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Photophysical and photochemical properties of Ni(II), Pd(II) and Pt(II) aryloxo and alkylthio derivatised phthalocyanine

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Several aryloxo (**3a**–**6a** and **3b**–**6b**) and alkylthio (**3d** and **3e**) derivatised phthalocyanines were synthesized, characterized and the photochemical and photophysical properties investigated along with those of the previously reported (**3c**–**5c**, **4d**, **5d**, **4e** and **5e**) complexes. The effects of open-shell metals (Ni(II), Pd(II) and Pt(II)) on the photophysical and photochemical properties of the phthalocyanine ligands were investigated. Palladium and platinum improved the triplet quantum yield and singlet oxygen generation capacities of the unmetalated phthalocyanines (**3a**–**3e**) making their complexes candidates for further investigation in photocatalysis. Ni(II)Pc analogues gave poor results compared with their Pd(II)Pc and Pt(II)Pc counterparts.

1. Introduction

Metallophthalocyanine (MPc) complexes containing diamagnetic central metals are well known as photosensitizers in photodynamic therapy [1,2]. This is due to their ability to efficiently produce singlet oxygen [1], which mediates photosensitized reactions of MPc complexes. Generally, diamagnetic metals promote intersystem crossing (ISC), producing long lived triplet excited states [3–9].

Because of considerable d–π interactions which quench the excited states, short triplet state lifetimes (τ_T) are observed for open-shell MPc complexes. In spite of this theoretical shortcoming PdPcs are being investigated in the areas of photocatalysis [10,11] because of their high photostability. The short triplet state lifetimes implies that MPc complexes decay from the electronically excited state to the ground state primarily by non-radiative pathways, releasing their energy in several forms, including heat. Thus the possibility exists of producing local photosensitized hyperthermal effects with open shell phthalocyanines leading to specific damage of the cells and tissues containing the photosensitizer, without affecting healthy tissues [12]. This is the basis for photothermal therapy (PTT) of cancer, and nickel octabutyloxyphthalocyanine and nickel octabutyloxynaphthalocyanine have gained a lot of attention in this area [13]. Thus, systematic investigation of the photophysical properties of MPcs containing open-shell metals, especially Ni(II), Pd(II) and Pt(II) is essential for possible applications, such as in PTT. Such studies are scarce in the literature for these MPc complexes.

This work reports on the syntheses, and photophysical and photochemical characterization of metal-free, Ni, Pd and Pt phenoxy (**3a**–**6a**) and benzyloxyphenoxy **(3b**–**6b)** phthalocyanine complexes. The syntheses of unmetalated alkylthio derivatives (**3d**, **3e**) are also reported. The choice of substituents (**a**) (phenoxy) and (**b**) (benzyloxyphenoxy) is based on our previous study of these substituents on MPc complexes containing other central metals (e.g. OTi(IV), ClIn(IV), ClGa(IV), Cd and Pb) where these ligands were found to prevent aggregation in some cases, hence enhancing photochemical and photophysical behavior of the MPc complexes [14–18]. NiPc complexes in particular are known to be highly aggregated even when bulky ligands are employed [19].

The effects of substituents and central metals on the photochemical and photophysical properties for **3a**–**6a**, **3b**–**6b** and **3d**, **3e** are compared with those of previously reported pentylthio, octylthio and dodecylthio substituted NiPc (**4c**–**4e**) and PdPc (**5c**–**5e**) derivatives and unmetalated pentylthio Pc (**3c**) [20,21].

2. Experimental

2.1. Materials

Nickel chloride hexahydrate, palladium chloride and platinum chloride, potassium carbonate, 8-diazabicyclo{5.4.0}-undec-7-ene (DBU), diphenylisobenzofuran (DPBF), and phenol were purchased

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from Sigma Aldrich. Chloroform, methanol (MeOH), 1-chloronaphthalene(1-CNP), 1-pentanol, tetrahydrofuran (THF), dimethylformamide (DMF), deuterated chloroform ($CDCl_3$) deuterated pyridine (Pyr-d_5) were obtained commercially and dried where necessary before use. Dimethylsulphoxide (DMSO) was purchased from SAARCHEM, and dried in alumina before use. Column chromatography was performed on silica gel 60 (0.04–0.063 mm). The syntheses of the phthalonitriles: 1,2-dichloro-4,5-dicyanobenzene (**1**) [22], 1,2-diphenoxy-4,5-dicyanobenzene (**2a**) [18], 1,2-bis(benzyloxyphenoxy)-4,5-dicyanobenzene (**2b**) [18,23], 1,2-bis(octylthio)-4,5-dicyanobenzene (**7d**) [20] and 1,2-bis(dodecylthio)-4,5-dicyanobenzene (**7e**) [24] have been reported in literature. The syntheses of phthalocyanine complexes: metal-free 2,3,9,10,16,17,23,24-octakis(pentylthiophthalocyanine) (**3c**), 2,3,9,10,16,17,23,24-octakis(pentylthiophthalocyaninato) nickel(II) (**4c**), 2,3,9,10,16,17,23,24-octakis(pentylthiophthalocyaninato) palladium(II) (**5c**), 2,3,9,10,16,17,23,24-octakis(octylthiophthalocyaninato) nickel(II) (**4d**), 2,3,9,10,16,17,23,24-octakis(octylthioph-thalocyaninato) palladium(II) (**5d**), 2,3,9,10,16,17,23,24-octakis(dodecylthiophthalocyaninato) nickel(II) (**4e**) and 2,3,9,10,16,17,23,24-octakis(dodecylthiophthalocyaninato)palladium(II) (**5e**), have been reported before [20,21].

2.2. Equipment

Triplet absorption and decay kinetics were recorded on a laser flash photolysis system; the excitation pulses were produced by a Nd: YAG laser (Quanta-Ray, 1.5 J/8 ns) pumping a dye laser (Lambda Physic FL 3002, Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360). The kinetic curves were averaged over 256 laser pulses. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

For singlet oxygen determination the irradiation was carried out with a tungsten lamp (100 W, 30 V) perpendicular to the direction of measurement. A water filter and an interference filter (with a wavelength close to the absorption maximum of the sensitiser) were placed in the light beam path of the tungsten lamp. The light intensity was measured with a power meter. The decay of DPBF absorption at 421 nm was recorded after each photolysis cycle. UV–Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer. Fluorescence emission and excitation spectra were recorded on Varian Eclipse spectrofluorimeter. ^1H NMR spectra were obtained, in deuterated solvents, using a Bruker EMX 400 MHz NMR or Bruker Avance II+ 600 MHz NMR spectrometer. FT-IR spectra (KBr pellets) were recorded on a Perkin–Elmer spectrum 2000 FT-IR spectrometer. MALDI-TOF mass spectra were recorded ABI Voyager DE-STR Maldi TOF instrument at University of Stellenbosch using alpha-cyano-4-hydroxycinnamic acid as a matrix.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by a comparative method [25,26], using Eq. (1):

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

where F and F_{Std} are the areas under the fluorescence curves of the MPc derivatives and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, and n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc in DMSO was used as a standard, $\Phi_F = 0.20$ [27], for the determination of fluorescence quantum yields of all the MPcs synthesized. The sample and the standard were excited at the same relevant wavelength.

