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The synthesis and photophysical properties of peripherally and non-peripherally substituted ball-type Mg(II) and Zn(II) phthalocyanines[†]

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Newly synthesized ball-type Zn(II) and Mg(II) phthalocyanines containing four 1,1'-binaphthol substituents at peripheral and non-peripheral positions are presented. The structures of the synthesized compounds were characterized by using elemental analysis, UV-vis, FT-IR, ¹H-NMR and mass spectroscopies. The $\Phi_{\rm F}$ values were 0.33, 0.08, 0.20 and 0.08 for **6–9**, respectively. The $\Phi_{\rm T}$ values were 0.56, 0.85, 0.64 and 0.88 for **6–9**, respectively. All the complexes showed reasonably large triplet lifetimes with $\tau_{\rm T}$ values of 710 (**6**), 170 (**7**), 1490 (**8**) and 380 µs (**9**) in DMSO. These complexes offer potential as photosensitizers in photodynamic therapy.

1. Introduction

Metallophthalocyanines (MPcs) have been studied as materials for many applications, including molecular electronics,¹ non-linear optics,² liquid crystals,³ photosensitizers^{4,5} and electrocatalysis.⁶ There is considerable interest in MPc complexes containing nontransition metals for use as photosensitizers in the relatively new method of cancer treatment called photodynamic therapy (PDT).^{4,5,7-10} The mode of operation in PDT is based on visible light excitation of a tumor-localized photosensitizer. After excitation, energy is transferred from the photosensitizer (in its triplet excited state) to ground state oxygen $({}^{3}O_{2})$, forming singlet oxygen $({}^{1}O_{2})$. High triplet state quantum yields and long triplet lifetimes are required for efficient photosensitization. The synthesis, spectroelectrochemical and electrocatalytic behaviour of ball-type phthalocyanine derivatives have been extensively studied since these molecules were published in the literature for the first time in 2002.^{11,12} Ball-type phthalocyanine derivatives show spectroscopic and electrochemical properties that differ significantly from their parent monomer.13 However, studies on non-peripherally substituted ball-type MPc derivatives and those containing bulky substituents (hence less aggregated) are still limited. The photophysical behaviour of ball-type molecules have also not received much attention.

Our interest in ball-type complexes is due to the possibility of intramolecular interactions between the Pc rings and/or the metal centres of these compounds. The electronic properties of ball-type Pcs can change dramatically, depending on the bridging compounds or the central metal. The distance between the two Pc units affects the degree of interaction between the rings.

Due to these interactions, the Q-bands in the electronic spectra of ball-type MPc complexes and their voltammetric signals are usually much broader (or split) compared to those for their parent monomers. In this study, the photophysical properties of ball-type complexes are presented by us for the first time.

Thus, in this paper, we describe the synthesis and photophysical properties of new symmetrically-substituted ball-type MgPc and ZnPc complexes containing substituents at the non-peripheral and peripheral positions (Scheme 1). We compare the effects of α vs. β substitution on their photophysical properties.

2. Experimental

2.1 Materials

3-Nitrophthalonitrile (1) and 4-nitrophthalonitrile (2) were synthesized as reported in the literature.¹⁴ 1,1'-Binaphthyl-8,8'-diol (3) was obtained from commercial suppliers. Anhydrous magnesium(II) chloride and zinc(II) acetate were purchased from Sigma-Aldrich. Dimethylsulfoxide (DMSO) and chloroform were obtained from Saarchem. Silica gel for column chromatography was purchased from Merck. All solvents were dried and purified as described by Perrin and Armarego.¹⁵ All other reagents were used as received.

2.2 Equipment

UV-vis absorption spectra were obtained using a Varian Cary 500 UV-Vis/NIR instrument. Fluorescence excitation and emission spectra were recorded using a Varian Eclipse spectrophotometer. FT-IR data (KBr pellets) were recorded using a Perkin-Elmer spectrum 2000 FTIR spectrometer. ¹H NMR spectra were obtained using a Bruker EMX 400 MHz spectrometer. Elemental analyses were performed on a Vario-Elementar Microcube EL III

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Scheme 1 A synthetic scheme for non-peripherally and peripherally substituted ball-type metallophthalocyanines.

analyser. Mass spectra data were collected by a Bruker AutoFLEX III Smartbeam MALDI/TOF mass spectrometer. The instrument was operated in positive ion mode using an m/z range of 400–3000. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. Reflector 1 and 2 voltages were set at 21 and 9.7 kV, respectively. Spectra were acquired using dithranol as the MALDI matrix using a 354 nm Nd:YAG laser.

