

## SYTHESIS, CHARACTERIZATION AND Pd(II) IONS COORDINATION EQUILIBRIUM STUDIES OF $\alpha$ -OCTASUBSTITUTED OCTYLTHIO- AND DODECYLTHIO-DERIVATSED PHTHALOCYANINES

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### ABSTRACT

Two metal-free phthalocyanines, 1,4,8,11,15,18,22,25,-octakis(octylthio)phthalocyanine (H<sub>2</sub>OOPc) and 1,4,8,11,15,18, 22,25,-octakis(dodecylthio)phthalocyanine (H<sub>2</sub>ODPc) were synthesized and characterized using Elemental analysis, IR, <sup>1</sup>H NMR, and UV/Vis absorption spectroscopies. The Pd(II) coordination extent and sequence were investigated for the two molecules at room temperature. The extent and nature of the two processes were different for the two molecules. The numbers of Pd(II) ions bound by H<sub>2</sub>OOPc and H<sub>2</sub>ODPc were 5 and 4 respectively, showing significant contribution from variation in chain length. The longer chain H<sub>2</sub>Pc behaved differently by disallowing Pd(II) ion coordination in its cavity. There was also a direct correlation between the carbon chain length and equilibrium constants, with the longer chain showing a lower equilibrium constant of  $1.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$ .

**Keywords:** Equilibrium Constant, Phthalocyanines, Coordination, Octylthio, Dodecylthio, Palladium Ions

### INTRODUCTION

The kinetics and thermodynamics of formations of complexes have been very crucial to the successes of many industrial and biological processes. Dyes and pigment formation, analytical chemistry, metal extractions, chemotherapy of cancer and photosynthesis are, among others, the processes taking advantage of rich chemistry of coordination molecules. However, like any other class of compounds, varieties of factors determine, not just the extents, but also the types of reactions that each of this class of compounds engage in, thereby making certain applications exclusive to specific types of compounds.

The concept of formation of coordination complexes by EDTA and dimethylglyoxime is employed in metal ions sequestration and analysis. Cyanides complexes of silver and gold are important to the processes of extraction of these metals. Naturally occurring complexes, which include chlorophyll, hemoglobin and Vitamin B<sub>12</sub> perform vital functions. The possibility of formation of soluble metal chelate complexes has been employed in the removal of harmful radioactive and other toxic elements like Pb<sup>2+</sup> from the body. Coordination of metal ions such as Ru<sup>2+</sup>, Pd<sup>2+</sup>, Au<sup>2+</sup>, Pt<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> by biological and synthetic ligands have been widely investigated

(Ivanova and Mayer-Figge, 2005; Ivanova *et al.*, 2005; Ivanova, 2007; Koleva *et al.*, 2007; Koleva *et al.*, 2008a; Koleva *et al.*, 2008b) for better understanding of their roles in biological processes and possibility of synthesizing their mimics for the same biological functions or deployment in other applications.

Dissociation and association equilibrium constants exploit variations, even seemingly insignificant ones, in the structures and compositions of molecules to widen their applications. Cisplatin, carboplatin and oxaliplatin are all platinum-based anti-tumor drugs with widely varying anti-tumor activities and different tumor annihilation pathways. This variation in activities has been related to the equilibrium constants of formation of the monoaquated analogues of these complexes (McGowan *et al.*, 2005; Aris and Farrell, 2009). Due to similar reason cisplatin and transplatin, the two isomers of diamminedichloroplatinum(II), are so chemically different that the former is used as an anti-tumor drug while the later does not exhibit comparable pharmacological effect (Aris and Farrell, 2009).

These far reaching consequences of equilibrium constants led to its investigation in various

phthalocyanine (Pc) ligands in the exploration of the deployment of phthalocyanines (Pcs) having thio functionalities as Palladium ions extracting agents and in Palladium ions dosimetry. The equilibrium constant under this circumstance represents a measure of recoverability of the metal ions. Phthalocyanines are a wide variety of macrocyclic compounds that possess an array of solid-state properties that make them notable examples of adaptable functional organic materials. The details of their binding process in this respect and the effect of molecular architecture on the process have been reported (Bilgin *et al.*, 2006; Meryem *et al.*, 2006; Kandaz *et al.*, 2007; Ogunbayo and Nyokong, 2009).

Aggregation occurred when tetrasubstituted thio-functionalized Pcs were used (Bilgin *et al.*, 2006; Meryem *et al.*, 2006 and Kandaz *et al.*, 2007). This problem was defeated with the use of octasubstituted ones proving the effect of inter-substituents distance on the molecular integrity of the binding products and robustness of the coordination process (Ogunbayo and Nyokong, 2009). The positions of substitution ( $\alpha$  or  $\beta$ ) through their effects on inter-substituent distances also impacted the binding process, with the  $\alpha$ -substituted showing a more robust binding process. This present work investigates the effect of chain length on the extent and nature of the binding process of novel  $\alpha$ -substituted metal-free phthalocyanines ( $H_2Pc$ ). The effects of chain length on the equilibrium constants of the processes were also explored.