2.3.2. Triplet quantum yields and lifetimes

Triplet quantum yields were determined using a comparative method based on triplet decay, using Eq. (2):

$$\Phi_T^{\text{Sample}} = \Phi_T^{\text{Std}} \frac{\Delta A_T^{\text{Sample}} \cdot \varepsilon_T^{\text{Std}}}{\Delta A_T^{\text{Std}} \cdot \varepsilon_T^{\text{Sample}}} \tag{2}$$

where $\Delta A_T^{\text{Sample}}$ and ΔA_T^{Std}. are the changes in the triplet state absorbance of the MPc derivatives and the standard, respectively. $\varepsilon_T^{\text{Sample}}$ and $\varepsilon_T^{\text{Std}}$ are the triplet state extinction coefficients for the MPc derivatives and standard, respectively. Φ_T^{Std} is the triplet state quantum yield for the standard, ZnPc in 1-CNP, $\Phi_T^{\text{Std}} = 0.67$ [28].

2.4. Photochemistry

2.4.1. Singlet oxygen quantum yields

The singlet oxygen quantum yield (Φ_Δ) determinations were carried out using solutions containing DPBF (90 μM) and the Pcs (absorbance ~0.2 at the irradiation wavelength). A solution of the complex (2 ml) contained in a quartz cuvette (1 cm × 1 cm) was saturated with oxygen and irradiated using the set-up described above. The irradiation and measurement were repeated until around 80% decay of DPBF was observed [29]. The DPBF absorbance was corrected for the absorbance of sensitizer at the respective detection wavelength.

The DPBF quantum yield Φ_{DPBF} was calculated using Eq. (3) and the determined extinction coefficient of DPBF in 1-chloronaphthalene ($\varepsilon_{\text{1-CNP}} = 20{,}287\ \text{M L}^{-1}\ \text{cm}^{-1}$).

$$\Phi_{\text{DPBF}} = \frac{(C_0 - C_t)V_R}{I_{\text{abs}} \cdot t} \tag{3}$$

where C_0 and C_t are the DPBF concentrations prior to and after irradiation, respectively; V_R is the solution volume; t is the irradiation time per cycle and I_{abs} is defined by Eq. (4).

$$I_{\text{abs}} = \frac{\alpha \cdot A \cdot I}{N_A} \tag{4}$$

where $\alpha = 1 - 10^{-A(\lambda)}$, $A(\lambda)$ is the absorbance of the sensitizer at the irradiation wavelength, A is the irradiated area (3.142 cm^2), I is the intensity of light (8.92×10^{15} photons $cm^{-2}\ s^{-1}$) and N_A is Avogadro's constant. The singlet oxygen quantum yields Φ_Δ were calculated using Eq. (5) [30].

$$\frac{1}{\Phi_{\text{DPBF}}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi\Delta} \cdot \frac{k_d}{k_a} \cdot \frac{1}{[\text{DPBF}]} \tag{5}$$

where k_d is the decay constant of singlet oxygen in respective solvent and k_a is the rate constant of the reaction of DPBF with $O_2(^1\Delta_g)$. The intercept obtained from the plot of $1/\Phi_{\text{DPBF}}$ versus 1/DPBF gives $1/\Phi_\Delta$.

The values of the fraction of the excited triplet state quenched by ground state molecular oxygen (S_Δ) were determined using Eq. (6):

$$S_\Delta = \frac{\Phi_\Delta}{\Phi_T} \tag{6}$$

2.5. Synthesis

2.5.1. Metal-free – 2,3,9,10,16,17,23,24-octakis(phenoxy)phthalocyanine (*3a*)

A mixture of compound **2a** (2.00 g, 6.40 mmol) and DBU (6.20 ml, 4.00 mmol) was refluxed in 1-pentanol (8 ml), under a blanket of nitrogen for 8 h. The reaction mixture was allowed to cool, thereafter, methanol (80 ml) was added and the mixture stirred. After stirring, the mixture was filtered, and the resulting solid sequentially washed with methanol and water and then dried. The crude product was purified using column chromatography and DCM as the eluting solvent to afford the title compound as a dark green solid. Yield: 0.14 g (78%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 706 (5.31), 672 (5.62), 642 (4.72), 610 (4.58). ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$) 8.53 (8H, s, Pc—H), 7.20–7.38 (40H, m, phenyl—H). Calc. MS (ESI–MS) m/z: Calc. 1250.30; Found: 1250.29. [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3289 (N—H), 3061, 3042, 1613, 1270 (C—O—C), 989, 874, 743, 687. $C_{80}H_{50}N_8O_8{\cdot}H_2O$. Calc.: C, 75.71; H, 4.10; N, 8.83. Found, C, 74.72; H, 4.07, N, 9.02%.

*2.5.2. Nickel – 2,3,9,10,16,17,23,24-octakis(phenoxy)phthalocyanine (**4a**)*

A mixture of compound **2a** (1.00 g, 3.20 mmol), $NiCl_2{\cdot}6H_2O$ (0.36 g, 1.50 mmol) and DBU (3.20 ml, 2.00 mmol) in 1-pentanol (8 ml), was refluxed under a blanket of nitrogen for 14 h. The reaction mixture was allowed to cool, thereafter, methanol (80 ml) was added and the mixture stirred for 1 h, then filtered, and the resulting solid sequentially washed with methanol and water and then dried. The crude product was purified by column chromatography, using DCM as the eluting solvent to afford the title compound as a dark green solid. Yield: 0.08 g (75%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 678 (5.29), 650 (4.65), 610 (4.59). ^{1}H NMR (600 mHz); δ ppm (Pyr-d$_5$) 8.45 (8H, s, Pc—H), 7.20–7.36 (40H, m, phenyl—H). Calc. MS (ESI–MS) m/z: Calc. 1306.98; Found: 1306.71. [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3061, 3032, 1599, 1260 (C—O—C), 965, 801, 748, 687. $C_{80}H_{48}N_8O_8Ni{\cdot}H_2O$. Calc.: C, 72.46; H, 3.62, N, 8.45. Found, C, 71.92; H, 3.52, N, 6.98%.

