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The synthesis and fluorescence behaviour of phthalocyanines unsymmetrically substituted with naphthol and carboxy groups

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ABSTRACT

Unsymmetrically substituted phthalocyanines 8,15,22-tris-(naphtho)-2-(carboxy)phthalocyanine, [8,15,22-tris-(naphtho)-2-(carboxy)phthalocyanato]zinc(II), 8,15,22-tris-(naphtho)-4,5-(3-carboxy-1,2-dioxyphenyl)phthalocyanine and [8,15,22-tris-(naphtho)-4,5-(3-carboxy-1,2-dioxyphenoxy)phthalocyanato]zinc(II) were prepared using the mixed phthalonitrile cyclotetramerization of 3-(1-naphthoxy) phthalonitrile with a carboxylic acid phthalonitrile. The phthalocyanines were separated using column chromatography employing a mixture of THF, ammonia and water. The novel compounds were characterized using UV–Vis, IR, ^{1}H NMR and mass spectrometry as well as elemental analysis. Fluorescence quantum yields were found to range from 0.05 to 0.16.

1. Introduction

Although phthalocyanines (Pcs) enjoy widespread use as conventional dyes and pigments, they have also found importance in a number of applications including photodynamic therapy, owing to their good singlet oxygen generation ability [1–6]. Interest in improving the photo-physical properties of the Pc ring system continues, resulting in interest in securing novel Pcs whose structures promote good photo-physical behavior [7–12].

This paper concerns the synthesis and fluorescence behaviour of unsymmetrically substituted metal-free and zinc Pcs which contain three naphthol units and one carboxylic acid functional group. The molecules may be attached to biological molecules as the COOH group can interact with the amino group of the former. The naphthol group was used to enhance solubility and reduce aggregation owing to the well-known effect of such bulky substituents on steric hindrance [7].

The possibility of synthesizing unsymmetrical Pcs with substituents situated at specific positions enables fine-tuning of physical properties, thereby enhancing the technological applications of the phthalocyanines [7,13–15]. The presence of different functional groups in the same molecule may provide additional features such as increased solubility and reactivity.

Pcs that comprise three identical (A) and one different (B) isoindole units (A_3B type) have been prepared using a non-selective statistical condensation method that is based on the reaction of the two differently substituted phthalonitriles to afford a mixture of six compounds, with the A_3B type Pc being of highest yield [7,16–18]. MPc molecules which are symmetrically tetra (or octa) substituted with naphthol [19] or carboxy [20,21] groups have been reported. This work reports the synthesis of unsymmetrically substituted zinc phthalocyanines (ZnPcs) containing both naphthol and carboxyl groups.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF), 25% aq ammonium hydroxide solution, dimethylformamide (DMF), dichloromethane (DCM), dimethylsulfoxide (DMSO), chloroform ($CHCl_3$), glacial acetic acid and pentanol were purchased from Saarchem. Potassium carbonate, zinc acetate, dihydroxy carboxylic acid (**5**) and lithium metal were purchased form Sigma–Aldrich. Silica gel for column chromatography was purchased from Merck. 3-Nitrophthalonitrile (**1**) and 4,5-dichlorophthalonitrile (**4**) were synthesized as reported in literature [22,23].

2.2. Equipment

UV–Vis absorption spectra were obtained using the Varian Cary 500 UV–Vis/NIR. Fluorescence excitation and emission spectra were recorded with Varian Eclipse spectrophotometer. IR data (KBr pellets) was obtained using the Perkin–Elmer spectrum 2000 FTIR

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spectrometer. ^{1}H NMR spectra were recorded using a Bruker AMX 400 MHz spectrometer. Elemental analysis was done using a Vario-Elementar Microcube ELIII. MALDI-TOF mass spectrometry was carried out at the University of Stellenbosch using ABI voyager DE-STR MALDI-TOF instrument.