## MATERIALS AND METHOD

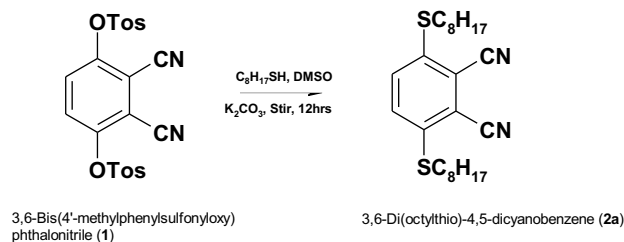
1-Pentanol, dimethylformamide (DMF), octanethiol, dodecanethiol, dimethylsulfoxide (DMSO), methanol, 1,8-diazabicyclo[5, 4, 0] undec-7-ene (DBU), potassium carbonates, chloroform, dichloromethane (DCM), chloronaphthalene (CNP) and palladium (II)

chloride were purchased from Sigma-Aldrich. Methanol, ethanol and chloroform were purchased from Merck. Chromatography was performed on silica gel 60 (0.04-0.063 mm). 3,6-Bis(4'-methylphenylsulfonyloxy) phthalonitrile (**1**) was synthesized as reported in literature (Mbambisa *et al.*, 2007). UV-Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer.  $^1H$  NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR.

## Synthesis

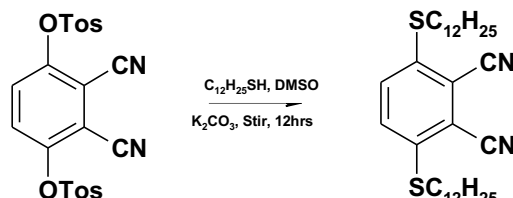
### 3,6-di(octylthio)-4,5-dicyanobenzene (**2a**)

Following literature methods for synthesis of substituted phthalonitriles (Mbambisa *et al.*, 2007) **2a** was synthesized as follows: octanethiol (2.01 g, 20 mmol) was dissolved in absolute dimethylsulfoxide (DMSO) (15 ml) under nitrogen and **1** (2 g, 10 mmol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (6 g, 43.4 mmol) was added portion-wise within 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 12 h. Water (30 ml) was added and the product was extracted from the aqueous phase with chloroform (3 x 20 ml). The combined extracts were treated first with sodium carbonate solution (5%), then with water and the aqueous phase was removed. The solvent (chloroform) was evaporated and the product was crystallized from ethanol. Yield: 2.4 g (78.9%). IR (KBr pellets)  $\nu_{max}$  /  $cm^{-1}$ : 3085, 2951, 2930, 2864, 2379 (S-C), 2226 (CN), 1444, 1283, 1202, 1181, 1173, 1145, 877, 847, 827, 725, 547, 447.  $^1H$ -NMR (400 MHz);  $\delta$  ppm ( $CDCl_3$ ) 7.52 (2H, s, Ar-H), 3.06–3.02 (4H, t,  $-CH_2$ ), 1.74–1.68 (4H, m,  $-CH_2$ ), 1.48–1.45, (4H, m,  $-CH_2$ ), 1.31–1.29, (16H, m,  $-(CH_2)_4$ ), 0.92–0.89 (6H, m,  $-CH_3$ ).



**3,6-di(dodecylthiol)-4,5-dicyanobenzene (2b)**

The same method used for the synthesis of **2a** was also used for **2b** except dodecylthiol was employed instead of octanethiol. The reagents used were dodecanethiol (3.01 g, 20 mmol), **1** (2 g, 10 mmol), potassium carbonate (6 g, 43.4 mmol). Yield: 4.4 g (85%). IR (KBr pellets)  $\nu_{\max}$  /  $\text{cm}^{-1}$ :



3,6-Bis(4'-methylphenylsulfonyloxy)phthalonitrile (**1**)

3,6-Di(dodecylthio)-4,5-dicyanobenzene (**2b**)

**Metal-free 1,4, 8, 11, 15, 18, 22, 25,-octakis(octylthio)phthalocyanine(H<sub>2</sub>OOPc) (3a)**

3,6-Bis(octylthio)-4,5-dicyanobenzene (**2a**) (0.42 g, 1 mmol) and DBU (1.70 g, 11.17 mmol) were added to refluxing pentanol (10 ml). The solution was heated to reflux for 5 hrs. The solution was then allowed to cool and the solvent removed under reduced pressure, followed by titration with cold methanol to precipitate the product. The black precipitate was dissolved in DCM and passed through a silica column. DCM was used as the eluting solvent to afford **3a**, which was purple in colour. Yield: 0.25 g (60%). UV/Vis [(DCM,  $\lambda_{\max}$ /nm, (log  $\epsilon$ )] 812 (5.21), 719 (4.61). <sup>1</sup>H-NMR (400 MHz);  $\delta$  ppm (CDCl<sub>3</sub>) 7.76 (8H, s, H<sub>arom</sub>), 3.29 (16H, t, SCH<sub>2</sub>-), 1.97-1.95 (16H, m, CH<sub>2</sub>-), 1.42 (16H, m, -CH<sub>2</sub>), 1.27-1.60 (64H, m, -(CH<sub>2</sub>)<sub>4</sub>), 0.94 (24H, m, CH<sub>3</sub>), 0.34 (2H, s, N-H). [IR (KBr pellets)  $\nu_{\max}$  /  $\text{cm}^{-1}$ ]; 3454 (N-H), 2948, 2857, 1669, 1411, 1332, 1337, 1078, 1027, 941, 871, 753, 671 (C-S-C). C<sub>96</sub>H<sub>146</sub>N<sub>8</sub>S<sub>8</sub>Calc.: C, 69.09; H, 8.82, N, 6.71, S, 15.37. Found, C, 68.03; H, 8.53, N, 6.29, S, 14.02%

