Contents lists available at ScienceDirect



Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

Research paper

Photo-physico-chemical properties of 1,3-benzenediol-substituted face-toface phthalocyanines



Mevlüde Canlıca

Chemistry Department, Inorganic Chemistry Division, Yıldız Technical University, Davutpasa Campus, 34220 Esenler, Istanbul, Turkiye

lifetime of 1100 µs.

A R T I C L E I N F O A B S T R A C T Keywords: Ball-type phthalocyanine Face-to-face interaction Fluorescence quantum yield Singlet oxygen quantum yield Singlet oxygen quantum yield Triplet life time A B S T R A C T Here, we report the synthesis of new ball-type phthalocyanines that are symmetrically substituted with Mg–Mg, and Co–Co centers and contain four 1, 3-benzenediol substituents at the beta positions. The structures and photophysical properties, including the fluorescence quantum yield, triplet quantum yield, and photochemical properties with singlet oxygen quantum yield, of these compounds were investigated. Moreover, the applicability of these molecules as photosynthesizers in cancer nanomedicines is discussed. Furthermore, the photodegradation quantum yield of the complexes with the inclusion of Co binuclear phthalocyanine was examined, and their fluorescence and triplet lifetimes were studied in dimethyl sulfoxide. The obtained Uv–Vis

1. Introduction

Phthalocyanines (Pcs) were accidentally discovered in 1907 [1] and first characterized in the 1930s [2,3]. Since then, they have attracted a great deal of attention by researchers worldwide. Pcs are stable aromatic macrocyclic compounds with $18-\pi$ electron conjugated systems, which enables strong absorption in the red region of the visible spectrum. There are many potential applications of Pcs in chemical sensors, liquid crystals, optical data storage, and as carrier or generation materials in near-infrared devices [4,5].

Furthermore, *Pc* derivatives containing metal ions, such as Zn and Mg, show promise for second-generation photosensitizers for use in photodynamic therapy (PDT) for cancer [6,7]. In PDT, photosensitizer, vis ible light and oxygen as singlet oxygen ($^{1}O_{2}$) and triplet oxygen ($^{3}O_{2}$) are used to induce a photodynamic effect that damages the living tissue in the target region. An ideal photosensitizer exhibits strong absorption in the wavelength range of 670–800 nm. In addition, as molecular oxygen quantum yield of the photosensitizer is of particular significance in PDT. However, researchers have yet to identify an optimal photosensitizer that can be utilized as a light-sensitive drug for alternative cancer treatments.

To date, several types of Pcs with various properties have been investigated [8]. One type of binuclear Pc is the ball-type Pc, which was first synthesized by the Zefirove group in 2002 [9,10]. This ball-type Pc

exhibits unique spectroscopic properties such as a broad Q band. Later, the Bekaroglu group focused on the electrochemical properties of ball-type Pcs including the nonlinear optical properties. Generally, their ultraviolet–visible light (Uv–Vis) spectra differ from those of monomers in that they exhibit high B bands and broad Q bands. In addition, the Uv–Vis spectra often reveal noteworthy interactions between the *Pc* rings or the two metal centers and substituents. However, in one study, ball-type H₂Pc was compared with metalPcs but was not found to exhibit the necessary properties for use as a photosensitizer [6]. To date, other studies of ball-type MgPc and H₂Pc derivatives with various substituents provide limited information about the photochemical behaviors of ball-type Pcs [11–27].

spectra exhibited unexpected results; for instance, H_2Pc exhibited a broad and peculiar Q band with D4h symmetry. Moreover, H_2Pc was found to have a triplet lifetime of 460 μ s whereas ZnPc had a higher triplet

Other binuclear Pcs include clamshell-type Pcs (i.e., co-facial Pcs), including 1,8-Naphthalene and 1,8-Anthracene [28] exhibit both magnetic circular dichroism (MCD) and electrochemical properties. Kobayashi et al. extensively reported the synthesis of binuclear balltype Pcs and their MCD properties [29,30] Seotsanyana [31] reported the photochemical properties of such molecules and demonstrated that they can be used as possible photosensitizers for PDT. Hence, both balltype and clamshell-type Pcs are of interest in terms of face-to-face interaction although each Pcs are different structurally in that ball-type Pcs has four substituent while clamshell Pcs has only one substituent. As far as I know, nevertheless, the photochemical behaviors of neither balltype Pcs nor clamshell Pcs as being ball-type Pcs have not been widely studied [9–39]. As O. Bekaroglu reported the synthesis of the ball-type

https://doi.org/10.1016/j.ica.2020.119830

Received 7 May 2020; Received in revised form 10 June 2020; Accepted 10 June 2020 Available online 12 June 2020

0020-1693/ © 2020 Published by Elsevier B.V.