Fluorescence lifetimes were measured using a time-correlated single photon counting (TCSPC) setup (Fluo Time 200, Picoquant GMbH) with a diode laser as the excitation source (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, Picoquant GmbH). Fluorescence was detected under the magic angle with a peltier cooled photomultiplier tube (PMT) (PMA-C 192-N-M, Picoquant GmbH) and integrated electronics (PicoHarp 300E, Picoquant GmbH). A monochromator with a spectral width of about 4 nm was used to select the required emission wavelength. The response function of the system, which was measured with a scattering Ludox solution (DuPont), had a full-width at halfmaximum (FWHM) of about 300 ns. The ratio of stop to start pulses was kept low (below 0.05) to ensure good statistics. All luminescence decay curves were measured at the maximum of the emission peak. The data were analyzed with the program FluoFit (Picoquant GmbH). The support plane approach¹⁶ was used to estimate the errors of the decay times.

Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physic FL 3002 dye (Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as the detector. Signals were recorded with a two-channel 300 MHz digital real-time oscilloscope (Tektronix TDS 3032C); kinetic curves were averaged over 256 laser pulses. Triplet lifetimes were determined by exponential fitting of the kinetic curves using the program OriginPro 7.5.

2.3 Syntheses

The target precursors were prepared by a nucleophilic aromatic substitution reaction between 3-nitrophthalonitrile (1) or 4-nitrophthalonitrile (2) and 1,1'-binaphthyl-8,8'-diol (3) in the solid phase in the absence solvent or catalysts (Scheme 1).

2.3.1. 3,4'-(1,1'-Binaphthyl-8,8'-diylbis(oxy))diphthalonitrile (4). Compound 3 (3.31 g, 11.6 mmol) was dissolved in dry DMSO (15 mL) and compound 1 (4.0 g, 23.1 mmol) was added under an inert atmosphere. To this reaction mixture was added finely ground anhydrous potassium carbonate (3.19 g, 23.1 mmol). After 4 h of stirring at room temperature, further potassium carbonate (0.79 g, 5.8 mmol) was added, and this same amount was added again after 24 h of stirring. After a total of 96 h of stirring, the reaction mixture was poured into water (50 mL), resulting in the formation of a light yellow precipitate. The crude product was centrifuged and further purified by chromatography over a silica gel column using CHCl₃ as the eluent. The product was recrystallized from ethanol, and then the pure product was dried using P₂O₅. Yield: 2.5 g. IR(KBr) v_{max} /cm⁻¹: 3080 (Ar-CH), 2230 (C = N), 1570 (C = C), 1259 (C - O - C).¹H NMR (DMSO- d_6): δ/ppm 8.21 (2H, d, Ar-H), 8.08 (2H, d, Ar-H), 7.63 (2H, t, Ar-H), 7.59 (2H, t, Ar'-H), 7.51–7.57 (4H, m, Ar-H), 7.37 (2H, d, Ar'-H), 7.34 (2H, t, Ar'-H), 7.26 (2H, d. Ar'-H). Calc. for C₃₆H₁₈N₄O₂: C, 80.29; H, 3.37; N, 10.40%. Found: C, 79.37; H, 3.68; N, 9.96%.