**Metal-free 1,4, 8, 11, 15, 18, 22, 25,-octakis(dodecylthio)phthalocyanine(H<sub>2</sub>ODPc) (3b).**

The same method used for **3a** was employed for the synthesis of **3b**, except **2b** was employed instead of **2a**. The reagents used includes 3,6-bis(dodecylthio)-4,5-dicyanobenzene (**2b**) (0.53 g, 1 mmol) and DBU (1.70 g, 11.17 mmol). Yield: 0.30 g (56%). UV/Vis [(DCM,  $\lambda_{\max}$ /nm, (log  $\epsilon$ )] 812 (5.25), 719 (4.64). <sup>1</sup>H-NMR (400 MHz);  $\delta$  ppm

3089, 2951, 2930, 2864, 2362 (S-C), 2228 (CN), 1444, 1283, 1202, 1181, 1173, 1145, 877, 847, 827, 725, 547, 447. <sup>1</sup>H-NMR (400 MHz);  $\delta$  ppm (CDCl<sub>3</sub>): 7.52 (2H, s, Ar-H), 3.04–3.01 (4H, t, -CH<sub>2</sub>), 2.71–2.68 (4H, m, -CH<sub>2</sub>), 1.70–1.66, (12H, m, -(CH<sub>2</sub>)<sub>3</sub>), 1.29–1.24, (12H, m, -(CH<sub>2</sub>)<sub>3</sub>), 0.93–0.90 (18H, m, -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>).

(CDCl<sub>3</sub>) 7.79 (8H, s, H<sub>arom</sub>), 3.32 (16H, t, SCH<sub>2</sub>-), 2.01-1.96 (16H, m, CH<sub>2</sub>-), 1.68-1.66 (16H, m, CH<sub>2</sub>-), 1.26-1.61 (128H, m, (CH<sub>2</sub>)<sub>8</sub>), 0.92-0.84 (24H, m, CH<sub>3</sub>), 0.37 (2H, s, N-H). [IR (KBr pellets)  $\nu_{\max}$  /  $\text{cm}^{-1}$ ]; 3451 (N-H), 2964, 2931, 2861, 1667, 1575, 1402, 1333, 1319, 1068, 1031, 939, 873, 748, 672 (C-S-C). C<sub>128</sub>H<sub>210</sub>N<sub>8</sub>S<sub>8</sub>Calc.: C, 72.60; H, 10.00, N, 5.29, S, 12.11. Found, C, 71.97; H, 10.51, N, 5.16, S, 12.12%.

**Palladium ion Assembly and its Equilibrium Studies**

For all studies, PdCl<sub>2</sub> was dissolved in ethanol and the Pcs in DCM. In order to minimize dilution effects, PdCl<sub>2</sub> stock solution (0.14 M) were added in microliters to the 2 mL of the Pc solution. For binding and kinetic studies, gradual addition of PdCl<sub>2</sub> solution was done and response monitored from spectroscopic changes. Varying amount of PdCl<sub>2</sub> stock solution was added to a fixed concentration (5 x 10<sup>-6</sup> M) of the Pc derivatives to form various PdCl<sub>2</sub> concentrations (from 4 x 10<sup>-3</sup> to 1 x 10<sup>-1</sup> M), and the absorbance changes accompanying each addition monitored.

The steady increase in absorbance at the  $\lambda_{\max}$  of Pd bound Pc (product) with increase in Pd (II) ion concentration was noted and used in the determination of the binding constant, as well as number of bound Pd (II) ions, according to equation 1 (Ogunbayo and Nyokong, 2009).

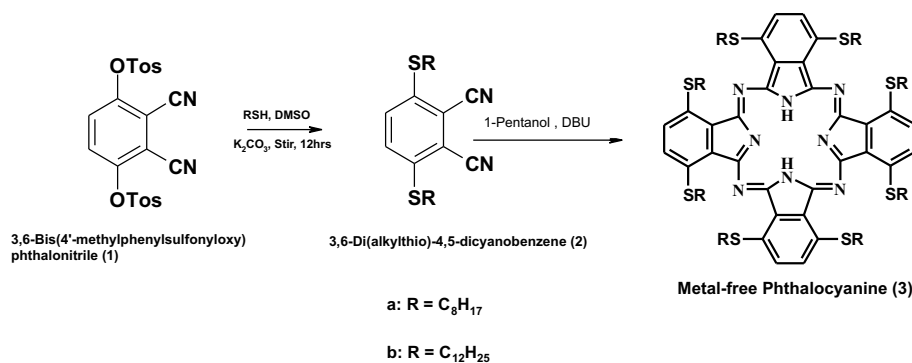
$$\log \left[ \frac{(A_{eq} - A_o)}{(A_{\infty} - A_{eq})} \right] = \log K + n \log [Pd^{2+}] \quad (1)$$

Where  $A_{cq}$  is the equilibrium absorbance of the Pd-bound Pc (product). This was the final absorbance of the product after each addition of  $\text{PdCl}_2$  solution to the reaction.  $A_0$  is the initial absorbance at the wavelength at which the product was monitored; and  $A^\infty$  is the maximum attainable absorbance of the product taken when further addition of  $\text{PdCl}_2$  to the reaction mixture no longer resulted in spectral changes.  $K$  is the binding constant, while  $n$  is the number of bound  $\text{Pd}^{2+}$  ions.

