and photochemical properties of phthalocyanines **4–7** in DMSO.

Complex	λmax/nm											
	λ_{Abs} (logε)*	λ_{Ems}	λ_{Exc}	$\Delta\lambda_{Stokes}$	Φ_F	Φ_T*	Φ_Δ	S_Δ	Φ_d ($\times 10^{-6}$)	ISC	τ_F (ns)	τ_T (μs)
	684 (3.78)	698	687	14	0.033	0.86	0.065	0.076	2.42	0.90	6.67	50
5	670/701 (4.14)	694	681	24	0.084	0.77	0.054	0.070	0. 47	0.86	4.61	110
6	672 (4.52)	…	…	…	…	…	…		0.58	…		…
7	681 (4.32)	692	683	11	0.058	0.75	0.350	0.467	2.20	0.59	2.95	440

*Excitation λ_{max}: 676, 672, 674 for **4, 5,** and **7,** respectively.
***log**ε/ dm^{-3}. moL^{-1}. $cm^{-1.}$

state. The lower values may also be explained by the tendency of these molecules to aggregate in DMSO, as aggregation reduces the likelihood of radiative deactivation, as well as by effects of the catechol groups on the substituent and the interaction between the two rings [30–33,35,26].

Fluorescence lifetimes were 6.672 ns for complex **4**, 4.613 ns for **5**, and 2,918 ns for **7** [31]. These values reflect the effect of the Pc skeleton and decreasing yield due to the heavy atom effect.

3.3. *Triplet quantum yield (Φ_T) and lifetime (τ_T)*

Table 1 also lists the Φ_T and τ_T values of complexes **4**, **5**, and **7** in DMSO. Fitting of the triplet decay curves for complex **7** are shown in Fig. 4 (see Fig. S4 in supplementary information for the decay curves of the other complexes). The high triplet state quantum yield values were 0.86 for complex **4**, 0.77 for **5**, and 0.75 for **7**. These high Φ_T values (corresponding to low Φ_F values) suggest more efficient ISC in the presence of the catechol substituents. The metastable triplet state properties intrinsic to phthalocyanines are particularly sensitive to changes that deactivate fluorescence. Therefore, factors that induce spin orbital coupling will promote the triplet excited state. This triplet excited state of MPcs in solution is strongly influenced by the nature of the central metal ion, as heavy diamagnetic metal ions or paramagnetic metal ions are known to enhance the triplet state yield.

Apart from triplet absorption detection, flash photolysis also provides information on the excited state lifetime of transient species. Fig. 4 shows a typical triplet state decay curve for complex **7**. Obtained lifetimes were 50 μs for complex **4**, 110 μs for **5**, and 440 μs for **7**. In general, ring substituents reduce triplet state lifetimes, while solvents such as DMSO can increase triplet state lifetimes. This stabilizing effect may be attributed to the highly viscous nature of DMSO. Phthalocyanines containing heavy central metal ions are expected to exhibit shorter lifetimes due to the heavy atom effect, which induces ISC from the excited triplet state to the ground state. Catechol groups, which are weakly electron donating, and the interactions between the two rings

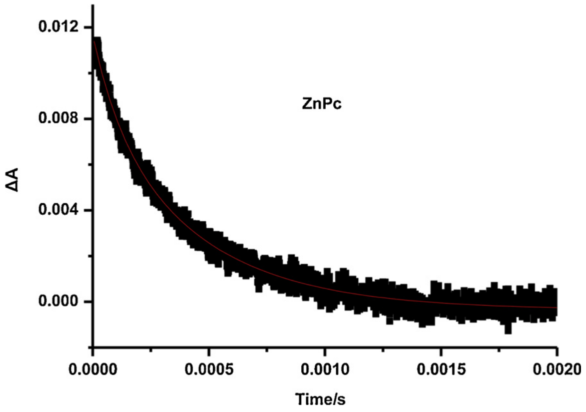

Fig. 4. Mono-exponential triplet decay curve for complex **7** in DMSO.

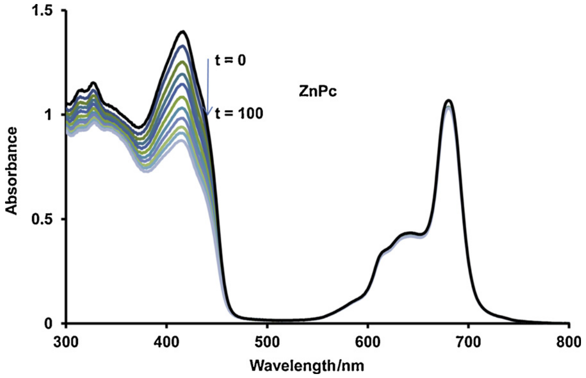

Fig. 5. Time-dependent photobleaching of DPBF absorption in the presence of complex **7** and DMSO as the solvent.

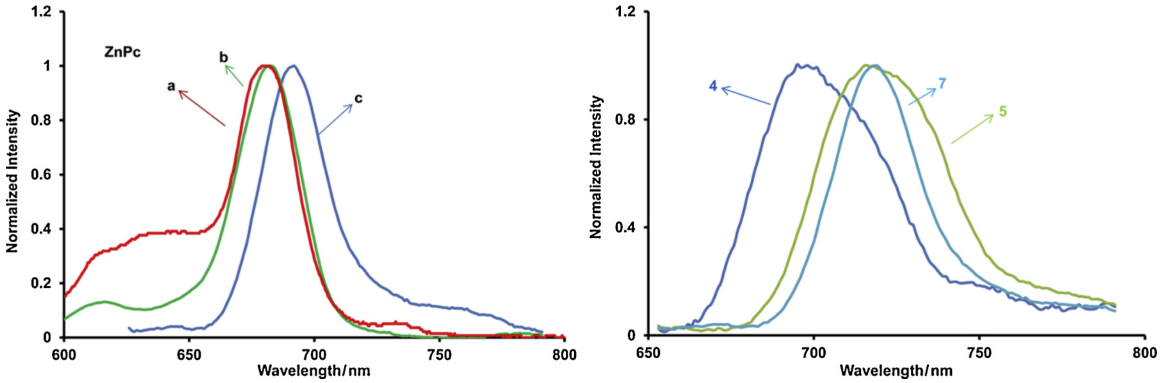

Fig. 3. Absorbance (a), excitation (b), and emission (c) spectra (top panel) of complex **7** and comparison of the emission spectra (bottom) of all complexes in DMSO, Excitation λ_{max}: 612 nm.