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2.3.2 4,4' - (1,1' - Binaphthyl - 8,8' - diylbis(oxy))diphthalonitrile (5). The synthesis of 5 was the same as that for 4, except that compound 2 was employed instead of 1; the amounts of the reagents were the same. Yield: 2.1 g. IR(KBr) (v_{max} /cm⁻¹: 3072 (Ar-CH), 2232 (C=N), 1586 (C=C), 1278 (C-O-C). ¹H-NMR (DMSO- d_6): δ /ppm 8.20 (2H, d, Ar-H), 8.08 (2H, d, Ar-H), 7.85 (2H, d, Ar-H), 7.55 (2H, t, Ar'-H), 7.49 (2H, s, Ar-H), 7.39 (2H, t, Ar-H), 7.30 (2H, d, Ar'-H), 7.16 (2H, d, Ar'-H), 6.93 (2H, d, Ar'-H). Calc. for C₃₆H₁₈N₄O₂: C, 80.29; H, 3.37; N, 10.40%. Found: C, 79.43; H, 4.05; N, 9.83%.

General synthetic procedure for complexes 6–9

A mixture of complex 4 or 5 (100 mg) and magnesium(II) chloride (100 mg) for 6 and 8, respectively, and zinc acetate (100 mg) for 7 and 9, respectively, was ground in a quartz crucible and heated in sealed glass tube for 15 min (6 and 8) or for 10 min (7 and 9), under an argon atmosphere at 550 °C (6 and 8) or at 500 °C (7 and 9). After cooling to room temperature, the dark-green reaction products were washed with hot methanol and hot water. The products were separated by column chromatography on silica gel using chloroform and a gradient of chloroform–methanol up to 50%. Finally, pure dark-green products were obtained by column chromatography over silica gel and eluting with chloroform.

2.3.3 1',11',15',25' - [Tetrakis(4,4' - (1,1' - binaphthyl-8,8' - diyl-(oxy))diphenyl)]bis-phthalocyaninatodimagnesium(II) (6). Yield: 0.038 g. UV-vis (CHCl₃) λ_{max} /nm (log ε /dm⁻³ mol⁻¹ cm⁻¹): 698 (4.98). IR[(KBr) ν_{max} /cm⁻¹: 3054 (Ar-CH), 1581 (C=C), 1243 (C-O-C). ¹H NMR (DMSO-*d*₆): δ /ppm 8.10–7.22 (64H, Ar-H), 7.05 (8H, d, Ar'-H). Anal. calc. for C₁₄₄H₇₂N₁₆O₈Mg₂: C, 78.51; H, 3.29; N, 10.17%. Found: C, 78.09; H, 3.48; N, 9.91%. MALDI-TOF-MS *m*/*z* calc. 2202.82. Found [M + H]⁺: 2203.54.

2.3.4 1',11',15',25' - [Tetrakis(4,4' - (1,1' - binaphthyl-8,8' - diyl-(oxy))diphenyl)]bis-phthalocyaninatodizinc(II) (7). Yield: 0.037 g. UV-vis (CHCl₃) λ_{max} /nm (log ε /dm⁻³ mol⁻¹ cm⁻¹): 696 (4.60). IR[(KBr) ν_{max} /cm⁻¹: 3055 (Ar-CH), 1579 (C=C), 1245 (C-O-C). ¹H-NMR (DMSO-d₆): δ /ppm 8.10–7.20 (64H, Ar-H), 7.02 (8H, d. Ar'-H). Anal. calc. for C₁₄₄H₇₂N₁₆O₈Zn₂: C, 75.69; H, 3.18; N, 9.81%. Found: C, 75.10; H, 3.24; N, 9.73%. MALDI-TOF-MS *m*/*z* calc. 2285.50. Found [M]⁺: 2285.50.

2.3.5 2',10',16',24' - [Tetrakis(4,4' - (1,1' - binaphthyl-8,8' - diyl-(oxy))diphenyl)]bis-phthalocyaninatodimagnesium(II) (8). Yield: 0.035 g. UV-vis (CHCl₃) λ_{max}/nm (log ε/dm^{-3} mol⁻¹ cm⁻¹): 690 (4.42). IR[(KBr) ν_{max}/cm^{-1} : 3054 (Ar-CH), 1581 (C=C), 1231 (C-O-C). ¹H-NMR (DMSO-*d*₆): δ /ppm 8.23–7.16 (64H, d, Ar'-H), 6.95 (8H, d, Ar'-H). Anal. calc. for C₁₄₄H₇₂N₁₆O₈Mg₂: C, 78.51; H, 3.29; N, 10.17%. Found: C, 77.88; H, 3.36; N, 10.09%. MALDI-TOF-MS *m/z* calc. 2202.82. Found [M]⁺: 2202.69.