E-mail address: mcanlica@yildiz.edu.tr.

Pcs are difficult but has their remarkable properties [26]. In the literature there still are limited papers any information about comparing of the results which obtained with any properties of ball-type Pcs based on face-to-face interaction effect.

The aim of this study is to synthesize metal-free, magnesium, zinc and cobalt ball-type Pcs bearing 1,3-benzenediol moieties and investigate their photo-physico-chemical behaviors. The centers and substituents of these molecules can be modified to manipulate the π electron conjugated ring system and intramolecular π - π^* interactions in the interest of making them more suitable for PDT. For example, an ideal Type II-photosensitizer should exhibit a relatively long triplet state lifetime (τ_T , microsecond range) [6]. It is also important to consider the fluorescence quantum yield (Φ_F), triplet quantum yield (Φ_T), singlet oxygen quantum yield (Φ_{Δ}) photodegradation quantum yield (Φ_d), fluorescence lifetime (τ_F) and triplet lifetime (τ_T) in order to design a suitable sensitizer. Moreover, the MCD properties of the synthesized ball-type Pcs are evaluated.

2. Results and discussion

Phthalonitriles widely used as the starting material due to their high yields for the desired *Pc* complexes [40]. Here, a diphthalonitrile, 4-nitrophthalonitrile, was used to synthesize ball-type Pcs according to the simplified preparation and purification methods that were developed previously as shown in Scheme 1. Ball-type Pcs were obtained in a low yield from 4, 4'-(1,3-phenylenebis (oxy)) diphthalonitrile, 3. Complexes 4–7 were purified by column chromatography on silica gel using chloroform (CHCl₃), tetrahydrofuran (THF), methanol (MeOH) and dimethyl sulfoxide (DMSO), respectively, as the mobile phase. The structures and purities of the H₂–, Mg-, Zn- and Co- *Pc* derivatives were confirmed by Uv–Vis, ¹H nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy and mass spectrometry and elemental analyses.

The IR spectra of **3** clearly exhibit a $-C \equiv N$ vibrational peak at 2235 cm⁻¹. After conversion into Pcs, this characteristic $-C \equiv N$ stretch disappeared from the spectrum, which confirms that metalled- and metal-free Pcs were formed. The remaining IR spectra for compound **3** and those of **4**–7 were quite similar in that they exhibited Ar-O-Ar peaks at 1247, 1083, 1094, 1124, 1089 cm⁻¹, respectively.

The ¹H NMR spectra of **3** and **4–6** in DMSO were difficult to interpret but confirmed that presence of aromatic protons in the aromatic region as expected. The ¹H NMR spectra of **4–6** show that the aromatic protons were present at concentrations of almost 6.50–8.50 ppm, which is attributed to the 1,3-benzenediol substitution in the ball-type complexes. On the other hand, the inner protons of the H₄Pc₂ ring were not observed as reported previously. Moreover, the obtained peaks were very broad, which is typical of face-to-face complexes [37].

The complexes were further characterized by MALDI-MS using 2,5dihydroxy benzoic acid as the matrix, which is known to intensify the fragmentation process [41]. Compounds 4–7 exhibited complicated spectra due to the presence of mixed isomers of these complexes. In the positive-ion and negative-ion MALDI-MS spectra of purified 4–7 (Fig. S1, supplementary information), the protonated, molecular ion peak and fragment ions as adducted Li and H₂O were observed [27]. This indicates that leaving groups are available for complexes 4 and 5 under the MALDI matrix conditions.

Pcs generally have two characteristic bands: a low-intensity B band between 300 and 400 nm and a relatively intense Q band in the range of 600–800 nm with a molar absorptivity often exceeding 10^{-5} L mol⁻¹ cm⁻¹ due to the π – π * transition from the macrocyclic structure. The Q band is also accompanied by one or two weak vibronic bands (Q_{vib}). For ball-type Pcs, the intensity of the B band is typically higher than that of the Q band, possibly due to intramolecular interactions between the *Pc* rings.

As shown in Fig. 1, in DMSO, complexes 4–7 exhibit approximately 10^{-5} M of Q band absorption at 682, 670/702, 680, and 672 nm,



Scheme 1. i: DMSO, 7 days, K₂CO₃ ii: n-pentanol, DBU, reflux, overnight, metal salt.

M. Canlıca



Fig. 1. Ground-state electronic absorption spectra for 4-7 plotted on the same axes.

Table 1

Uv–Vis absorption (Q band), emission and excitation spectral data, and photophysical and photochemical data for the phthalocyanines complexes in DMSO.