*2.5.3. Palladium – 2,3,9,10,16,17,23,24-octakis(phenoxy)phthalocyanine (**5a**)*

Synthesis and purification of **5a** was as outlined for **4a** except that $PdCl_2$ was employed instead of $NiCl_2$. The amount of reagents employed were: 1-pentanol (8 ml), compound **2a** (1.00 g, 3.20 mmol), $PdCl_2$ (0.27 g, 1.50 mmol) and DBU (3.20 ml, 2.00 mmol). Yield: 0.07 g (65%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 668 (5.11), 640 (4.41), 602 (4.44). ^{1}H NMR (600 mHz); δ ppm (Pyr-d$_5$) 8.43 (8H, s, Pc—H), 7.25–7.42 (40H, m, phenyl—H). MS (ESI–MS) m/z: Calc. 1354.14; Found: 1354.20. [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3072, 3039, 1589, 1269 (C—O—C), 988, 882, 746, 688. $C_{80}H_{48}N_8O_8Pd{\cdot}H_2O$ Calc.: C, 69.94; H, 3.50, N, 8.16. Found, C, 68.92; H, 4.12, N, 6.69%.

*2.5.4. Platinum – 2,3,9,10,16,17,23,24-octakis(phenoxy)phthalocyanine (**6a**)*

Synthesis and purification of **6a** was as outlined for **4a** except that $PtCl_2$ was employed instead of $NiCl_2$. The amount of reagents employed were: 1-pentanol (8 ml), compound **2a** (1.00 g, 3.20 mmol), platinum chloride (0.40 g, 1.50 mmol) and DBU (3.20 ml, 2.00 mmol). Yield: 0.07 g (61%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 658 (5.06), 636 (4.53), 593 (4.43). ^{1}H NMR (600 mHz); δ ppm (Pyr-d$_5$) 8.63 (8H, s, Pc—H), 7.23–7.45 (40H, m, phenyl—H). Calc. MS (ESI–MS) m/z: Calc. 1443.36; Found: 1443.60. [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3063, 3033, 1602 (C═C), 1251(C—O—C), 966, 852, 745, 688. $C_{80}H_{48}N_8O_8Pt{\cdot}H_2O$. Calc.: C, 65.70; H, 3.28, N, 7.67. Found, C, 64.29; H, 4.13, N, 8.11%.

*2.5.5. Metal-free – 2,3,9,10,16,17,23,24-octakis(benzyloxyphenoxy)phthalocyanine (**3b**)*

A mixture of compound **2b** (1.68 g, 3.20 mmol) and DBU (4.80 ml, 3.00 mmol) was refluxed in 1-pentanol (8 ml), under a blanket of nitrogen for 12 h. The reaction mixture was allowed to cool, thereafter, methanol (80 ml) was added and the mixture was stirred for 1 h. The mixture was then filtered and dried. The crude product was purified with column chromatography, using THF as the eluting solvent to afford the title compound as a dark green solid. Yield: 0.15 g (88%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 708 (5.31), 674 (5.24), 643 (4.76), 611 (4.62). ^{1}H NMR (400 mHz), δ, ppm: ($CDCl_3$) 8.62 (8H, s, Pc—H), 7.60–7.00 (72H, m, phenyl—H), 5.10 (16H, s, CH_2). [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3253(N—H), 3063, 3033, 1602, 1222 (C—O—C), 945, 836, 737. Anal. Calc. For $C_{136}H_{98}N_8O_{16}$: C, 77.77; H, 4.90, N, 5.34. Found, C, 76.41; H, 5.12, N, 6.79%.%.

*2.5.6. Nickel – 2,3,9,10,16,17,23,24-octakis(benzyloxyphenoxy)phthalocyanine (**4b**)*

A mixture of compound **2b** (1.68 g, 3.20 mmol), $NiCl_2{\cdot}6H_2O$ (0.36 g, 1.50 mmol) and DBU (4.80 ml, 3.00 mmol) was refluxed in 1-pentanol (8 ml), under a blanket of nitrogen for 24 h. The reaction mixture was allowed to cool, thereafter, methanol (8 ml) was added and the mixture stirred. The mixture was then filtered and dried. The crude product was purified by column chromatography, using THF as the eluting solvent to afford the title compound as a dark green solid. Yield: 0.13 g (74%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 680 (5.40), 648 (4.69), 610 (4.66). ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$): 8.72 (8H, s, Pc—H), 7.65–7.10 (72H, m, phenyl—H), 5.00 (16H, s, CH_2). [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3052, 3031, 1611, 1224 (C—O—C), 955, 820, 734, 694. $C_{136}H_{96}N_8O_{16}Ni$: Calc.: C, 75.73; H, 4.49, N, 5.19. Found, C, 73.92; H, 5.18, N, 5.12%.

*2.5.7. Palladium – 2,3,9,10,16,17,23,24-octakis(benzyloxyphenoxy)-phthalocyanine (**5b**)*

Synthesis and purification of **5b** was as outlined for **4b** except that $PdCl_2$ was employed instead of $NiCl_2$. The amount of reagents employed were: 1-pentanol (8 ml), compound **2b** (1.68 g, 3.20 mmol), palladium chloride (0.27 g, 1.50 mmol) and DBU (4.80 ml, 3.00 mmol). Yield: 0.11 g (62%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 670 (5.25), 603 (4.58). ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$) 8.62 (8H, s, Pc—H), 7.60–7.00 (72H, m, phenyl—H, phenyl—H), 5.10 (16H, s, S—CH_2). [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3065, 3035, 1648, 1207 (C—O—C), 962, 827, 733, 693. $C_{136}H_{96}N_8O_{16}Pd$ Calc.: C, 74.09; H, 4.39, N, 5.08. Found, C, 73.64; H, 5.90, N, 5.89%.

*2.5.8. Platinum – 2,3,9,10,16,17,23,24-octakis(benzyloxyphenoxy)-phthalocyanine (**6b**)*

Synthesis and purification of **6b** was as outlined for **4b** except that $PtCl_2$ was employed instead of $NiCl_2$. The amounts of reagents employed were: 1-pentanol (8 ml), compound **2b** (1.68 g, 3.20 mmol), platinum chloride (0.40 g, 1.50 mmol) and DBU (4.80 ml, 3.00 mmol). Yield: 0.09 g (49%). UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 703 (4.13), 660 (5.22), 594 (4.54). ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$) 8.60 (8H, s, Pc—H), 7.70–6.96 (72H, m, phenyl—H), 4.95 (16H, s, CH_2) [IR (KBr pellets) $\nu_{\max}$ (cm^{-1})]; 3052, 3037, 1634, 1261 (C—O—C), 949, 801, 741, 671. $C_{136}H_{96}N_8O_{16}Pt$. Calc.: C, 71.23; H, 4.22 N, 4.89. Found, C, 68.70; H, 4.55, N, 5.11%.