2.3.6 2',10',16',24' - [Tetrakis(4,4' - (1,1' - binaphthyl-8,8' - diyl-(oxy))diphenyl)]bis-phthalocyaninatodizinc(II) (9). Yield: 0.038 g. UV-vis (CHCl₃) λ_{max}/nm (log $\varepsilon/dm^{-3}mol^{-1}cm^{-1}$): 684 (4.85). IR[(KBr) v_{max}/cm^{-1} : 3054 (Ar-CH), 1579 (C=C), 1232 (C-O-C). ¹H NMR (DMSO-*d*₆): δ/ppm 8.20–7.15 (64H, Ar'-H), 6.93 (8H, d, Ar'-H). Anal. calc. for C₁₄₄H₇₂N₁₆O₈Zn₂: C, 75.69; H, 3.18; N, 9.81%. Found: C, 75.97; H, 3.94; N, 9.44%. MALDI-TOF-MS *m/z* calc. 2285.50. Found [M]⁺: 2285.37.

2.4. Photophysical Studies

2.4.1 Fluorescence quantum yields. Fluorescence quantum yields ($\Phi_{\rm F}$) were determined by the comparative method^{17,18} (eqn (1)):

$$\Phi_{\rm F} = \Phi_{\rm F(Std)} \frac{FA_{\rm Std} n^2}{F_{\rm Std} A n_{\rm Std}^2}$$
(1)

where *F* and *F*_{Std} are the areas under the fluorescence curves of **6–9** and the standard, respectively, *A* and *A*_{Std} are the respective absorbances of the sample and standard at the excitation wavelength (which was ~0.05 in all solvents used), and *n* and *n*_{std} are the refractive indices of the solvents used for the sample and standard, respectively. ZnPc ($\Phi_{\rm F} = 0.20$ in DMSO) was employed as the standard.¹⁹

2.4.2 Triplet quantum yields and lifetime

The solutions for triplet quantum yields and lifetimes were introduced into a 1.0 mm path length UV-visible spectrophotometric cell de-aerated using nitrogen and irradiated at the Q-band maximum. Triplet state quantum yields (Φ_T) of **6–9** were determined by the triplet absorption method²⁰ using zinc phthalocyanine (ZnPc) as a standard; eqn (2):

$$\Phi_{\rm T} = \Phi_{\rm T}^{\rm Std} \frac{\Delta A_{\rm T} \varepsilon_{\rm T}^{\rm Std}}{\Delta A_{\rm T}^{\rm Std} \varepsilon_{\rm T}} \tag{2}$$

where $\Delta A_{\rm T}$ and $\Delta A_{\rm T}^{\rm Std}$ are the changes in the triplet state absorbances of **6–9** and the standard, respectively, $\varepsilon_{\rm T}$ and $\varepsilon_{\rm T}^{\rm Std}$ are the triplet state molar extinction coefficients for **6–9** and the standard, respectively and $\Phi_{\rm T}^{\rm Std}$ is the triplet quantum yield for the standard, ZnPc ($\Phi_{\rm T} = 0.65$ in DMSO²¹). $\varepsilon_{\rm T}$ and $\varepsilon_{\rm T}^{\rm Std}$ were determined from the molar extinction coefficients of the respective ground singlet state ($\varepsilon_{\rm S}$ and $\varepsilon_{\rm S}^{\rm Std}$) and the change in absorbance of the ground singlet state ($\Delta A_{\rm S}$ and $\Delta A_{\rm S}^{\rm Std}$) according to eqn (3):

$$\varepsilon_{\rm T} = \varepsilon_{\rm S} \frac{\Delta A_{\rm T}}{\Delta A_{\rm S}} \tag{3}$$

Quantum yields of internal conversion (Φ_{ISC}) were obtained from eqn (4), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion) jointly deactivate the excited singlet state of complexes **6–9**.