Complex λmax (nm)	4	5	6	7
λ_{Abs} (loge)* ^a λ_{Ems}	682(3.79) 691	670/ 702(4.31) 707	680(4.61) 690	672(4.62)
λ_{Exc}	683	701	681	
$\Delta \lambda_{\text{Stokes}}$	9	35	11	
$\Phi_{\rm F}$	0.06	0.06	0.04	
$\Phi_{T}^{*^{b}}$	0.43	0.65	0.33	
Φ_{Δ}	0.27	0.54	0.72	
ISC	0.67	0.40	0.24	
S_{Δ}	0.63	0.83	2.18	
Φ _d (x10-6)	1.38	2.2	2.88	0.107
$\tau_{\rm F}$ (ns)	5.34	4.49	2.89	
τ _T (μs)	460	110	1100	

[a] $\log \epsilon$: dm³. moL₁⁻¹cm⁻¹.

[b] Excitation λ_{max} : 663, 671, and 662 for **4–6**, respectively.

respectively, as summarized in Table 1; further, their molar absorptivities were calculated as 3.79 for H_4Pc_2 , 3.91 for Mg_2Pc_2 , 4.62 for Zn_2Pc_2 and 4.78 for Co_2Pc_2 . Unexpectedly, B band of complex **6** was lower than that which is typical of ball-type Pcs, which may be due to the Zinc metal ion. Complex **4** has a broad single Q band that is typical of metalled *Pc* complexes with D_{4h} symmetry. In contrast, the absorption of complex **5** resembles that of a metal-free *Pc*. These findings provide evidence that both metalled and metal-free Pcs had aggregated in the solution [42,43]. The aggregated complexes exhibited both broad Q_{vib} and a shoulder on the high-energy side of the Q band, which can be attributed to intramolecular interactions. The fact that a split Q band is observed for metalled species but not metal-free species confirms that intramolecular coupling occurred between the two halves of the binuclear complexes as reported in other studies [44,31,33–36].

The absorption and MCD spectra for complexes 4-7 in DMSO were

recorded from the same solution at the same time; those of complex **6** are shown in Fig. 2 (others are shown in Fig. S2, supplementary data). Table 2 summarizes the measured MCD and Uv–Vis absorption data. The MCD spectra exhibit dispersion-type signals with peaks and troughs at + 617, +677 and – 692 nm for **4**, +600, -657 and – 691 nm for **5**, +619, +676 and – 690 nm for **6**, +607 and – 646/–665 nm as shoulders and –684 nm for **7**, corresponding to the Q band absorption. Complexes **4**–7 exhibited cross-over points at 683, 628, 681, and 641 nm, respectively. These points describe the Q band maxima for ball-type complexes **4** and **6** and are related to the main π - π * excited state, which retains its orbital degeneracy and results in curve splitting with the Faraday A term. Excited state degeneracy was also observed in B band region with cross-over points at 347, 329, 349, and 333 nm, respectively.

The MCD spectra of complexes **5** and **7** are relatively similar in shape in the Q band region and can explain the behaviors of the aggregated Pcs [37], as noted previously by Kobayashi. Further, the balltype MCD spectra exhibited similarities with those of co-facial binuclear molecules, which indicates the occurrence of face-to-face interactions.

The absorption and fluorescence excitation spectra of complex **6** in DMSO are shown in Fig. 3 (the others are shown in Fig. S3, supplementary information). The excitation, absorption, and emission spectral data are listed in Table 1. Fluorescence emission peaks were observed at 691 nm for **4**, 707 nm for **5**, and 690 nm for **6**. While complexes **4** and **6** exhibited typical behaviors, complex **5** had some abnormal properties, which may be explained by its tendency to aggregate in this solvent. The Stokes shifts for **4–6** were 9, 35, 11 nm, respectively [45,27]. Further, Mg₂Pc₂ again exhibited different behavior, which can be attributed to the polarity of the singlet state.

The fluorescence quantum yield, Φ_F values are typical of MPc complexes [27]. The Φ_F values are 0.060, 0.064, and 0.043 in DMSO for **4–6**, respectively. Low Φ_F values are often predicted for aggregated MPcs.³¹ This result may be attributed to the fact that 1,3 benzenediol groups showing the interaction between the two rings were minimal The complexes generally had lower fluorescence quantum yields corresponding to higher triplet quantum yields. Fluorescence lifetimes are



Fig. 2. The ground-state electronic absorption spectrum of MCD and ball-type ZnPc in DMSO.

5.34 ns for **4**, 4.49 ns for **5** and 2.89 ns for **6** [46]. These values show the effect of the Pc skeleton and decrease due to atom effect.

The obtained triplet quantum yield (Φ_T) and lifetime (τ_T) data of the complexes are shown in Table 1. The high triplet state quantum yield values in DMSO are 0.43, 0.65 and 0.33 for **4–6**, respectively. The values of Φ_T values suggest more efficient intersystem crossing (ISC) in

the presence of the 1, 3-benzenediol substituents for substituted complexes, corresponding to low $\Phi_{\rm F}$ values. This data of complexes are lower when compared to those of ball-type Pcs in the same solvent as described in a previous study.