## RESULTS AND DISCUSSION

### Syntheses and Characterization of the Metal-free Phthalocyanines

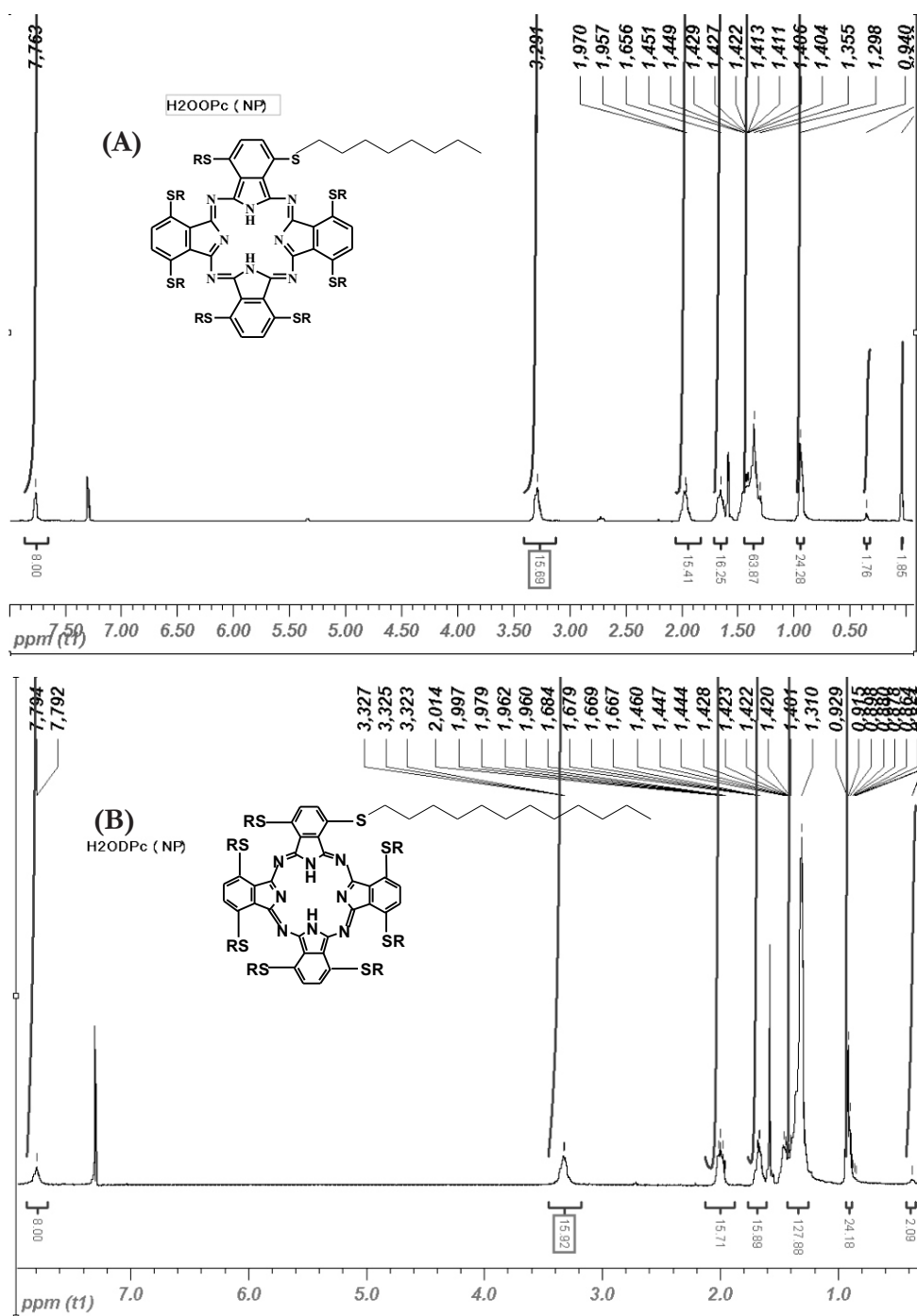
The precursors, thio-substituted phthalonitriles (**2a** and **2b**) were prepared via a base-catalysed ( $\text{K}_2\text{CO}_3$ ) nucleophilic aromatic displacement reaction of the tosyl group with a thiol. The metal-free phthalocyanines (**3a** and **3b**) were then prepared through the conventional reaction of thio-substituted precursors in the presence of DBU (**Scheme 1**).