2.3. Synthesis

2.3.1. 3-(1-Naphthoxy) phthalonitrile (**3**)

1-Naphthol (**2**, 2.11 g, 14.6 mmol) was dissolved in dry DMSO (13 mL) and 3-nitrophthalonitrile (**1**, 2.5 g, 14.4 mmol) was added under inert atmosphere. To this reaction mixture finely ground anhydrous potassium carbonate (4.15 g, 30 mmol) was added. After 4 h of stirring at room temperature further potassium carbonate (1.06 g, 7.66 mmol) was added and this same amount was added again after 24 h of stirring. After 48 h of stirring, the reaction mixture was poured into water (50 mL) resulting in the formation of brown precipitates. Thin layer chromatography (TLC) was performed to determine the consumption of the starting materials and complete conversion of compound **1** was observed after 48 h. The brown product was centrifuged and recrystallised from methanol.

Yield: 3.7 g (67%). IR [(KBr) ν_{max}/cm^{-1}]: 2228 (CN), 1273 (C–O–C). ^{1}H NMR (DMSO-d_6): δ, ppm 8.21 (1H, d, Ar′–H), 7.95 (1H, t, Ar′–H), 7.85 (1H, d, Ar′–H), 7.75 (1H, t, Ar–H), 7.7–7.55 (4H, m, Ar′–H), 7.35 (1H, d, Ar–H), 7.15 (1H, d, Ar–H).

2.3.2. 4,5-(3-Carboxy-1,2-dioxyphenyl) phthalonitrile (**6**)

A mixture of 4,5-dichlorophthalonitrile (**4**, 6 g, 30.5 mmol), 3,4 dihydroxy carboxylic acid (**5**, 4.72 g, 30.5 mmol) and dry DMSO (23 mL) was stirred at 90 °C, whilst finely ground anhydrous potassium carbonate (2.12 g, 15.3 mmol) was added every five minutes until eight portions were added. The reaction was stirred for 60 min and cooled to room temperature. Water (50 mL) was added to the reaction mixture and the pH of this solution was dropped to one, with stirring, using a 10% HCl solution. The product was extracted with ethyl acetate and the organic extract was washed with water and dried under $MgSO_4$. The product was obtained as a brown solid.

Yield: 4.3 g (71%). IR [(KBr) ν_{max}/cm^{-1}]: 3050 (OH), 2235 (CN), 1718 and 1337 (C–O). ^{1}H NMR (DMSO-d_6): δ, ppm 7.80–7.84 (2H, d, Ar–H), 7.64–7.58 (1H, d, Ar′–H), 7.32 (1H, s, Ar′–H), 7.10–7.14 (1H, d, Ar′–H).

2.3.3. Synthesis of unmetallated phthalocyanines (**7a**, **8a**)

In 25 mL of dry pentanol, one equivalent of **5** (for **7a**) or **6** (for **8a**) and three equivalents of **3** were stirred under reflux in an argon atmosphere at 140 °C for 10 min. 100 mg of lithium was then added and the reaction mixture was refluxed for a further 2 h. Thereafter the reaction mixture was left to cool to room temperature. Glacial acetic acid (40 mL) was added to the mixture resulting in unmetallated phthalocyanines. The resulting precipitates were centrifuged and washed with water. The product was purified by repeated re-precipitation from THF into methanol followed by column chromatography on silica gel as substrate using THF:NH_4OH:H_2O in a 1:1:1 ratio as the eluting solvent mixture. Under these conditions, Pcs with polar side chains (COOH groups) are expected to be easily retained by the silica and hence are slower to elute through the column. Essentially the first fraction eluted is expected to be the four naphthoxy-substituted Pc followed by the desired mono-functionalized Pc. Three fractions were observed on the column, the third fraction remained at the top of the column.

*2.3.3.1. [8,15,22-Tris-(naptho)-2-(carboxy)phthalocyanine] (**7a**).* Yield: <5% UV–Vis [(THF/λ_{max}/nm (log ε))] 714 (4.96), 684 (4.93), 653 (4.46), 621 (4.33), 351 (4.59). Calcd. for: $C_{70}H_{66}N_8O_5$: C, 76.48: H, 6.05: N, 10.19%; found C, 75.14: H, 5.91; N, 9.23%. IR [(KBr)ν_{max}/cm^{-1}]: 2958–2869 (carboxylic acid OH), 1157 (C–O), 1096 (N–H). ^{1}H NMR (THF-d_8): δ, ppm 8.80 (2H, s, Pc–H), 7.22 (3H, broad s, Pc–H), 6.32–5.10 (28H, m, Ar–H, Pc–H), −1.02 (2H, s, H_2Pc). MALDI-TOF-MS m/z Calc: 984.28; Found (M$^-$): 985.0.