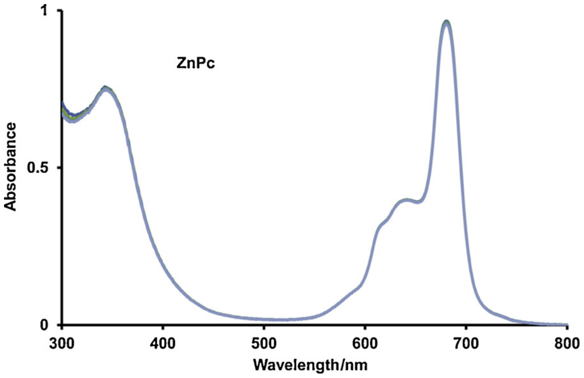

Fig. 6. The photodegradation spectrum for complex **6** in DMSO.

may also influence excited state lifetime.

3.4. Singlet oxygen quantum yields (Φ_Δ)

Fig. 5 shows the spectral changes over 60 min during photolysis of complex **7** in the presence of DPBF. Table 1 summarizes the results for all the complexes (see Fig. S5 in supplementary information for individual photolysis data of each complex). Degradation of complexes **4**, **5**, and **7** by DPBF was monitored by Uv–Vis spectroscopy at 414, 410, and 416 nm, respectively. A blue-shift of almost 2 nm was observed, so the measurement period was sufficient for determination of Φ_Δ values.

The light intensity used for singlet oxygen studies was 5×10^{15} photons $s^{-1}.cm^{-2}$. H_2Pc was not changed, MgPc was slightly increased, and ZnPc slightly decreased, but generally there were no changes in Q band intensities, confirming that these complexes were not degraded during singlet oxygen studies [26]. Complex **4** exhibited a Φ_Δ value of 0.065**,** **5** a value of 0.054, and **7** a value of 0.350. Generally, the Φ_Δ values of the complexes were high, corresponding to high Φ_T values (Table 1) in the same solvent. The rank order of the Φ_Δ values among the substituted complexes was **7** > **4** > **5** in DMSO, which may reflect the propensity of each complex to aggregate because the singlet oxygen quantum yield is strongly sensitive to aggregation [61].

All the three compounds demonstrated efficient generation of singlet oxygen as reflected by the SΔ values (Table 1). The SΔ value was largest for complex **7** while values were similar for complexes **4** and **5**. SΔ values are generally thought to be related to the lifetimes of the triplet state. The low SΔ for complexes in DMSO may also be due to partial oxidation as well as the interaction between the two rings.

3.5. Photodegradation quantum yields (Φ_d)

The photodegradation quantum yields of complexes **4–7** were determined in DMSO by monitoring the decrease in Q band intensity under irradiation over 60 min. Fig. 6 shows the photodegradation spectrum for complex **6** (see Fig. S6 in supplementary information for spectra of the other complexes) and Table 1 summarizes the results for all the complexes. This parameter is especially important when considering photocatalyst applications [62]. The degradation of phthalocyanine molecules often occurs *via* attack by singlet oxygen in an oxidative process, while DMSO partially shields the Pc from oxidative attack. In addition, substituents can also provide stability [63,64].

Complexes **7** and **5** exhibited decreased Q band intensity whereas complexes **4** and **6** showed little or no change under irradiation. Photodegradation of MPcs is characterized by reduced absorption in the Q and B band regions without the appearance of new bands in the visible region or a shift in the maxima on exposure to intense light. Thus, all the four complexes are highly stable in the solvent used. Stability may also reflect the peripheral substitutions or be a consequence of the initial partial oxidation and low Φ_Δ values [63]. The order of stability among the substituted complexes was **4** > **7** > **6** > **5** in DMSO. The quantum yields of the MPcs increased with metal atomic number, but quantum yields were still higher for H_2Pc, indicating that the Pc skeleton has a stronger influence than the metal weight.

4. Conclusions

Four new ball-type phthalocyanines (denoted **4–7**) were synthesized from 4,4′-(1,2-phenylenebis(oxy))diphthalonitrile (compound **3)** at the peripheral position. The complexes were characterized by elemental analysis, Uv–Vis, ^{1}H-NMR, FT-IR, and mass spectroscopy, and then examined for photophysical and photochemical properties useful for PDT. All compounds possess low fluorescence quantum yields and high triplet quantum yields. The ZnPc complex also possesses good singlet oxygen quantum yield. MgPc exhibits a split in its Q band, while H_2Pc shows only a single Q band, consistent with previous measures of non-metal-containing ball-type Pcs. Although all the four complexes tend to aggregate, the singlet oxygen quantum yield of ZnPc is reasonable. The photodegradation quantum yield shows that all the four molecules are highly stable in DMSO, indicting relatively good photostability. Among complexes, ZnPc has particularly long fluorescence and triplet lifetimes, properties especially suitable for PDT. In this study, the effects of aggregation were carefully documented, which should serve as a template for future reports on novel Pcs.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2019.112043.

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