**Scheme 1:** Synthesis of metal-free 1,4,8,11,15,18,22,25,-akylthiophthalocyanines, **3a** and **3b**.

Column chromatography with silica gel was employed to obtain the pure products with yields of 56% and 60% respectively for **2a** and **2b**. UV-Vis, IR and  $^1\text{H}$  NMR spectroscopies, and elemental analyses, were employed to characterize the Pc derivatives. The analyses were consistent with the predicted structures as shown in the experimental section. The disappearance of the sharp CN vibration at  $2226\text{ cm}^{-1}$  and  $228\text{ cm}^{-1}$  present in **2a** and **2b** respectively in the IR spectra of **3a** and **3b** confirmed the cyclotetramerisation of phthalonitriles **2a** and **2b** to form the metal-free phthalocyanines. The symmetrical nature of the phthalocyanines gave rise to simple  $^1\text{H}$  NMR spectra as represented by **Figure 1b** for the longer chain thio-derivatized phthalocyanine, **3b**. The

NMR data obtained in  $\text{CDCl}_3$  was in accordance with the expected structures. The aromatic non-peripheral ring protons were observed as a singlet at 7.76 ppm (**Figure 1**) for **3a** and 7.79 for **3b**, integrating for eight protons for each molecule. The methylene and methyl proton shifts belonging to the thio-alkyl side chain were clearly observed in the  $^1\text{H}$  NMR spectrum. Unsubstituted phthalocyanines were sparingly soluble but substitution at the peripheral ( $\beta$ ) and non-peripheral ( $\alpha$ ) positions improved solubility with substitution at the non-peripheral position resulting in higher solubility relative to peripheral substitution (Beck *et al.*, 199; Bakboord *et al.*, 2000). The two Pcs were soluble in solvents such as DCM,  $\text{CHCl}_3$  and chloronaphthalene (CNP).



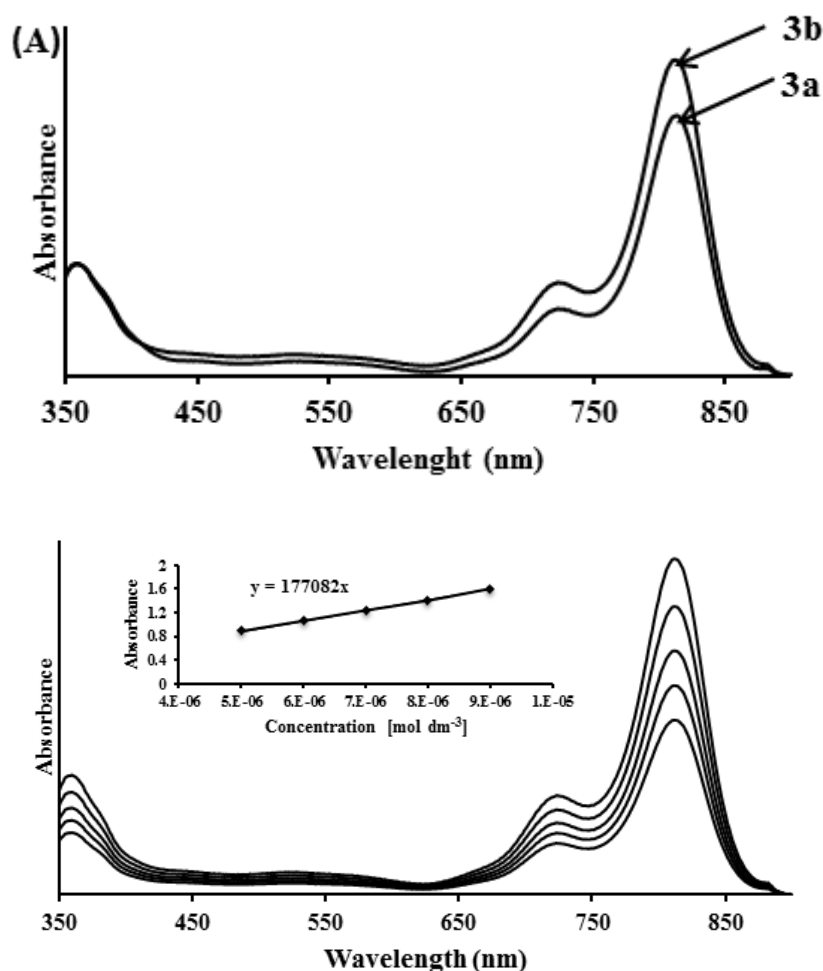
**Figure 1:**  $^1\text{H}$  NMR spectra of (A) **3a** (B) **3b** in  $\text{CDCl}_3$

The two phthalocyanines have similar UV-Vis spectrum with the Q band observed at 812 nm in DCM for the two molecules (**Figure 2A**). These are slightly red shifted compared to what was observed during characterization of octapentylthio analogue with its Q-band at 801 nm leading to the conclusion that length of the substituent chain has a significant effect on their spectra (Ogunbayo and Nyokong, 2009). The same trend was observed in the characterization

of the peripherally substituted analogues (Ogunbayo and Nyokong, 2010). The spectra of **3a** and **3b** did not show the typical split Q band expected for unmetalated phthalocyanines; The resolution of the split of the Q band is known to decrease with increasing wavelength hence for these two, the appearance of the Q-band at the unusually large wavelength resulted in the low resolution of the split and the consequent disappearance (Kobayashi *et al.*, 2003). Similar

result was observed in the characterization of the pentylthio-derivatised phthalocyanine (Ogunbayo and Nyokong, 2009). In DCM, Beer–Lambert law was obeyed by the molecules only at lower

concentrations ( $>1 \times 10^{-5} \text{ mol dm}^{-3}$ ), as shown in **Figure 2B**. The deviation at higher concentrations was due to formation of aggregates.