*2.3.3.2. [8,15,22-Tris-(naptho)-4,5-(3-carboxy-1,2-dioxyphenyl)phthalocyanine] (**8a**).* Yield: <5% UV–Vis [(THF/λ_{max}/nm (log ε))] 710 (4.51), 680 (4.47), 646 (4.05), 617 (3.93), 354 (4.29). $C_{76}H_{68}N_8O_5$: C, 75.72: H, 5.69: N, 9.30%; found C, 75.27: H, 5.62; N, 10.08%. IR [(KBr) ν_{max}/cm^{-1}]: 3053–2853 (carboxylic acid OH), 1246 (C–O), 1082 (N–H). ^{1}H NMR (THF-d_8): δ, ppm 9.00 (2H, s, Pc–H), 7.15 (3H, m, Ar–H), 6.40 (4H, m, Pc–H), 5.93 (5H, d, Pc–H), 5.80–5.25 (21H, m, Ar–H), −2.00 (2H, s, H_2Pc). MALDI-TOF-MS m/z Calc: 1090.29; Found (M$^-$): 1090.9.

2.3.4. Synthesis of zinc phthalocyanines (**7b**, **8b**)

The unmetallated phthalocyanines (**7a** or **8a**) were refluxed for 1 h in the presence of excess zinc (II) acetate in pentanol (20 mL). To the resulting product, methanol (30 mL) was added to precipitate out the dark green crude products. For purification, the procedure of **7a** and **8a** was followed.

*2.3.4.1. [8,15,22-Tris-(naptho)-2-(carboxy)phthalocyanato]zinc(II) (**7b**).* Yield: <5% UV–Vis [(THF/λ_{max}/nm (log ε))] 680 (4.15), 651 (3.40), 614 (3.44), 357 (3.95). $C_{70}H_{64}N_8O_5Zn$: C, 72.19: H, 5.71: N, 9.62%; found C, 71.44: H, 5.87; N, 8.07%. IR [(KBr) ν_{max}/cm^{-1}]: 2955–2854 (carboxylic acid OH), 1244 (C–O). ^{1}H NMR (THF-d_8): δ, ppm 10.82 (2H, s, Pc–H), 9.10 (3H, broad s, Pc–H), 8.22–6.91 (28H, m, Ar–H, Pc–H). MALDI-TOF-MS m/z Calc: 1046.19; Found (M$^+$): 1045.7.

*2.3.4.2. [8,15,22-Tris-(naptho)-4,5-(3-carboxy-1,2-dioxyphenoxy)phthalocyanato]zinc(II) (**8b**).* Yield: <5% UV–Vis [(THF/λ_{max}/nm (log ε))] 685 (3.98), 654 (3.21), 355 (3.60). $C_{76}H_{66}N_8O_5Zn$: C, 70.83: H, 5.39: N, 10.82%; found C, 69.94: H, 6.12; N, 10.14%. IR [(K Br) ν_{max}/cm^{-1}]: 3052–2849 (carboxylic acid OH), 1237 (C–O). ^{1}H NMR (THF-d_8): δ, 9.00 (1H, br s, OH), 8.25 (3H, br d, Pc–H), 7.78 (6H, m, Pc–H), 7.60–7.19 (21H, m, Ar–H), 7.15 (2H, d, Pc–H), 6.80 (3H, d, Ar–H).

MALDI-TOF-MS m/z Calc: 1152.20; Found (M$^-$): 1153.2.

2.4. Photo-physical properties

2.4.1. Flourescence quantum yields

The comparative method was used to determine the fluorescence quantum yields (Φ_F) of the phthalocyanine complexes using equation (1) [24].