A triplet decay curve of the change in absorbance (ΔA) versus time (in seconds) was obtained experimentally and used to derive the triplet

Table 2

Ground-state electronic absorption and MCD spectral values for ball-types phthalocyanines for **4** to **7** in DMSO.

	B/nm		Q _{vib} /nm	Q ₀₀ /nm	
4 H ₂ Pc					
ABS	346		616	680	
MCD		-374	+617	+677	-692
5 MgPc					
ABS	330		616	665	696
MCD	+324	- 356	+600	-657/-691	-743
6 ZnPc					
ABS	349		616	678	
MCD	+ 339	-371	+619/+635	+676	-690
7 CoPc					
ABS	333		614/631	672	
MCD	+313	- 347	+607	-646/-665	-684

lifetime. A typical triplet state decay curve for Zn_2Pc_2 is shown in Fig. 4 (those of the other complexes are shown in Fig. S4, supplementary information). The obtained lifetimes were 460, 110 and 1100 µs for 4–6, respectively. The triplet lifetime of complex 6 was the longest, which may be attributed to the interactions between the two rings. These results show that Pcs with 1,3-benzenediol substituents in the same position but bearing different metals in the central cavity also exhibit different triplet lifetimes and quantum yields.

Next, the spectral changes were observed during the photolysis of the complexes in the presence of DPBF were measured over time (0-140 sec) by Uv–Vis spectroscopy; the experimental results for complex **6** are shown in Fig. 5 (those of the other complexes are shown in Fig. S5, supplementary information) and the data are summarized in Table 1. The spectra show no changes in the Q band intensities, confirming that the complexes are not degraded in the singlet oxygen studies [47,31].

The Φ_{Δ} values for **4–6** were 0.27, 0.54 and 0.72, respectively.

Generally, high triplet oxygen quantum yields in Pc complexes are accompanied by high singlet oxygen quantum yield; the complex 6 which is among the complexes **4–6** synthesized in this study exhibited higher singlet oxygen quantum yield. This may indicate that the complexes have ball-type structures with face-to-face interactions.

Overall, the S_{Δ} values in Table 1 show that singlet oxygen is generated efficiently in DMSO. The high S_{Δ} values for complexes **4–6** may be due to the interaction between the two rings. The S_{Δ} value for complex **6** was the largest and that of **5** was the lowest. This trend can be attributed to the lifetimes of the triplet states.

In order to evaluate the stabilities of these derivatives under singlet oxygen attack due to intense light exposure, the photodegradation quantum yields (Φ_d) of complexes 4–7 were measured in DMSO by monitoring the photo-induced decomposition in terms of the decrease in the intensity of the Q band under irradiation over 60 min. The photodegradation spectrum for complex 7 is shown in Fig. 6 (those of complexes 4–6 are shown in Fig. S6, supplementary information) and the results are summarized in Table 1. The peak absorbance of complex 7 decreased and blue-shifted by 9 nm in the presence of light as observed under heating in DMSO. After accounting for the effects of the differences in the maximum wavelength of the Q band on the starting maximum wavelength, the order of stability of the substituted complexes in DMSO was 6 > 5 > 4 > 7. The data further indicates that the molecules are highly stable in the solvent that was used [48,49].

3. Conclusions

In this study, novel ball-type Pcs were successfully synthesized and characterized. Pcs were found to be prone to aggregation in solution. All complexes studied exhibited spectroscopic similarities in that they had monomeric structures and were either metal-free or metalled complexes, demonstrating that the present work may be useful as a model method. Further, the obtained spectra of aggregated Pcs confirm



Fig. 3. Absorbance (dashed line), excitation (solid line) and emission (pink dotted line) spectra of complex 6 in DMSO; excitation λ_{max} : 611 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Mono-exponential triplet decay curve for 6 in DMSO.

that their properties were similar to those previously described in the literature [38,42,45]. This observation may be explained by orbital degeneracy due to symmetric changes in the shapes of the Q bands for H_4Pc_2 and Mg_2Pc_2 in DMSO. All of the compounds exhibited low fluorescence quantum yields and high triplet quantum yields. Moreover, Zn_2Pc_2 exhibited high singlet oxygen quantum yield. The photo-degradation quantum yields of all complexes showed that the molecules are highly photostable in the solvent used. Although all complexes were found to have good triplet lifetimes, that of Zn_2Pc_2 indicated it to be superior to the others. The photo-physico-chemical behaviors of these complexes, and particularly those of Zn_2Pc_2 , were found to be suitable

for PDT. Another interesting finding was that Co_2Pc_2 underwent a blue shift when exposed to light and heat; this would be an interesting topic of further research.