$$\Phi_{\rm IC} = 1 - (\Phi_{\rm F} + \Phi_{\rm T}) \tag{4}$$

3. Results and discussion

3.1. Synthesis and characterization

New ball-type binuclear Mg(II)Pc and Zn(II)Pc complexes **6–9** were prepared by the reaction of compounds **4** and **5** with MgCl₂ and zinc acetate. The cyclotetramerization of phthalonitrile derivatives **4** and **5** to form MPc derivatives **6–9** was accomplished without a solvent in the presence of metal salts at 500 and 550 °C. Column chromatography on silica gel using CHCl₃ as the mobile phase (or a gradient of chloroform and methanol) was used to purify complexes **4–9**. The structure and purity of the MPc derivatives was confirmed by UV-vis, IR and mass spectral data, and elemental analyses. The results of elemental analysis differed

by less than 1% from the calculated values, showing the purity of the complexes.

The IR spectra of **4** and **5** clearly indicate the absence of OH groups in **3**. The C=N vibrational peaks were observed at 2230 and 2232 cm⁻¹ for compounds **4** and **5**, respectively. A diagnostic feature of the formation of **6–9** from the phthalodinitrile derivatives is the disappearance of the sharp –CN vibration at 2230 and 2232 cm⁻¹ for **4** and **5**, respectively. The IR spectra of **4–9** showed Ar–O–Ar peaks at 1235–1255 cm⁻¹.

The ¹H NMR spectra of 4 and 5 show the aromatic protons appearing between δ 8.21–7.26 and 8.08–6.93, respectively, integrating to a total of 18 for 4 and 5. In the ¹H NMR spectrum of 5, a sharp singlet signal was observed at δ 7.49 belonging to Ar-H. The spectrum of 4 has three triplets at δ 7.63, 7.59 and 7.34, whereas the spectrum of 5 shows triplets at δ 7.55 and 7.39. The ¹H NMR spectra of Pcs 6–9 were recorded in DMSO and were similar to each other. The aromatic protons appeared at δ 8.10–7.22, 8.10–7.20, 8.23–7.16 and 8.20–7.15, and δ 7.05, 7.02, 6.95 and 6.93, respectively, and integrating to a total of 72 for 6-9. The elemental analysis results were also consistent with the proposed structures of 4-9. The purified monofunctional phthalocyanines were further characterized by mass spectroscopy. The expected mass values corresponded to the found values for all the complexes using dithranol as the matrix. The protonated molecular ion peak of complexes 6 and the molecular ion peak complex of 7-9 were observed at 2203.54, 2285.50, 2202.69 and 2285.37 amu, respectively. These values are for the most abundant isotope (see the ESI, Fig. S1[†]).

The UV-vis spectra in CHCl₃, shown in Fig. 1, for **6–9** are also in agreement with the expected structures. The phthalocyanines show typical electronic spectra with two absorption bands, one in the UV region in the range 300–400 nm (B band) and the other in the visible region in the range 600–700 nm (Q band). The characteristic Q band transition of metallophthalocyanines with D_{4h} symmetry is observed as a single band of high intensity in the visible region. The aggregation behaviour of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes, and is dependent on the concentration, nature of the solvent, substituents, metal ions and temperature.²² Aggregation in MPcs is typified by a broadened or split Q-band, with the high energy band being due to the aggregate and the low energy band being due to the monomer.

Complexes 6 and 7 show Q band absorptions at 690 and 693 nm, whereas complexes 8 and 9 show Q band absorptions at 685 and 684 nm in DMSO. The band maxima are listed in Table 1 in both $CHCl_3$ and DMSO. Complexes 6 and 7 show Q-band



Fig. 1 Absorption spectra of complexes **6–9** in DMSO, concentration = 1×10^{-5} mol dm⁻³.

absorptions at 698 and 696 nm, whereas complexes **8** and **9** have Qband absorptions at 690 and 684 nm in CHCl₃ (Table 1). It is well known that α -substitution results in a red-shifting of the spectra of MPcs.^{23,24} This is due to the electron density enhancement caused by substitution at the α -position.