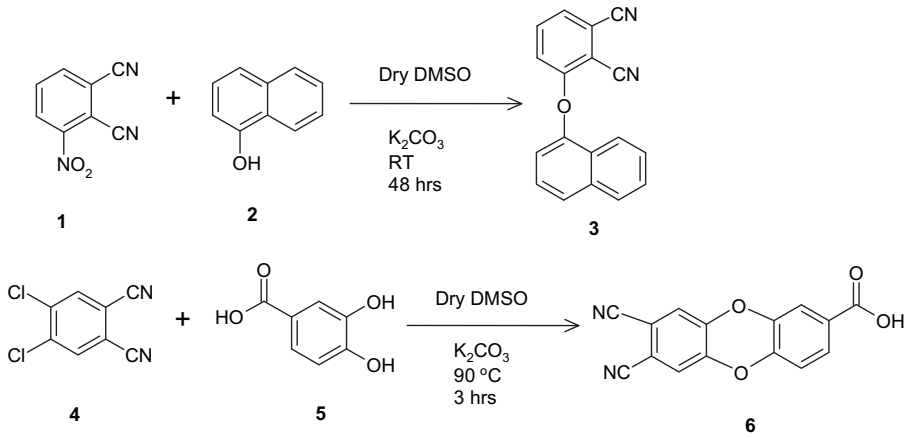
$$\Phi_F = \Phi_F(\mathrm{Std})\frac{F \cdot A_{Std} \cdot n^2}{F_{Std} \cdot A \cdot n^2_{Std}} \quad (1)$$

where F and F_{std} are the areas under the fluorescence curves of the complexes and the standard respectively. A and A_{std} are the respective absorbances of the sample and the standard at the excitation wavelength and n and n_{std} are the refractive indices of the solvents used for the sample and standard respectively. ZnPc was used as a standard in DMSO where $\Phi_F = 0.20$ [25].

3. Results and discussion

3.1. Synthesis and characterization

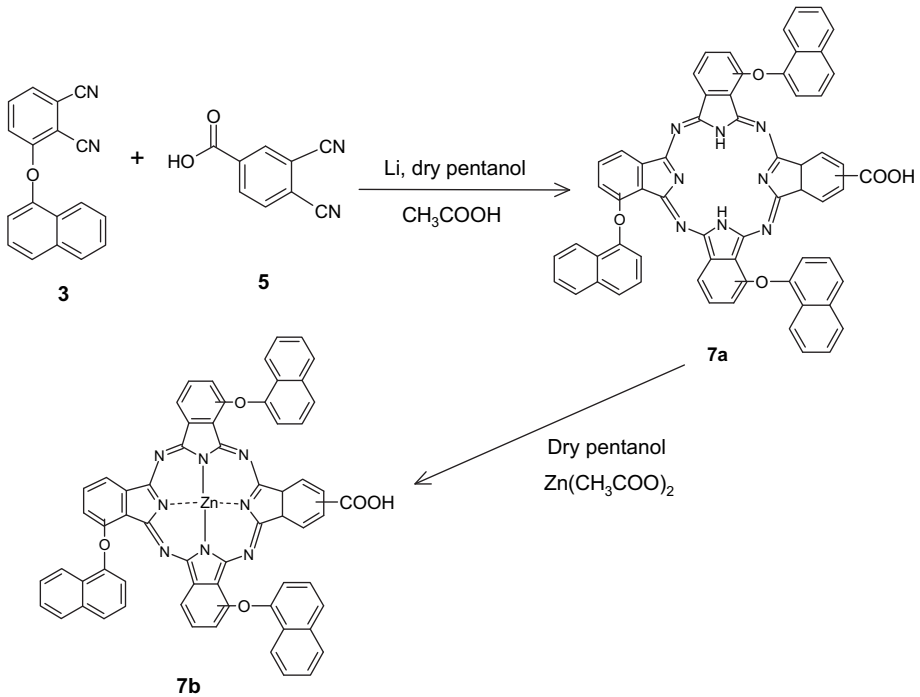
The synthesis of the dinitrile precursors; 3-nitrophthalonitrile (**1**) and 4,5-dichlorophthalonitrile (**4**) was carried out as according to literature [22,23]. Scheme 1 shows the synthetic procedures used to obtain 3-(1-naphthaenyloxy) phthalonitrile (**3**) and 4,5-(3-carboxy-1,2-dioxyphenyl) phthalonitrile (**6**). The electron-withdrawing