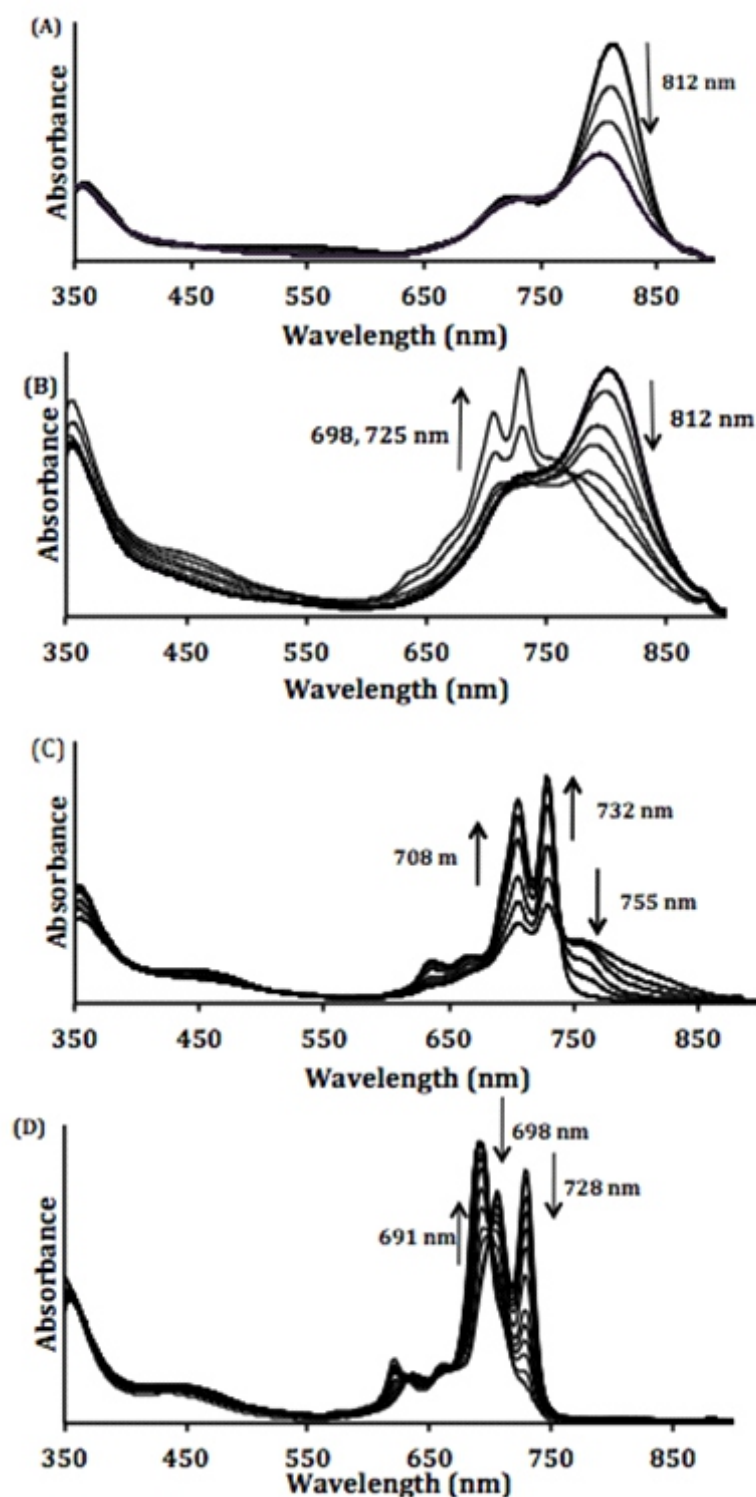


**Figure 2:** (A) Electronic absorption spectra of **3a** and **3b** in DCM. Concentration:  $1 \times 10^{-5} \text{ M}$ . (B) Absorption spectra of compound **3b** in DCM at different concentrations. Inset: Beer–Lambert Plot Pd(II) ion Assembly and its Equilibrium Studies

#### Metal-free **1**, **4**, **8**, **11**, **15**, **18**, **22**, **25**-octakis(octylthio)phthalocyanine( $\text{H}_2\text{OOPc}$ ) (**3a**)

The major structural difference between the Pcs is the length of the thio substituent chain. Octylthio and dodecylthio-substituents were compared with what was observed for pentylthio-substituted.

The processes involved and spectral changes were similar to what was observed with pentylthio-derivatised with significant differences. There are two areas of attachment available to the metals on these two phthalocyanine ligands: the thio groups on the periphery or the core nitrogen of the ligands. Addition of Pd(II) to the solution of **3a** led to spectral changes in **Figure 3**.



**Figure 3:** UV-Vis spectral changes observed on addition of PdCl<sub>2</sub> in ethanol to **3a** (concentration  $\sim 5 \times 10^6$  M) in DCM. The first spectrum in (B) is the same as the last spectrum in (A), the first spectrum in (C) is the same as the last spectrum in (B), and so on.