The results presented here for benzene-1,3-diol (**A**) were compared with those reported in an unpublished paper with the same substituent, catechol(benzene-1,2-diol (**B**) [50], and a different substituent containing a carboxyl group in the peripheral position, catechol-4-carboxylic acid (**C**) [27]. The Q band maximum wavelengths of these Pcs in DMSO were similar to each other [55,61,45,51]. The Q band was not split at 684 nm for the 1,2-benzene or at 682 nm 1,3-benzene in H₄Pc₂ while that of catechol-4-carboxylic acid at 675/702 nm was split as



Fig. 5. Time-dependent photobleaching of DPBF absorption in the presence of 6 in DMSO.



Fig. 6. Absorbance spectra for complex 7 during photodegradation in DMSO.

expected for H₄Pc₂. On the other hand, Mg₂Pc₂s was split at 670/ 702 nm for 1,3-benzene, at 670/701 nm for 1,2-benzene, and at 668/ 698 nm for catechol-4-carboxylic acid. This result may be attributed to the intramolecular coupling of ball-type Pcs (A). However, the effects of the substituent were not observed for Co2Pc2 and Zn2Pc2 at 672 and 680 nm, respectively. The triplet lifetimes of MgPcs were consistent: 110, 110, and 130 µs for A, B, and C, respectively. However, the triplet lifetimes of Zn₂Pc₂s differed: 1100, 440 and 60 µs for A, B, and C, respectively. Finally, the singlet oxygen quantum yields of the Zn₂Pc₂s were 0.21, 0.35, and 0.01 for A, B, and C, respectively. Considering this data, it could be said that the carboxyl group decreases the photochemical properties of ball-type Pcs. Further, it is important to note that ball-type ZnPcs exhibited good singlet oxygen quantum yields, making them promising candidates as photosensitizers. On the other hand, I believe that the present paper will be remarkable in that it report both the photochemical and MCD properties of ball-type Pcs all at once.

4. Materials and methods

Previously reported materials, equipment and methods were used in this study [11-27] to synthesize ball-type derivatives **4–7** from 4, 4'-(1, 3-phenylenebis (oxy)) diphthalonitrile (**3**) using *n*-pentanol in the presence of DBU at the reflux temperature as shown in Scheme 1.

Synthesis of 4, 4'-(1, 3-phenylenebis (oxy)) diphthalonitrile (3) [52]: Compound 2 (1.272 g) was dissolved in dry DMSO (10 mL) and compound 1 (4.00 g, 28.90 mmol) was added under inert atmosphere. Finely ground anhydrous potassium carbonate (8.00 g) was added to this reaction mixture and stirred for 10 h at 70 °C. After stirring at room temperature for 7 days, the reaction was monitored by thin layer chromatography (TLC) as it proceeded under Ar. Finally, the reaction mixture was poured onto ice and crystalized from ethanol to form a light yellow precipitate. The pure product was dried using P_2O_5 under a vacuum for 15 days. The yield was 2.80 g or 70%. The following FT-IR (ATR) signals were observed (v_{max}/cm^{-1}): 3120/3093/3074 (Ar–CH),

2235 (C=N), 1587/1593 (C=C), 1310/1285/1247 (C-O-C). ¹H NMR (DMSO- d_6), δ (ppm): 8.14 (2H, d, Ar-H), 7.93 (2H, d, Ar-H), 7.61 (H, t, Ar-H), 7.56 (H, d, Ar-H), 7.57 (H, d, Ar-H) 7.15 (2H, s, Ar-H), 7.14 (H, s, Ar-H). Anal. calcd. for C₂₂H₁₀N₄O₂ C, 72.92; H, 2.78; N, 15.46, found C, 72.65; H, 2.29; and N, 15.75%. LC-MS, *m*/*z* anal. calcd. 362.34, found [M]⁺: 362.09, and [M + H₂O]⁺: 380.12.

Typical Synthesis Procedures for Ball-Type Pcs 4-7: Under Ar gas without metal salt, an excess of magnesium(II) chloride (0.050 g, 0.52 mmol), zinc(II) acetate (0.050 g, 0.23 mmoL) and cobalt(II) acetate (0.050 g, 0.20 mmol) was added to a solution of diphthalonitrile, 3 (0.100 g, 0.28 mmoL) in 4 mL of n-pentanol and stirred for 2-3 min. at reflux temperature. Then, ten drops of DBU were added to form ball-type binuclear H₄Pc₂, Mg₂Pc₂, Zn₂Pc₂, and Co₂Pc₂. The reaction was monitored by Uv-Vis spectroscopy and TLC over the course of 20 h. After the reaction was complete, the mixture was cooled to room temperature and the excess n-pentanol was removed under reduced pressure. The crude product was washed with methanol. Then, a large amount of water was added before the produced was purified by silica gel column chromatography using a gradient of CHCl₃, THF, MeOH, DMSO, then DMSO + HCI as the eluents. The ball-type Pcs were obtained as a deep green powder that has a melting point above 250 °C and is soluble in THF, DMSO, and DMF.