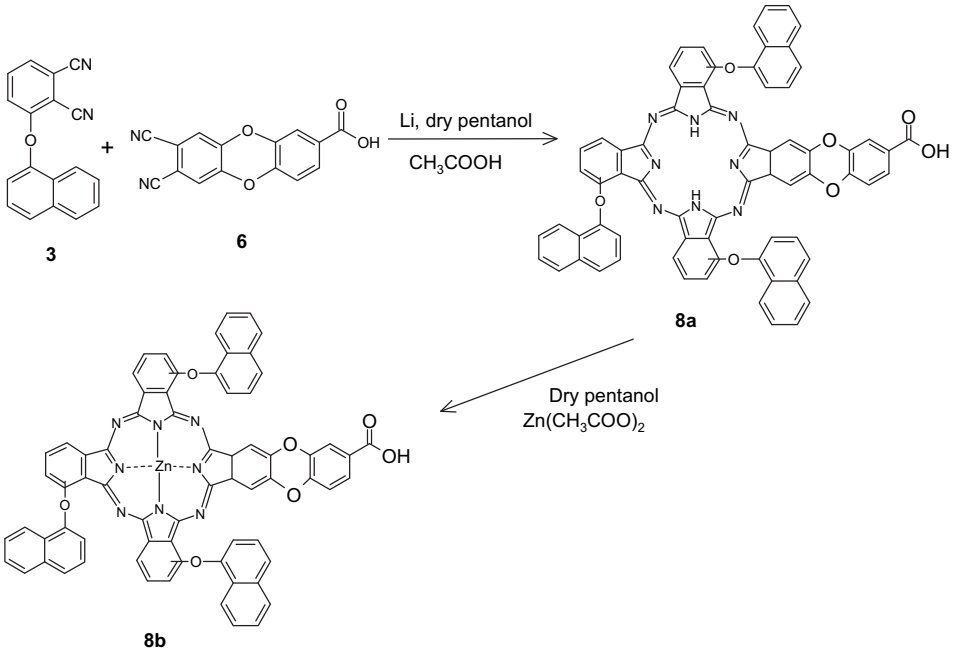
Scheme 1. Synthesis of carboxylated phthalonitriles **3** and **6**.

capability of the dinitrile functionalities makes **1** and **4** susceptible to nucleophilic attack. The base catalyzed nucleophilic substitution of the nitro and chloride groups was performed in dry DMSO at room temperature under inert nitrogen atmosphere. Good yields were obtained for both reactions. The synthetic procedure outlined in Schemes 2 and 3 show the statistical condensation approach used for the synthesis of the A_3B type Pcs. This method is based on the reaction of two differently substituted phthalonitriles in a ratio of 3:1. Chromatographic techniques were used for the isolation of the desired product and the A_3B type Pcs were isolated with very low (<5%) percentage yields. The asymmetric unmetallated phthalocyanines (**7a** and **8a**) were soluble in THF and only partially soluble in other organic solvents including ethanol, chloroform, DMF, DCM and DMSO. The metallation of Pcs **7a** and **8a** in dry pentanol using zinc (II) acetate gave Pcs **7b** and **8b** with low percentage yields after purification. The compounds were characterized by UV–Vis, IR, NMR and mass spectral data, as well as elemental analysis. The disappearance of the C≡N stretch at 2228 cm^{-1} and 2235 cm^{-1} in the IR spectra of phthalonitriles **3** and **6** confirmed the conversion into the corresponding phthalocyanine analogues (**7a** and **8a**). IR data also confirmed the conversion of **7a** and **8a** to the respective Zn phthalocyanines by the disappearance of the N–H stretches at 1096 and 1082 cm^{-1}. The disappearance of the inner cavity protons in the ^1H NMR spectra also confirmed metallation.