*2.5.9. Metal-free – 2,3,9,10,16,17,23,24,-octakis(octylthio)phthalocyanine (**3d**)*

The same method used for **3a** was employed for the synthesis of **3d**, except **7d** was employed instead of **2a**. The amounts of reagents were: Compound **7d** (0.42 g, 1 mmol), DBU (1.66 ml, 1 mmol). Yield: 0.37 g (74%), UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), ($\log \varepsilon$)] 737 (5.15), 710 (5.10), 673 (4.72), 638 (4.62), 452 (4.57). ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$) 8.23 (8H, s, H$_{\text{arom}}$), 3.40–3.37 (16H, t, SCH_2—), 2.10–2.00 (16H, m, CH_2—), 1.79–1.75 (16H, m, —CH_2), 1.58–1.35 (88H, m, —CH_2, CH_3). Calc. MS (ESI–MS) m/z: Calc. 1666.16; Found: 1666.46. [IR (KBr pellets) $U_{\max}$ (cm^{-1})]; 3452 (N—H), 2949, 2935, 2855, 1669, 1597, 1511, 1469, 1409, 1329, 1331, 1079, 1021, 939, 871, 751, 682 (C—S—C). $C_{96}H_{146}N_8S_8$ Calc.: C, 69.09; H, 8.82, N, 6.71. Found, C, 68.93; H, 8.75, N, 6.56%.

*2.5.10. Metal-free – 2,3,9,10,16,17,23,24,-octakis(dodecylthio)phthalocyanine **(3e)***

The same method used for **3a** was employed for the synthesis of **3e**, except **7e** was employed instead of **2a**. The amounts of reagents were: Compound **7e** (0.53 g, 1 mmol), DBU (1.66 ml, 1 mmol). Yield: 0.35 g (64%), UV/Vis [(1-CNP), $\lambda_{\max}$ (nm), (log ε)] 737 (5.18), 710 (5.11), 672 (4.72), 638 (4.62), 452 (4.57). ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$) 8.30 (8H, s, H_{arom}), 3.42–3.40 (16H, t, SCH_2—), 2.13–2.09 (16H, m, CH_2—), 1.80–1.69 (16H, m, CH_2—), 1.50–1.30 (152H, m, CH_2, CH_3). MS (ESI–MS) *m/z*: Calc. 2116.91; Found: 2117.19. [IR (KBr pellets) $U_{\max}$ (cm^{-1})]; 3449 (N—H), 2962, 2922, 2857, 1666, 1571, 1500, 1467, 1405, 1331, 1319, 1069, 1028, 937, 872, 748, 676 (C—S—C). $C_{128}H_{210}N_8S_8$ Calc.: C, 72.60; H, 10.00, N, 5.29. Found, C, 71.93; H, 10.42, N, 5.16%.

3. Results and discussion

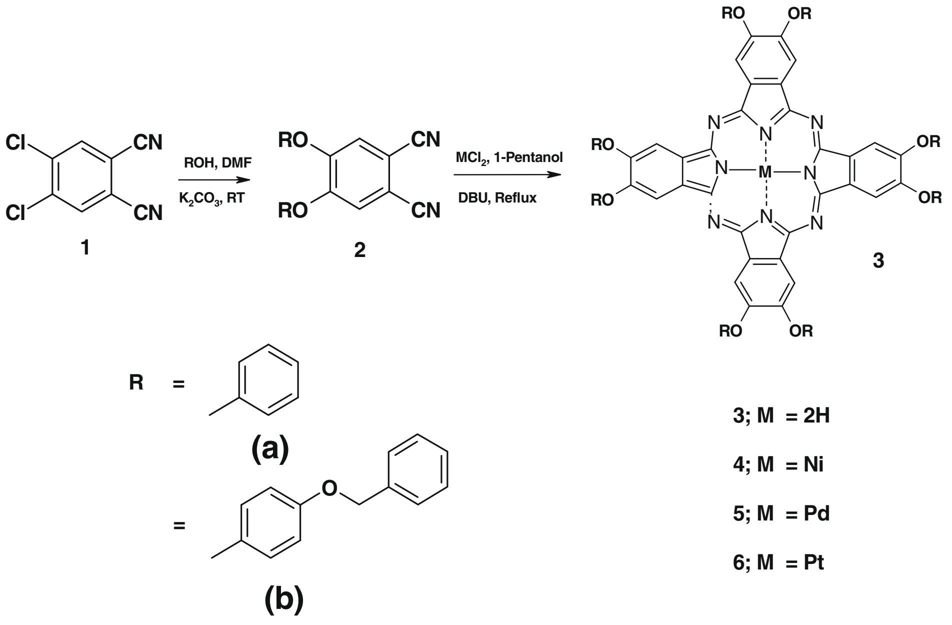
3.1. Syntheses and characterization

Phthalocyanines are prepared by cyclotetramerization of phthalonitriles. Octasubstituted phthalocyanines were synthesized from 4,5-diphenoxyphthalonitriles **(2a)**, 4,5-bis-(benzyloxyphenoxy)phthalonitrile **(2b)**, 4,5-dioctylthiophthalonitrile **(7d)** and 4,5-didodecylthiophthalonitrile **(7e)**. The syntheses of metallophthalocyanine complexes (**4a–6a**, and **4b–6b**) were achieved by treatment of respective phthalonitriles (**2a** and **2b**) with $NiCl_2$, $PdCl_2$ and $PtCl_2$, respectively in dry pentanol (Scheme 1). Metal salts were not included in the synthesis of metal-free phthalocyanines **(3a**, **3b**, **3d**, and **3e)**, Schemes 1 and 2. Column and preparative thin layer chromatography with silica gel was employed to obtain the pure products from the reaction mixtures. Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All complexes (**3a**–**6a**, **3b**–**6b**, **3d**, **3e**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF and toluene but they are only appreciably monomerised in 1-chloronaphthalene. The new compounds were characterized by UV–Vis, IR and NMR spectroscopies elemental and mass analysis. The analyses are consistent with the predicted structures as shown in the experimental section. ^{1}H NMR of all the molecules were done in deuterated chloroform except for **4a**, **5a** and **6a** that were also done in deuterated pyridine.