Synthesis and Purification of Ball-type H₂Pc (4): Complex 4 was synthesized and purified as described above in the general procedure, without any metal salt and using only compound 3 directly. The reaction conditions and amounts were as outlined above. The yield was 0.032 g or 32%. Uv–Vis (DMSO), λ_{max} (nm): 682, 621. FT-IR (ATR) (μ_{max} /cm⁻¹): 3296 (Ar–CH), 2238 (CN), 1717 (CO), 1596 (C=C), and 1121/1083 (C–O–C). ¹H NMR (DMSO- d_6), δ (ppm): 7.85–7.00 (44H, Ar-H). Anal. calcd. for C₈₈H₄₄N₁₆O₈: C, 72.72; H, 3.05; N, 15.42, found: C, 72.51; H, 3.42; and N, 15.85%. MALDI-TOF-MS, *m*/*z* calcd. 1453,39, found 1453.47 [M] + .

Synthesis and Purification of Ball-type MgPc (5): Complex 5 was synthesized and purified as described above in the general procedure using magnesium (II) chloride. The reaction condition and amounts were as outlined above. The yield was 0.012 g or 12%. Uv–Vis (DMSO), λ_{max} (nm): 702, 670, 618, 331. FT-IR (ATR) (μ_{max} /cm⁻¹): 3070 (Ar–CH), 1720 (CO), 1594 (C=C), and 1266/1255/1094 (C–O–C). ¹H NMR (DMSO- d_6), δ (ppm): 7.90–7.05 (40H, Ar-H). Anal. calcd. for C₈₈H₄₀N₁₆O₈Mg₂: C, 70.56; H, 2.69; N, 14.96, found: C, 70.41; H, 2.43; and N, 15.02%. MALDI-TOF-MS, *m/z* calcd. 1497.97, found 1546.97 [M + 2Na + 3H].

Synthesis and Purification of Ball-type ZnPc (6): Complex 6 was synthesized and purified as described above in the general procedure using zinc(II) acetate. The reaction condition and amounts were as outlined above. The yield was 0.029 g or 27%. Uv–Vis (DMSO), λ_{max} (nm): 680, 631, 614, and 350. FT-IR (ATR) (μ_{max} /cm⁻¹): 3092 (Ar–CH), 1716 (CO), 1593 (C=O), and 1263/1219/1124 (C–O–C). ¹H NMR (DMSO- d_6), δ (ppm): 7.70–7.03 (40H, Ar-H). Anal. calcd. for C₈₈H₄₀N₁₆O₈Zn₂: C, 66.89; H, 2.55; N, 14.18, found: C, 67.05; H, 2.54; and N, 14.15%. MALDI-TOF-MS: *m*/*z* calcd. 1580.18, found 1591.44 [M + Li + 4H]⁺.

Synthesis and Purification of Ball-type CoPc (7): Complex 7 was synthesized and purified as described above in the general procedure using cobalt (II) acetate. The reaction conditions and amounts were as outlined above. The yield was 0.017 g or 16%. Uv–Vis (DMSO), λ_{max} (nm): 672, 616, and 322. IR (ATR) (μ_{max} /cm⁻¹): 3072 (aromatic –CH), 1718 (CO), 1593 (C=C), and 1089 (C–O–C). Anal. calcd. for C₈₈H₄₀N₁₆O₈Co₂: C, 67.44; H, 2.57; N, 14.30, found: C, 67.01; H, 3.05; and N, 14.39%. MALDI-TOF-MS *m*/*z* calcd. 1567.23 found 1585.00 [M + H₂O]⁺.

Characterization of Photophysical and Photochemical properties: The fluorescence quantum yields (Φ_F), fluorescence lifetimes (τ_F), triplet quantum yields (Φ_T) and triplet lifetimes (τ_T) of complexes **4–6** were determined by a described previously using ZnPc as a standard [53–57]. For the photochemical studies, the quantum yields of singlet oxygen photogeneration (Φ_A) were determined in air using a relative method with ZnPc as reference and DPBF as a chemical quencher for singlet oxygen. Further, in order to determine the oxidative degradation of the Pcs, their photodegradation quantum yields (Φ_d) and MCD spectral properties were studied as described previously [58–60].