The well-defined band close to 620 nm in ball-type phthalocyanines is due to exciton coupling between the two Pc rings.¹³ The spectra of complexes 8 and 9 in DMSO show two bands at ~640 and 613 nm. The latter is attributed to intermolecular interactions between the rings, in agreement with the literature. This band is also observed for complexes 6 and 7. The band at ~640 nm is attributed to aggregation, as is typical for phthalocyanines. For complexes 6 and 7, this band is not observed; however, for complex 7, aggregation is evidenced by broadening of the Qband. Aggregation is not evident for complexes 8 and 9, which are peripherally substituted compared to non-peripherally substituted complexes 6 and 7, as is typical for phthalocyanines.²⁵ However, the Lambert–Beer law was obeyed for the complexes in CHCl₃ for concentrations of less than 1×10^{-5} M.

3.2. Fluorescence spectra, quantum yields and lifetimes

The absorption and fluorescence excitation spectra of complexes **6–9** in DMSO are shown in Fig. 2. The excitation, absorption and emission spectral data are listed in Table 1. All complexes showed a similar fluorescence behaviour. The absorption and excitation spectra show the same Q-band maxima. However, the absorption spectra are broadened compared to the emission and excitation spectra due to aggregation in the former. The peaks due to exciton coupling are, however, not clear upon excitation, suggesting relaxation of the coupling. The proximity of the wavelength of each

Table 1 UV-vis absorption (Q band) emission and excitation spectral data, and photophysical data for phthalocyanines 6–9

$\frac{\text{Solvent} \rightarrow}{\text{Complex} \downarrow}$	$\lambda_{\rm max}/{\rm nm} \left(\log \varepsilon/{\rm dm^{-3}\ mol^{-1}\ cm^{-1}}\right)$									
	$\frac{\text{CHCl}_3}{\lambda_{\text{abs}} (\log \varepsilon)}$	DMSO								
		λ_{abs}/nm	$\lambda_{\rm ems}/{\rm nm}$	$\lambda_{\rm exc}/{\rm nm}$	Stokes shift/nm	$arPsi_{ m F}$	$\tau_{\rm T}/\mu{ m s}$	$arPsi_{ ext{T}}$	$arPhi_{ m IC}$	$ au_{ m F}/ m ns$
6	698 (4.98)	690	697	689	8	0.33	710	0.56	0.11	5.38
7	696 (4.60)	693	699	693	6	0.08	170	0.85	0.07	2.35
8	690 (4.42)	685	695	686	9	0.20	1490	0.64	0.16	5.09
9	684 (4.85)	684	695	685	10	0.08	380	0.88	0.04	2.67





Fig. 2 (a) Absorbance, (b) excitation and (c) emission spectra of complexes 6-9 in DMSO. Excitation wavelength = 620, 616, 614 and 616 nm for 6-9, respectively.

component of the Q-band absorption to the Q-band maximum of the excitation spectrum for all the complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation. The emission spectra are mirror images of the excitation spectra. Stokes shifts ranged from 6 to 10 nm, typical of MPc complexes. The effect of the point of substitution is not clear from the nature of the excitation and emission spectra.

The $\Phi_{\rm F}$ values ranged from 0.08 to 0.33 in DMSO. The fluorescence quantum yield ($\Phi_{\rm F}$) values were typical²⁶ of MPc complexes for complex 8. The $\Phi_{\rm F}$ values were low for the ZnPc derivatives (7 and 9). This is attributed to the central Zn metal, which is heavier than Mg and hence encourages intersystem crossing to the triplet state, as will be confirmed below.

The fluorescence quantum yield of the octaphenoxy-substituted zinc phthalocyanine monomer has been reported to be 0.17 in DMF.²⁶ This value is much larger than that reported here for the ZnPc ball-type dimers (complexes 7 and 9), which may suggest a self-quenching process of the two Pc ring complexes in balltype complexes. Face-to-face interaction of the two monomers in dimers will decrease the energy gap between the singlet state and the triplet state, and enhance the formation of the triplet state (*i.e.* intersystem crossing increases), so decreasing fluorescence.²⁷ The $\Phi_{\rm F}$ values for complexes 7–9 will, however, also be underestimated due to aggregation. We believe that aggregation and the heavy atom effect are the predominant factors affecting the $\Phi_{\rm F}$ values of the complexes, since for complex 6, which is not aggregated, a $\Phi_{\rm F}$ value higher than that typical for monomeric phthalocyanines is observed.