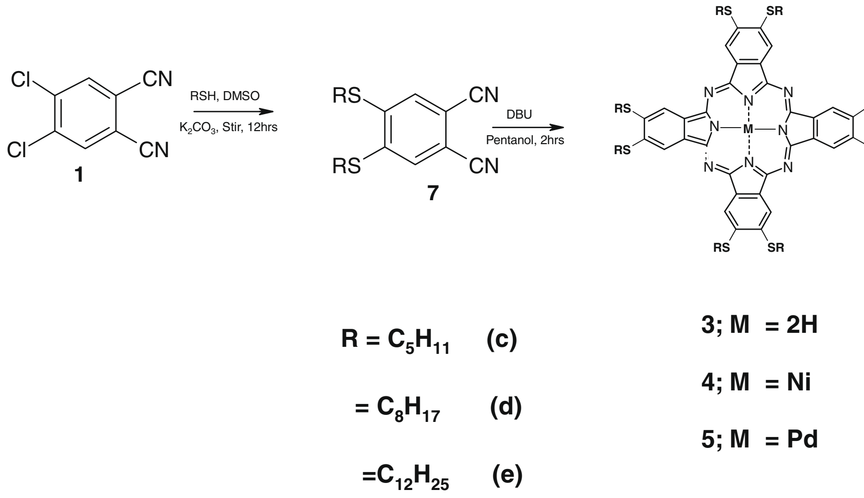
3.2. Ground state electronic absorption

UV/Vis spectra of the complexes showed characteristic absorptions in the Q-band, Figs. 1–3. The Q-bands were observed in the range 658–709 nm in 1-CNP, Table 1. The spectra of the complexes in 1-CNP, showed monomeric behavior, evidenced by a single (narrow) Q-band at 678, 668, 658 nm (for **4a**, **5a** and **6a**, respectively) and 680 nm, 670 nm and 660 nm (for **4b**, **5b** and **6b**, respectively), typical of unaggregated MPcs while spectra of metal-free analogues showed a typical split Q-band at 706 nm and 672 nm for **3a**, 708 nm and 674 nm for **3b** and 707 nm and 736 nm for both **3d** and **3e**, (Fig. 3), Table 1. The Q-band of all the thio derivatised complexes (substituents **c**, **d**, and **e**), Table 1, are red shifted compared to the aryloxy substituted. Red shifting is typical of all thio substituted phthalocyanine complexes [31].

The benzyloxyphenoxy PtPc complex (**6b**), Fig. 2a and b, also showed an additional peak on the red side of the Q-band around 709 nm but this extra peak was not noticed in phenoxy derivative **(6a)**. This extra peak is associated with partial demetallation of the complex since Pt^{2+} central metal is unable to completely enter the central cavity of Pc ring due to its large ionic size. Demetallation was solvent dependent in that the extra peak was observed in chlorinated solvents as was reported before for CdPc complexes [32]. Studies have shown that, in chlorinated solvents, MPcs undergo oxidation with the formation of HCl as a by-product [33] which in certain cases reacts with the MPc to cause demetallation. Fig. 2c shows that the extra peak disappeared in pyridine. It is also possible that demetallation occurred during synthesis, this was evidenced by the presence of the extra peak during synthesis in 1-pentanol, and addition of Zn acetate resulted in the disappearance of the peak as a result of the coordination of the Zn to the centre of the ring. Attempts to eliminate the demetallated species using chromatography and eluting with several solvents and their mixtures were not successful.



Scheme 1. Synthetic routes for oxy-derivatised phthalocyanines.



Scheme 2. Synthetic routes for thio-derivatised phthalocyanines.

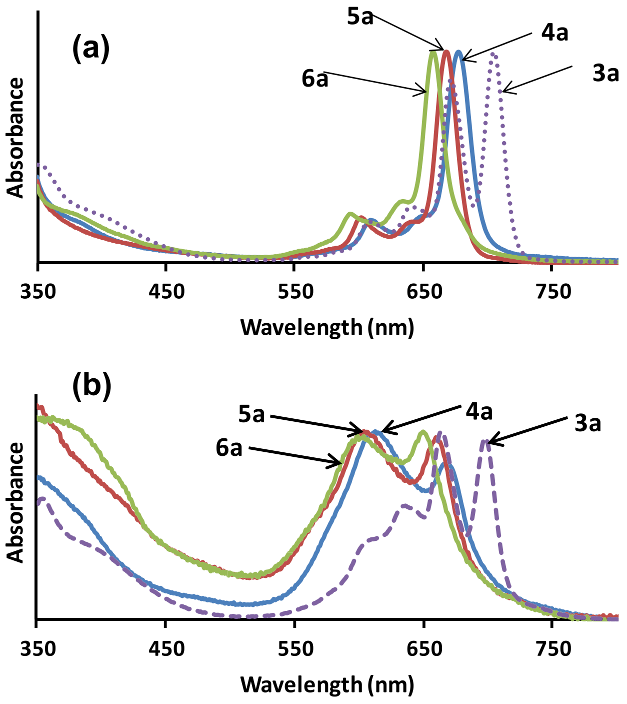


Fig. 1. UV–Vis spectra of complexes **3a**, **4a**, **5a**, and **6a**: (a) 1-CNP and (b) in DCM (concentration ~1×10^{-6} mol dm^{-3}).

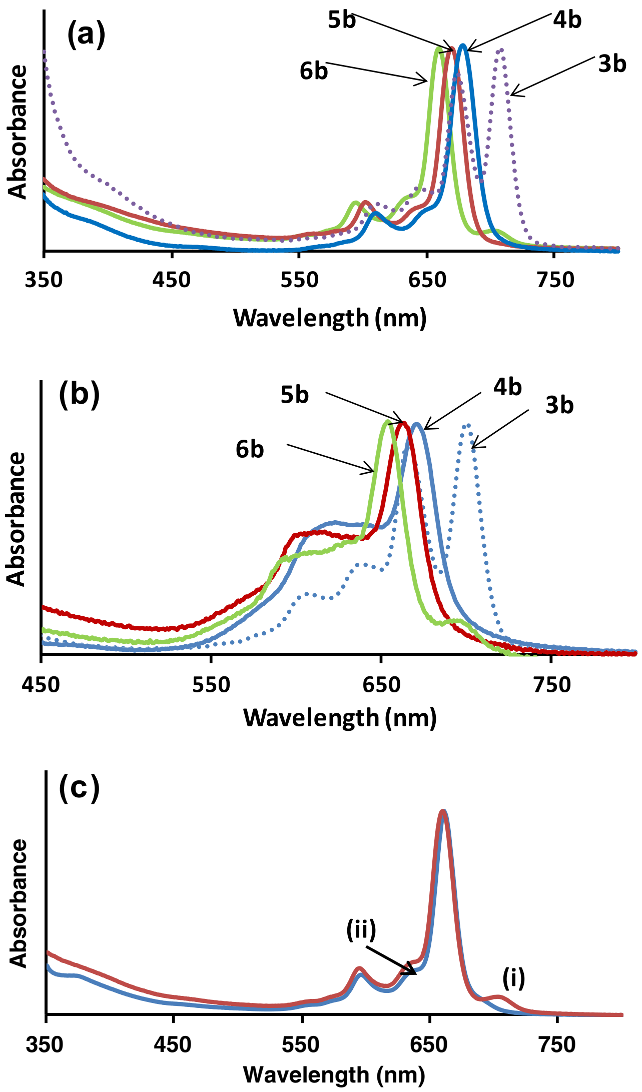


Fig. 2. UV–Vis spectra of complexes **3b, 4b, 5b**, and **6b** in (a) 1-CNP, (b) in DCM and (c) **6b** in 1-CNP (i) and pyridine (ii) (concentration ~1×10^{-6} mol dm^{-3}).