Figure 3A shows the spectra on the commencement of the addition of Pd(II) ions. Reduction in the intensity of the Q-band at 812 nm was observed. This was due to the

disappearance of the original form of the ligand from solution, most likely as a result of the conversion of the monomeric form of the ligand to aggregates with Pd(II) ions as bridges. But the

spectral changes were not clear enough to infer this transformation of monomers to aggregates with certainty. This conversion was demonstrated beyond reasonable doubt in the case of pentylthio-derivatized where there was observation of a new broad peak around 754 nm clearly representing the newly formed aggregates (Ogunbayo and Nyokong, 2009). In this work there was no clear new peak or any broadening of existing ones to reach a definite conclusion on these aggregates formation. The speculation of its occurrence, in spite of the aforementioned, was due to a sign of broadening observed around 761 nm. The inconspicuousness of these spectral changes might be due to low molar extinction coefficient of the new chemical species coupled with low quantity of the species in solution resulting in spectral responses too obscured for clear observation. Addition of more Pd(II) ions into the reaction mixture gave rise to the spectra in Figure 3B. It was at this point that appearance of new peaks became clearly noticeable. But instead of the broad peak suggesting aggregation, what appeared were two sharp peaks at 698 nm and 725 nm, the split Q-band suggesting loss of symmetry, consistent with the existence of an unmetallated Pc. Moving from the single to split Q-band in these spectra is consistent with the reason adduced for the single Q-band earlier. The single Q-band was due to decreasing resolution of the split at increasing wavelength. The appearance of the Q-band at long wavelength, in this case, was due to enhanced contribution to the electron density of the ring caused by the lone pairs of electron on the eight sulphur atoms of the thio substituents. Coordination of the thio groups with palladium using these lone pairs reduced the ring electron density leading to the blue shift of the Q band and the consequent higher resolution of the split of the Q-band. The split in Q band was a clear signal that a PdPc complex was not formed at this point and the complex was still metal-free

cavity phthalocyanine with Pd(II) ions coordinated to the alkylthio groups.

Further addition of Pd(II) ions to the reaction mixture led to the disappearance of the remnant of the original peak at 755 nm and the fine-tuning of the split Q band stabilizing at 708 nm and 732 nm (Figure 3C). This demonstrated the complete formation of the metal-free cavity octylthio-octasubstituted phthalocyanine. The observation of a clear isosbestic point around 740 nm suggests the existence of two chemical species in solution during this transformation: the aggregates of metal-free Pc and the one with palladium ions on the periphery. If the PdPc complex was formed with unsymmetrical substitution of Pd ions on the ring the nature of the split would not be as symmetrical as shown in Figure 3C. More addition of PdCl<sub>2</sub> to the reaction caused the reduction in the intensity of the split peaks at 708 nm and 732 nm (Figure 3D) suggesting the conversion of the chemical species represented, as discussed earlier, by these peaks. Simultaneously with this was also the appearance of a new peak at 691 nm blue shifted from the split Q band signaling the insertion of metal into the cavity of the phthalocyanine since the final spectrum is representative of metallated Pc. This sequence is comparable to the results obtained from previous work on pentylthio-phthalocyanines. Scheme 2 below is the summary of the coordination sequence for **3a**.

The equilibrium studies for the Pd(II) ions coordination to the phthalocyanine was carried

out using equation 1. A plot of  $\log \left[ \frac{(A_{\text{eq}} - A_0)}{(A_{\infty} - A_{\text{eq}})} \right]$

versus  $\log[\text{Pd}^{2+}]$  gave an equilibrium constant of  $1.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$  and  $n$  was found to be 5 (Figure 4).



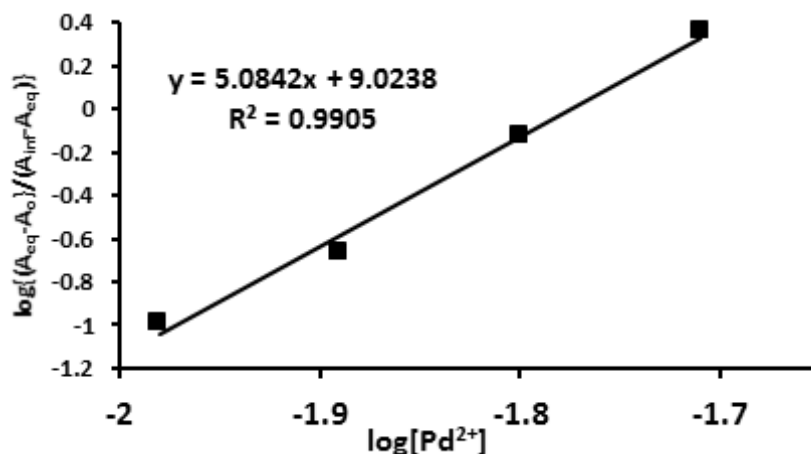
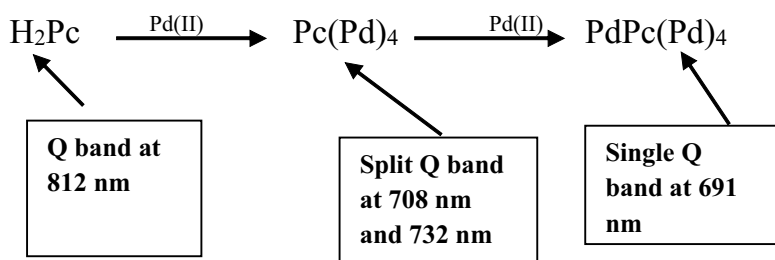


Figure 4: A plot of  $\log\left[\frac{(A_{\text{eq}} - A_o)}{(A_{\infty} - A_{\text{eq}})}\right]$  versus  $\log[\text{Pd}^{2+}]$  for **3a**