Non-peripherally substituted complex **6** showed a larger Φ_F compared to the corresponding peripherally substituted **8**, probably due to there being less aggregation in the former, as observed in Fig. 1. Aggregation reduces the likelihood of radiative deactivation through the dissipation of energy by aggregates.

The fluorescence decay profiles for the complexes were monoexponential. Due to the heavy atom effect, fluorescence lifetime (τ_F) values are higher for complexes 6 and 8 when compared to complexes 7 and 9. The τ_F values range from 2.35 to 5.38 (Table 1).

Triplet quantum yields (Φ_T) and lifetimes (τ_T)

The triplet quantum yields ($\Phi_{\rm T}$) and lifetimes of the complexes are listed Table 1; Fig. 3 shows a representative triplet decay curve for the complexes (using complex 7 as an example). $\Phi_{\rm T}$ represents the fraction of absorbing molecules that undergo intersystem crossing to the metastable triplet excited state. Therefore, factors that induce spin-orbit coupling will certainly populate the triplet excited state. High $\Phi_{\rm T}$ values, and correspondingly low $\Phi_{\rm F}$ values (for ZnPc derivatives 7 and 9), suggest a more efficient intersystem crossing (ISC). The $\Phi_{\rm T}$ values for 6–9 are 0.56, 0.85, 0.64 and 0.88, respectively. The low values of $\Phi_{\rm T}$ for the MgPc derivatives, when compared to the ZnPc derivatives, are accounted for by the heavy atom effect of the Zn central metal, which encourages intersystem crossing, resulting in larger Φ_{T} and correspondingly lower $\Phi_{\rm F}$ values, as discussed above. Complexes 6–9 have low \varPhi_{IC} values, which may be explained by strong intramolecular interactions between the Pc rings, probably due to the cofacial structure

All complexes showed reasonably large triplet lifetimes, with $\tau_{\rm T}$ ranging from 170 to 1490 µs. The MgPc derivatives (6 and 8) showed longer $\tau_{\rm T}$ values when compared to the ZnPc derivatives (7 and 9) due to the heavy atom effect of Zn.



Fig. 3 Triplet decay curve for complex 7.

Peripheral substitution resulted in longer $\tau_{\rm T}$ values compared to non-peripheral substitution when considering the same central metal; compare non-peripherally substituted complex **6** ($\tau_{\rm T}$ = 710 µs) and peripherally substituted complex **8** ($\tau_{\rm T}$ = 1490 µs) or non-peripherally substituted complex **7** ($\tau_{\rm T}$ = 170 µs) and peripherally substituted **9** ($\tau_{\rm T}$ = 390 µs). The value of $\tau_{\rm T}$ ~1.5 ms is longer compared to phthalocyanine complexes in general.²⁶ Also, complex **6** has a higher $\Phi_{\rm T}$ and a longer $\tau_{\rm T}$ when compared to its monomer.²⁸ This can be attributed to strong intramolecular interactions between the Pc rings. This is due to the fact that the face-to-face interaction of the two monomers in dimers will decrease the energy gap between the singlet state and the triplet state, and enhance the formation of the triplet state (as discussed above), consequently decreasing the fluorescence intensity but increasing the triplet state yield.²⁷

Conclusions

We have reported on the synthesis of two new phthalodinitrile derivatives for the preparation of novel binuclear Pcs of the ball-type, substituted at non-peripheral and peripheral positions with aromatic groups. The synthesis and photophysical properties of the new ball-type Mg(II)Pc and Zn(II)Pc complexes were presented. The $\tau_{\rm T}$ values are longer and $\Phi_{\rm T}$ values are lower for the non-peripherally substituted derivatives. The MgPc derivatives (6 and 8) showed longer $\tau_{\rm T}$ values when compared to the ZnPc derivatives (7 and 9). All the complexes showed reasonably high triplet state quantum yields and long triplet lifetimes, which are required for efficient photosensitization. Thus, these complexes show potential for the PDT of cancer.

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