There is a clear red shifting of the Q-band as the size of the central metal decreases on going from PtPc (**6a**, **6b**), to PdPc (**5a**, **5b**) and NiPc (**4a**, **4b**), Figs. 1 and 2. Red shifting of the Q-band in MPc complexes is due to the destabilization of the highest occupied molecular orbital (HOMO) [34]. There are some central metals such as Mn^{III}, Pb^{II} and Sn^{IV}, which show a large red shift compared to metals such as Ni^{II}, Zn^{II} [35]. The observed red shifting of NiPc derivative (**4a**, **4b**) compared to PdPc (**5a**, **5b**) and PtPc (**6a**, **6b**) derivatives, suggests that the former destabilizes the HOMO to a larger extent than the latter two complexes. In DCM the MPcs displayed aggregation as evidenced by the presence of a blue shifted non-vibrational band in the visible region, Figs. 1b and 2b. The Q-bands of the monomers in DCM were observed at 669, 660 and 650 nm for **4a**, **5a** and **6a**, respectively, Fig. 1b and 669, 662 and 652 for **4b**, **5b** and **6b**, respectively, Fig. 2b. The peaks due to the aggregates were observed at 613, 604, 599, 615, 597 and 590 nm, respectively for **4a**, **5a**, **6a**, **4b**, **5b** and **6b**.

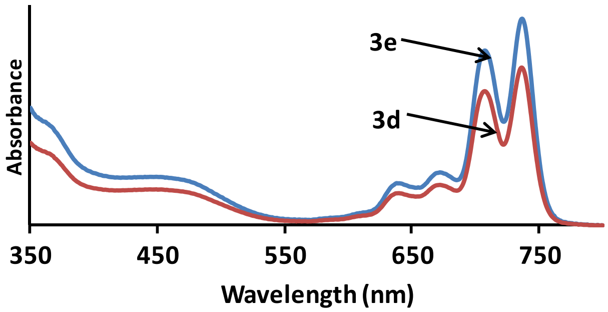


Fig. 3. UV–Vis spectra of complexes **3d** and **3e** in 1-CNP (concentration = 1 × 10^{-6} mol dm^{-3}).

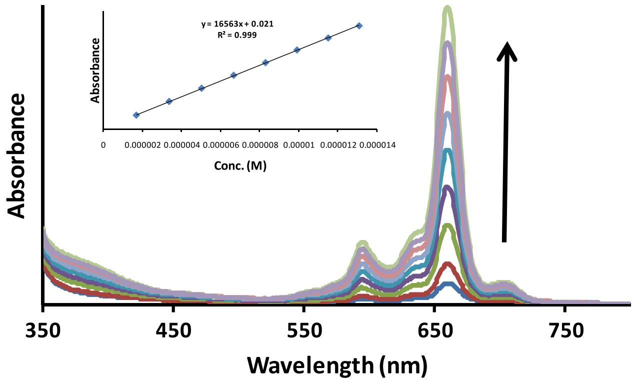


Fig. 4. UV–Vis spectral changes observed on increase in concentration of **6b** in 1-CNP. Inset: Beer–Lambert's plot for **6b** in 1-CNP. Concentration range: 1.0 × 10^{-6} mol dm^{-3} to 1.3 × 10^{-5} mol dm^{-3}).

The red shifting of the Q-band in 1-CNP compared to DCM might be due to aromatic nature of 1-CNP. Aromatic solvents have been known to bring about red shifting of Q-band relative to the non-aromatic ones [36]. Generally, aggregation is more pronounced in non-coordinating solvents. Thus the observed extensive aggregation in DCM compared to 1-CNP could be due to the coordinating nature of the later which reduces coplanar association of the Pc rings. Fig. 4 shows the concentration dependence of complex **6b** in 1-CNP. As the concentration was increased, the intensity of the Q-band also increased and there were no new band due to the aggregated species for the complex. The Beer–Lambert's law was obeyed for all of these compounds in 1-CNP for concentrations less than 1 × 10^{-5} mol dm^{-3}.

3.3. Fluorescence spectra and quantum yield

The absorption and fluorescence excitation spectra of the unmetalated derivatives (**3a**, **3b**, **3c**, **3d** and **3e**) are almost identical (Fig. 5a using **3a** as an example), implying that the absorbing species do not differ much from the fluorescing species. Metal-free Pcs are known to fluoresce with only one main peak in non-aqueous media which has been assigned as the 0–0 transition of the fluorescence [37], hence the observation of an unsplit fluorescence Q-band in Fig. 5a. The fluorescence excitation spectrum of the benzyloxyphenoxy derivative of PdPc **(5b)** is red shifted from the absorption spectrum by 11 nm (Table 1), suggesting a change in geometry upon excitation. Since for the Pt analogue (**6b**), the peak at 709 nm is due to partial demetallation discussed above, the excitation spectra is that of the unmetalated species which will fluoresce more efficiently than the metallated species. There will be more enhanced intersystem crossing in the metallated complex. The observed emission is that of the unmetallated species with emission Q-band maximum of 713 nm which is not too different from that of unmetallated **3b** at 716 nm (Table 1).

For complex **3d**, Fig. 5b, there is peak-to-peak matching between excitation and absorption spectra, but there is a decrease in intensity in the high energy band of the split pair. The excitation or emission spectra for **4a**, **4b**, **5a** and **6a** were too weak to be analysed accurately. The implication of this is that excited states of phenoxy derivatised Ni, Pd and Pt phthalocyanines were quenched faster than alkylthio (only for NiPc and PdPc complexes, attempts to synthesize PtPc alkylthio derivatives were not successful) and benzyloxyphenoxy (for PtPc and PdPc) derivatised analogues This might be due to a specific interactions between the central metals and phenoxy groups which quench the excited state faster than the alkylthio or benzyloxyphenoxy analogues.