The ^1H NMR spectra of all complexes in THF-d_8 were complicated and gave broadened peaks due to possible intermolecular aggregation of the Pc as well as the presence of isomers. The ^1H NMR spectra was used to confirm the number of protons expected for the complexes. For complexes **7a** and **7b**, 33 aromatic protons were obtained. In similar manner complexes **8a** and **8b** gave 35 aromatic protons respectively. In addition, ring cavity protons (2) for **7a** and **8a** were observed as a weak peaks at −1.02 and −2.00 ppm as anticipated. The non-peripheral ring protons were observed as two signals at 8.80 and 7.22 ppm for **7a** and at 7.15 and 6.40 for **7b**. The ^1H NMR spectra data for **7a** and **8a** were similar to that of respective complexes **7b** and **8b**, except that the proton signals for the latter (ZnPc derivatives) were deshielded, this may be caused by the electron-withdrawing effect caused by the



Scheme 2. Synthesis of 8, 15, 22-tris-(naptho)-2-(carboxy)phthalocyanine analogues.



Scheme 3. Synthesis of 8,15,22-tris-(naptho)-4,5-(3-carboxy-1,2-dioxyphenyl) phthalocyanine analogues.

insertion of the Zn metal. The carboxylic acid proton was only observed for complex **8b** as a broad peak at 9.00 ppm. The acid proton is often difficult to locate due to its varying chemical shift, also the presence of water and oxygen in the sample may lead to the OH not being seen as it is easily exchangeable with deuterated solvents and the exchange is too fast on the NMR timescale, hence the peak is hardly observed. The integration of the peaks corresponded suitably to the expected number of protons for all complexes, further confirming the relative purity of the complexes. The purified monofunctional phthalocyanines were further characterized by mass spectra. The expected mass values corresponded with the found values for all complexes. There was no indication of other substituted derivatives on all mass spectra.

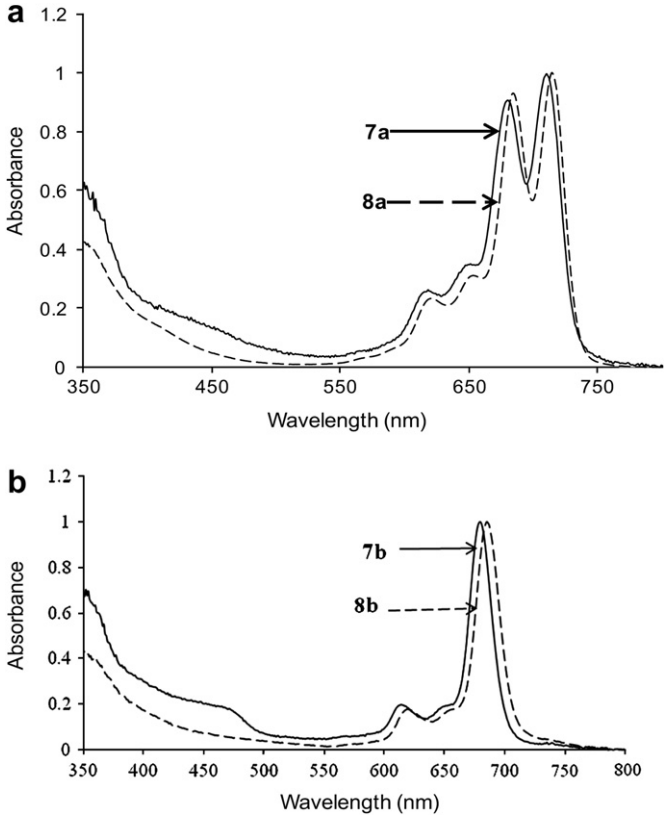


Fig. 1. Absorption spectra of (a) complex **7a**, **8a** and (b) **7b** and **8b** in THF. Concentrations $\sim 1 \times 10^{-6}$ mol L^{-1}.

3.2. Ground state electronic absorption, fluorescence spectra and quantum yields

The absorption spectra of the Pcs in THF show a characteristic sharp *Q* bands, Fig. 1. These $\pi-\pi^*$ transitions were observed at 710, 680 (**7a**), 715, 685 (**8a**), 680 (**7b**) and 685 (**8b**), Fig. 1. The *Q* band maxima of all the complexes are summarized in Table 1. There is a 5 nm difference between the Q-band positions of compounds **7** and **8**. This implies that the electron density of compound **8** is higher than that of compound **7** due to the dioxyphenyl substituent. This results in the lowering of the HOMO–LOMO gap of complexes **8a** and **8b**. The aggregation behavior of the Pcs were investigated in THF (Fig. 2 using complex **7a** as an example), no new bands were observed for all complexes signifying no aggregation behavior at these concentrations, probably due to the bulky nature of the ring substituents. Beer's law was observed for all complexes for concentrations less than 5×10^{-5} M. The complexes are unsymmetrically substituted and it would be expected that there is some *Q* band splitting due to loss of symmetry.