CRediT authorship contribution statement

Mevlüde Canlıca: Methodology, Project administration, Resources, Software, Supervision, Visualization, Writing - original draft, Writing review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Research Fund of the Yildiz Technical University (Project No: 2012-01-02-KAP12), Tubitak-BiDEB-2219 International Postdoctoral Research Scholarship Programme, Number: 1059B191401081, and the Yildiz Technical University in Istanbul, Turkey, the University of Illinois at Urbana-Champaign in the USA, and Rhodes University in Grahamstone, South Africa. The author is thankful to Prof. Kenneth K. Suslick for providing lab space to synthesize the compounds used in this study. The author is also grateful to Prof. Tebello Nyokong for providing the funds and lab facilities for conducting the photophysical and photochemical measurements.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119830.

References

- [1] A. Braun, J. Tcherniac, Ber. Deutsch. Chem. Ges. 40 (1907) 2709-2714.
- [2] R.P. Linstead, J. Chem. Soc. 42 (1934) 1016–1017.
 [3] J.M. Robertson, J. Chem. Soc. (1935) 615–621.
- [4] D. Dini, M. Hanack, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin
- Handbook, Academic Press, San Diego, 2003, 17, 1–36.
- [5] C.C. Leznoff, in: A.B.P. Lever, (Eds.), Phthalocyanines, Properties and Applications, VCH, New York, 1996.
- [6] H. Ali, J.E. van Lier, Chem. Rev. 9 (1999) 2379-2450.
- [7] T.J. Dougherty, M. HendersonDekker (Eds.), Photodynamic Therapy, Basic Principles and Clinical Applications, CRC Pres, New York, 1992.
- [8] G. de la Torre, G. Bottari, M. Sekita, A. Hausmann, M.G. Dirk, T. Torres, Chem. Soc. Rev. 42 (2003) 8049.
- [9] A.Y. Tolbin, A.V. Ivanov, L.G. Tomilova, N.S. Zefirov, Mendeleev Commun. 12 (2002) 96–97.
- [10] A.Y. Tolbin, A.V. Ivanov, L.G. Tomilova, N.S. Zefirov, J. Porphyr. Phtalocyan. 7 (2003) 162–166.
- [11] M. Canlıca, I.N. Booysen, T. Nyokong, Polyhedron 30 (2011) 508-514.
- [12] M. Canlıca, T. Nyokong, Dalton Trans. 40 (2011) 1497–1502.
- [13] M. Canlıca, T. Nyokong, Dalton Trans. 40 (2011) 5285–5290.
- [14] M. Canlica, T. Nyokong, Polyhedron 31 (2012) 704–709.
- [15] M. Canlica, M. Coskun, A. Altindal, T. Nyokong, J. Porphyr. Phtalocyan. 16 (2012) 855–860.
- [16] M. Canlica, A. Altindal, T. Nyokong, J. Porphyr. Phtalocyan. 16 (2012) 826-832.
- [17] E. Güzel, S. Güney, M. Kandaz, Dyes Pigm. 113 (2015) 416-425.
- [18] N. Njemuwa, J. Mack, J. Britton, T. Nyokong, New J. Chem. 41 (2017) 2020–2028.
 [19] N. Njemuwa, D.O. Oluvole, J. Mack, M. Louzada, S. Khene, J. Britton, T. Nyokong, Dyes
- Pigm. 140 (2017) 417.
 [20] A. Yazıcı, A. Avcı, A. Altındal, B. Salih, Ö. Bekaroglu, J. Porphyrins Phthalocyanines 22 (2018) 149–156
- [2016] 149–156.[21] N.N. Njemuwa, J. Mack, T. Nyokong, J. Photo. Photobio. A-Chem. 352 (2018) 73–85.
- [22] N. Njemuwa, A.J. Ojodomo, T. Nyokong, New J. Chem. 42 (2018) 6040–6050.
- [23] N. Njemuwa, J. Mack, T. Nyokong, Optical Mate. 82 (2018) 93-103.
- [24] N. Kocyigit, U.E. Ozen, M. Ozer, O. Bekaroglu, Electrochim. Acta 233 (2017) 237-248.
- [25] E. Kaki, A. Altindal, B.S. Bekir, O. Bekaroglu, Dalton Trans. 44 (2015) 8293-8299.
- [26] O. Bekaroglu, Turk. J. Chem. 38 (2014) 903-922.