The fluorescence quantum yield (Φ_F) values of **3a**, **3b**, **3c**, **3d** and **3e** in 1-CNP are 0.21, 0.25, 0.10, 0.13 and 0.15, respectively while those of the metallated derivatives are expectedly low (<0.01 and 0.012), **6b** displayed a higher fluorescence quantum yield (Φ_F) than **6a** probably because of the demetallation discussed above, Table 2. The low fluorescence quantum yield observed for the PdPc and PtPc complexes is due to open-shell nature of the metals involved

Table 1
Spectral data for all complexes in 1-CNP[a].

Complexes	Substituents	$\lambda_{Q(abs)}$ (nm)	$\lambda_{Q(exc)}$ (nm)	$\lambda_{Q(emm)}$ (nm)
3a (M=H_2)	—O—C_6H_5	672, 706	677, 711	720
4a (M=Ni)	—O—C_6H_5	678	–	–
5a (M=Pd)	—O—C_6H_5	668	–	–
6a (M=Pt)	—O—C_6H_5	658	–	–
3b (M=H_2)	—O—C_6H_4—O—CH_2—C_6H_5	674, 708	674, 709	716
4b (M=Ni)	—O—C_6H_4—O—CH_2—C_6H_5	680	–	–
5b (M=Pd)	—O—C_6H_4—O—CH_2—C_6H_5	670	681	682
6b (M=Pt)	—O—C_6H_4—O—CH_2—C_6H_5	660	709	713[c]
3c (M=H_2)	S—C_5H_{11}	707, 736	711, 738	745
4c (M=Ni)[b]	S—C_5H_{11}	696	695, 725	730
5c (M=Pd)[b]	S—C_5H_{11}	698	738	745
3d (M=H_2)	S—C_8H_{17}	707, 736	711, 738	745
4d (M=Ni) [b]	S—C_8H_{17}	707	662, 699	740
5d (M=Pd)[b]	S—C_8H_{17}	698	701	707
3e (M=H_2)	S—$C_{12}H_{25}$	707, 736	711, 738	745
4e (M=Ni)[b]	S—$C_{12}H_{25}$	709	727	730
5e (M=Pd)[b]	S—$C_{12}H_{25}$	698	703	709

[a] $\lambda_{Q(abs)}$ = Q-band absorption wavelength; $\lambda_{Q(exc)}$ = Q-band excitation wavelength; $\lambda_{Q(emm)}$ = Q-band emission wavelength.
[b] Values from Ref. [20].
[c] Due to demetalated species.

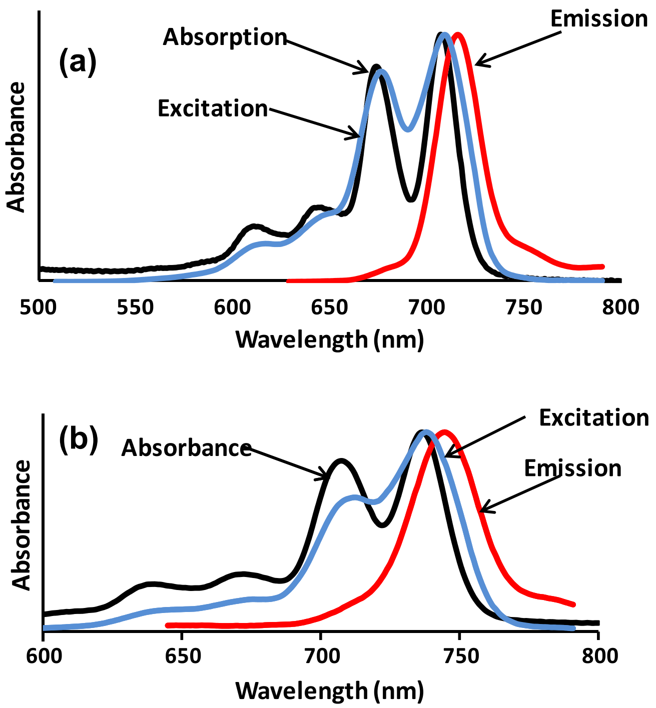


Fig. 5. Absorption and fluorescence (excitation and emission) spectra of (a) **3a** and (b) **3d** in 1-CNP excitation wavelength = 620 nm.

which promotes d–π interactions thereby quenching the singlet state of the complexes. Also the enhanced spin orbit coupling or low planarity might be responsible in lowering of fluorescence quantum yields [38].

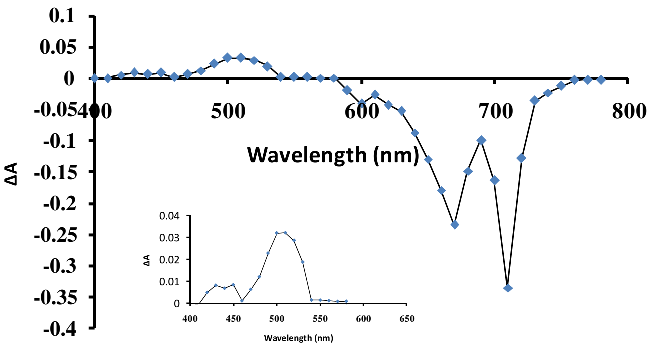


Fig. 6. Transient absorption curve for triplet decay curve of **3b** in 1-CNP at 520 nm. Excitation wavelength = 707 nm. Inset: transient absorption spectrum in the 500 nm region.

3.4. Triplet quantum yield and lifetime

Both the triplet quantum yields and lifetimes were determined by laser photolysis. Transient spectrum (Fig. 6) of complex **3b** in 1-CNP showed a split Q-band characteristic of unmetalated phthalocyanines. Of the octaphenoxy phthalocyanines, the metal-free (**3a**) complex showed a triplet quantum yield (Φ_T) of 0.40, while MPc complexes **5a** (Pd) and **6a** (Pt) containing the same substituent, gave $\Phi_T = 0.51$ and 0.62, respectively. The increase in the triplet quantum yield of the palladated and platinated octaphenoxy phthalocyanines (compared to unmetalated derivative, **3a**) is due to enhancement of intersystem crossing by the presence of heavy central metals. The Ni(II)Pc analogue (**4a**) did not show any triplet absorption peak suggesting an extremely short triplet lifetime or yield. The triplet lifetimes of the molecules reflect their open-shell nature. **3a** which was not metalated showed a lifetime of 55 μs while **5a** (Pd) and **6a** (Pt) showed lifetimes of 23 μs and 17 μs, respectively, Table 2, demonstrating the effect of d–π interaction characteristics of open-shell metal phthalocyanines, this normally results in lower excited state lifetime. The triplet decay curve in Fig. 7 obeyed first order kinetics suggesting minimum or absence of triplet–triplet recombination.