The excitation spectra for **7a** and **8a** were similar to the corresponding absorption spectra in that there was no change in *Q* band

Table 1
UV–Vis spectral parameters of H_2Pc (**7a**, **8a**) and ZnPc (**7b**, **8b**) analogues in THF.

MPc	Q_{abs} (nm)	Q_{ems} (nm)	Q_{exc} (nm)	Φ_F
7a	710,680	718	713, 678	0.16
8a	715, 685	722	716, 687	0.10
7b	680	685	680	0.05
8b	685	698	687	0.12

Q_{abs} = *Q* band absorption maximum; Q_{ems} = *Q* band emission maximum; Q_{exc} = *Q* band excitation maximum.

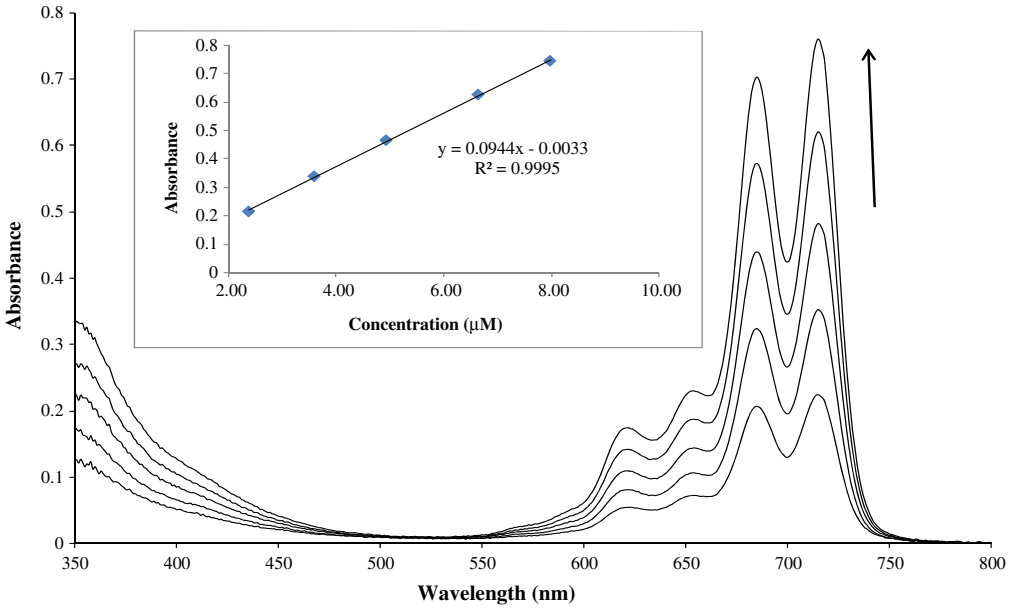


Fig. 2. Absorption spectra of compounds **7a** in THF at different concentrations. Inset a plot of Q-band absorbance versus concentration.

positions, but the relative intensities of the split pair were different, suggesting a slight change in symmetry upon excitation, Fig. 3a and b. Low symmetry Pc complexes, such as that of unmetallated Pcs [26], fluoresce with only one main peak and is assigned as the 0–0 transition of the fluorescence, hence the observation of a single main emission peak in Fig. 3a and b.