- [27] M. Canlica, B.C. Omur, B. Salih, Inorg. Chem. Comm. 103 (2019) 75-81.
- [28] N. Kobayashi, Y. Yanagisawa, T. Osa, H. Lam, C.C. Leznoff, Anal. Sci. 6 (1990) 813–817.
 [29] Z. Odabaş, F. Dumludağ, A.R. Ozkaya, S. Yamauchi, N. Kobayashi, O. Bekaroglu, Dalton Trans. 39 (2010) 8143–8152.
- [30] U. Salan, N. Kobayashi, O. Bekaroğlu, Tetrahedron Lett. 50 (2009) 6775-6778.
- [31] I. Seotsanyana-Mokhosi, S. Maree, D. Maree, T. Nyokong, J. Porph. Phthalo. 7 (2003) 167-175.
- [32] W.A. Nevin, W. Liu, A.B.P. Lever, Can. J. Chem. 65 (1987) 855.
- [33] A. Eisfeld, J.S. Briggs, Chem. Phys. 324 (2006) 376-384.
- [34] K. Sakamoto, E. Ohno-Okumura, Materials 2 (2009) 1127-1179.
- [35] K. Nakai, J. Usami, N. Kobayashi, J. Porphyr. Phtalocyan. 11 (2007) 222–227.
 [36] E.S. Dodsworth, A.B.P. Lever, P. Seymour, C.C. Leznoff, J. Phys. Chem. 89 (1985)
- 5698-5705.
- [37] C.C. Leznoff, S.M. Marcuccio, S. Greenberg, A.B.P. Lever, K.B. Tomer, Can. J. Chem. 63 (1985) 623–631.
- [38] A.Y. Tolbin, L.G. Tomilova, N.S. Zefirov, Russ. Chem. Rev. 77 (2008) 435–449.
- [39] S.M. Marcuccio, P.I. Svirskaya, S. Greenberg, A.B.P. Leznoff, K.B. Tomer, Can. J. Chem. 63 (1985) 3057–3069.
- [40] P. Yiru, H. Fenghua, L. Zhipeng, C. Naisheng, H. Jinling, Inorg. Chem. Commun. 7 (2004) 967–970.
- [41] A.Y. Tolbin, V.E. Pushkarev, G.F. Nikitin, L.G. Tomilova, Tetrahedron Lett. 69 (2009) 4848–4850.
- [42] Y. Yamada, K. Nawate, T. Maenoa, K. Tanaka, Chem. Commun. 54 (2018) 8226.
- [43] L.M. Moreira, A.B.F. Vieira dos Santos, A.J.P. Lyon, A.M. Maftoum-Costa, A.C. Pacheco-Soares, A.N. Soares da Silva, Aust. J. Chem. 61 (2008) 741–754.
- [44] B.G. Ongarora, Z. Zhou, E.A. Okoth, I. Kolesnichenko, K.M. Smith, M.G.H. Vicente, J. Porphyr. Phthalocyan. 18 (2014) 1021–1033.
- [45] P. Zhao, Y. Song, S. Dong, L. Niua, F. Zhang, Dalton Trans. 32 (2009) 6327-6334.
- [46] E.C. Kaya, M. Durmus, E. Yanmaz, H. Kantekin, Turk. J. Chem. 38 (2014) 1118-1134.
- [47] M. Durmus, T. Nyokong, Spectrochim. Acta 69 (2008) 1170–1177.
- [48] S. Maree, T. Nyokong, J. Porphyr. Phtalocyan. 5 (2001) 782–792.
- [49] L.K. Oleg, A.E. Lukyanets, G.N. Vorozhtsov, J. Porphyr. Phthalocyan. 3 (1999) 592-610.
- [50] M. Canlica, J. Photochem. Photobiol. A Chem. 384 (2019) 112043.
 [51] A.I. Awaji, B. Koksoy, M. Durmus, A. Aljuhani, S.Y. Alraqa, Molecules 24 (2019) 77.
- [51] A.I. Awaji, B. Rossoy, M. Dunnus, A. Alfunani, S.I. Anaqa, Molecules 24 (2019) 77
 [52] T.M. Keller, D.D. Dominguez, Polymer 46 (2005) 4614–4618.
- [53] S. Fery-Forgues, D. Lavabre, J. Chem. Ed. 76 (1999) 1260–1264.
- [54] J. Fu, X.Y. Li, D.K.P. Ng, C. Wu, Langmuir 18 (2002) 3843–3847.
- [55] A. Ogunsipe, A.D. Maree, T. Nyokong, J. Mol. Struct. 650 (2003) 131-140.
- [56] P. Kubát, J. Mosinger, J. Photochem. Photobiol. A Chem. 96 (1996) 93–97.
- [57] T.H. Tran-Thi, C. Desforge, C.C. Thiec, J. Phys. Chem. 93 (1989) 1226–1233.
- [58] P. Tau, A. Ogunsipe, S. Maree, M.D. Maree, T. Nyokong, J. Porphyr. Phtalocyan. 7 (2003) 439–446.
- [59] A. Ogunsipe, A.J.Y. Chen, T. Nyokong, New J. Chem. 28 (2004) 822-827.
- [60] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Roder, G. Schnurpfeil, J. Porphyr. Phtalocyan. 2 (1998) 145–158.