Of the octabenzyloxyphenoxy phthalocyanines, the metal-free analogue (**3b**) has $\Phi_T = 0.47$ while the Ni(II) analogue **(4b)** showed no triplet absorption peak as was the case for **4a**. Complexes **5b** (Pd) and **6b** (Pt) showed $\Phi_T = 0.65$ and 0.73, respectively (Table 2) due to enhancement of intersystem crossing by the presence of Pd and Pt. The lifetime followed the same pattern as octaphenoxy derivatives with **3b**, **5b** and **6b**, showing lifetimes of 50 μs, 20 μs and 13 μs, respectively.

The alkylthio derivatised phthlocyanines showed triplet quantum yields lower than their oxy-derivatised counterparts. The metal-free analogues (**3c**, **3d** and **3e**) gave Φ_T values of 0.39, 0.40 and 0.38, with triplet lifetimes of 62, 51, 44 μs, respectively, Table 2. Insertion of nickel into the cavities of these Pc ligands caused drastic reduction in Φ_T values of these molecules with complexes **4c**, **4d** and **4e** having triplet quantum yields of 0.09, 0.04 and 0.04 and reduced of lifetimes of 6, 4 and 2 μs, respectively. However, insertion of palladium metal into the ligands enhanced the triplet

Table 2
Photophysical properties of oxy and thio-derivatised phthalocyanines. References in brackets. Solvent = 1-CNP.

Compounds	Φ_F	Φ_T	τ_T (μs)	Φ_Δ	S_Δ
3a (M=H$_2$)	0.21	0.40	55	0.05	0.13
4a (M=Ni)	–	–	–	<0.01	–
5a (M=Pd)	–	0.51	23	0.49	0.96
6a (M=Pt)	–	0.62	17	0.42	0.68
3b (M=H$_2$)	0.25	0.47	50	0.01	0.02
4b (M=Ni)	–	–	–	<0.01	–
5b (M=Pd)	<0.01	0.65	20	0.43	0.66
6b (M=Pt)	0.012	0.73	13	0.39	0.53
3c (M=H$_2$)	0.10	0.39	62	0.04	0.1
4c (M=Ni)	<0.01 [20]	0.09	6	<0.01	<0.1
5c (M=Pd)	<0.01 [20]	0.47	15	0.42	0.89
3d (M=H$_2$)	0.13	0.40	51	0.04	0.1
4d (M=Ni)	<0.01 [20]	0.04	4	<0.01	0.25
5d (M=Pd)	<0.01	0.42	12	0.40	0.95
3e (M=H$_2$)	0.15	0.38	44	0.04	0.11
4e (M=Ni)	<0.01	0.04	2	<0.01	0.25
5e (M=Pd)	<0.01	0.40	10	0.39	0.98

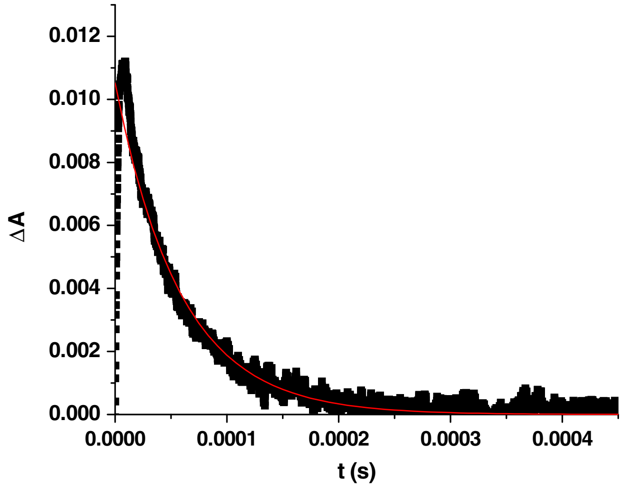


Fig. 7. Triplet decay curve for **3a** in 1-CNP. Excitation wavelength = 707 nm.

yields but also reduced the lifetime of the molecules with complexes **5c**, **5d** and **5e** showing triplet quantum yields to 0.47, 0.42 and 0.40 and triplet lifetimes to 15, 12 and 10 μs, respectively, Table 2. The increase in the quantum yield by insertion of heavy metal palladium is due to enhancement of intersystem crossing through spin–orbit coupling which also reduces the lifetimes. The nickel analogues of the alkylthio derivatised phthalocyanines were found to be slightly photoactive while that of oxy-derivatised showed no photoactivity. The non-display of photoactivity by nickel oxy-derivatised phathlocyanines is consistent with what was observed for nickel octabutoxylphthalocyanines and nickel octabutoxynaphthalocyanines [13] that made them good candidates for photothermal therapy (PTT). This suggest a specific interaction between aryloxy substituents and Ni(II) that efficiently quenches the excited states to a larger extent than the alkylthio substituents.

3.5. Singlet oxygen quantum yield

Singlet oxygen quantum yields were determined in 1-CNP using DPBF as a chemical quencher. The disappearance of DBPF was monitored using UV–Vis spectrometer. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including; triplet excited state energy, ability of substituents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. The trends in the of singlet oxygen quantum yields (Table 2) is as follows for the phenoxy and benzyloxyphenoxy complexes: Pd (**5**) > Pt (**6**) > H_2 (**3**) > Ni (**4**). This trend shows the PdPc derivatives to have higher Φ_Δ values than the Pt complexes, yet the latter showed larger triplet quantum yields. This suggests that the PtPc complexes are less efficient in generating singlet oxygen than the corresponding PdPc derivatives, with low S_Δ values for the former complexes. The magnitude of S_Δ (=Φ_Δ/Φ_T) represents the efficiency of quenching of the triplet excited state by singlet oxygen. The variation in the Φ_Δ values for the alkylthio complexes was: Ni < Metal-free < Pd.

4. Conclusions

Octakis(benzeloxyphenoxyl)phthalocyanine and octakis(phenoxyl)phthalocyanine complexes of Ni(II), Pd(II) and Pt(II) were successfully synthesized and characterized along with their metal-free analogue and alkylthio derivatised phthalocyanines. The effects of these open-shell metals on the photophysical and photochemical properties of these oxo and thio substituted phthalocyanine ligands were investigated. Palladium and platinum improved the singlet oxygen generation properties of the ligands while nickel reduced the capacity. Insertion of each of the metals led to reduction in the fluorescence quantum yield due to intersystem crossing and d–π interaction.

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