The corresponding zinc phthalocyanines (**7b** and **8b**) show excitation spectra which are similar to absorption spectra with both being mirror images of emission, Fig. 3c and d. The fluorescence quantum yield (Φ_F) values for the complexes were found to range from 0.05 to 0.16, with complex **7a** having the highest quantum yield, Table 1. The Φ_F values are in the range of MPc complexes [26]. Unmetallated complex **7a** gave a larger Φ_F values compared to **7b** containing the Zn central, this could be a result of intersystem crossing to the triplet state in the presence of the heavy Zn central metal, which then lowers the Φ_F values. However for **8a** and **8b**,

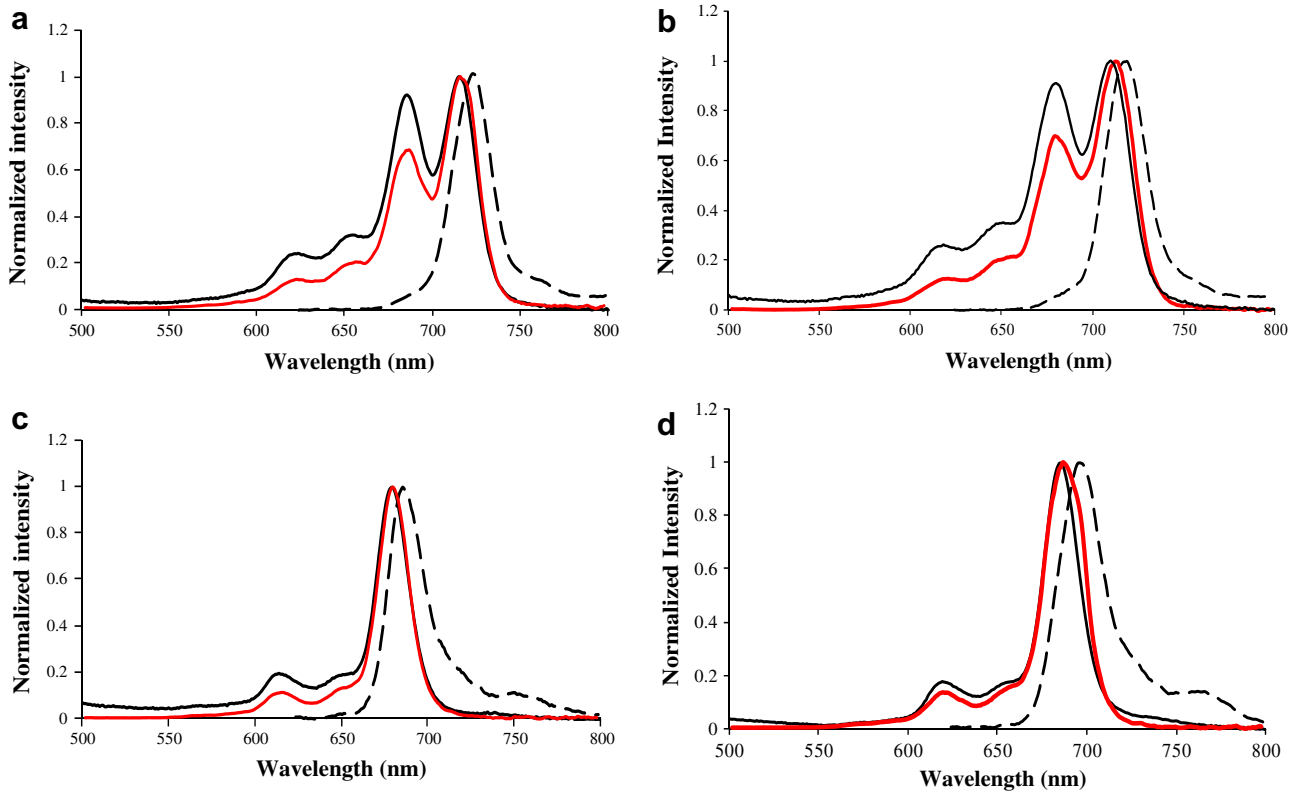


Fig. 3. Absorption (solid line), excitation (red line) and emission (dashed line) spectra of (a) **7a**, (b) **8a**, (c) **7b** and (d) **8b** in THF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the Φ_F values are quite similar, hence do not show the effects of Zn central metal.

4. Conclusion

In summary, we have successfully synthesized and characterized compounds **7a**, **8a**, **7b** and **8b**. The UV–Vis absorption and fluorescence spectra of the compounds in THF were determined. The results of the fluorescence spectra showed typical Pc behavior for all compounds with complex **7a** having the highest fluorescence quantum yield.

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