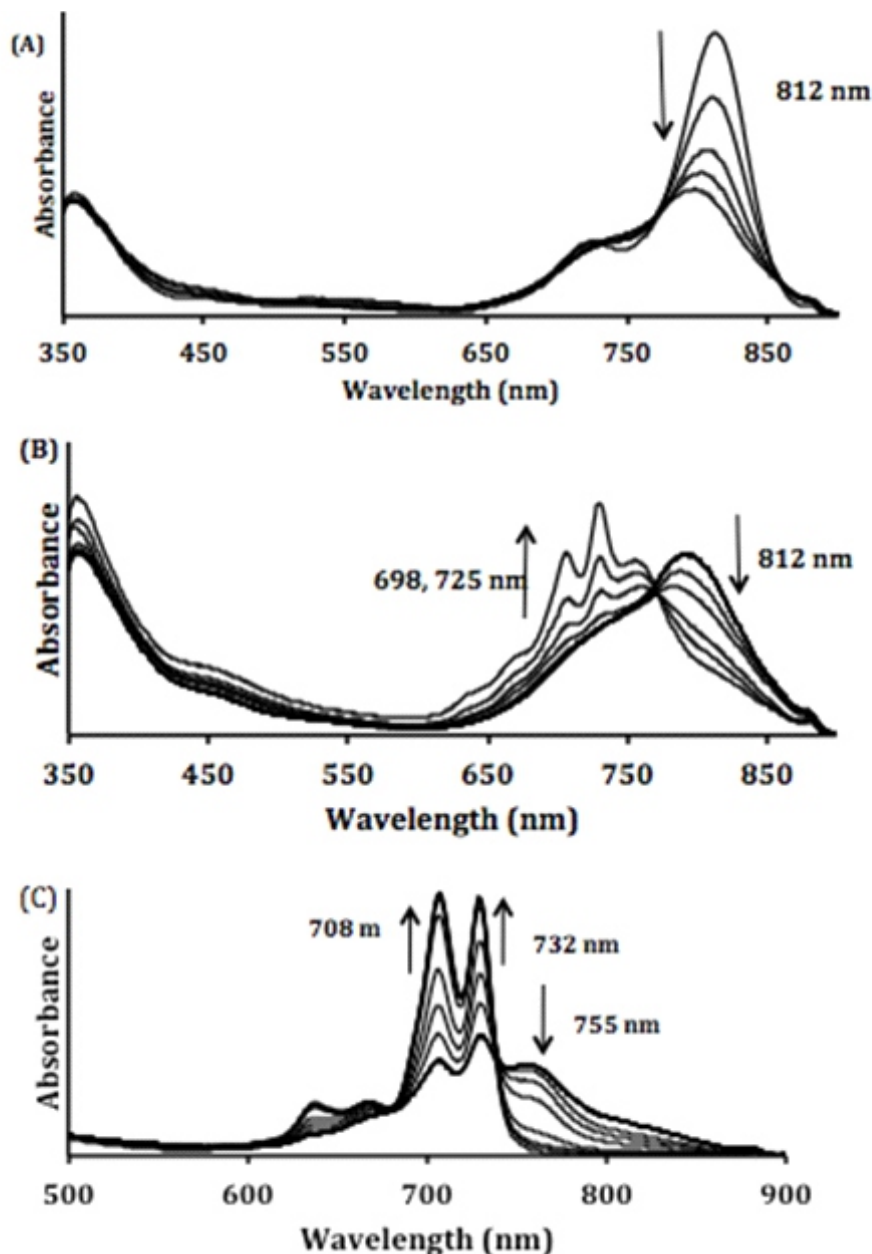
This obtained results illustrated in the sequence number of 5 Pd(II) ions: Four at the periphery and shown in Scheme 2 below accounted for a total one at the cavity.



Scheme 2: Processes involved in Pd(II) coordination to **3a**

**Metal-free 1,4, 8, 11, 15, 18, 22, 25,-octakis (dodecylthio)phthalocyanine( $\text{H}_2\text{ODPc}$ ) (**3b**)**  
The sequence of the coordination reaction of **3b** with Pd(II) ions was similar to what was observed for **3a**. The first stage was the reduction in the intensity of the original at 812 nm suggesting the

coordination of Pd(II) ions (Figure 5A). Following this was the appearance of split Q band suggesting the further coordination to the periphery of the phthalocyanine molecules, while still leaving the cavity empty (Figure 5B



**Figure 5:** UV-Vis spectral changes observed on addition of PdCl<sub>2</sub> in ethanol to complex **3b** (concentration  $\sim 5 \times 10^{-6}$  M) in DCM. The first spectrum in (B) is the same as the last spectrum in (A), the first spectrum in (C) is the same as the last spectrum in (B), and so on.

Further addition of Pd(II) ions led to Figure 4C which was just the complete conversion of the metal-free Phthalocyanines to the peripherally metallated analogue. Further addition did not lead to any change in the spectra. The equilibrium studies for the Pd(II) ions coordination to the

phthalocyanine was carried out using equation 1. This gave an equilibrium constant of  $3.0 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> and  $n$  was found to be 4 (Figure 6). Scheme 3 below is the summary of the coordination sequence for **3b**.

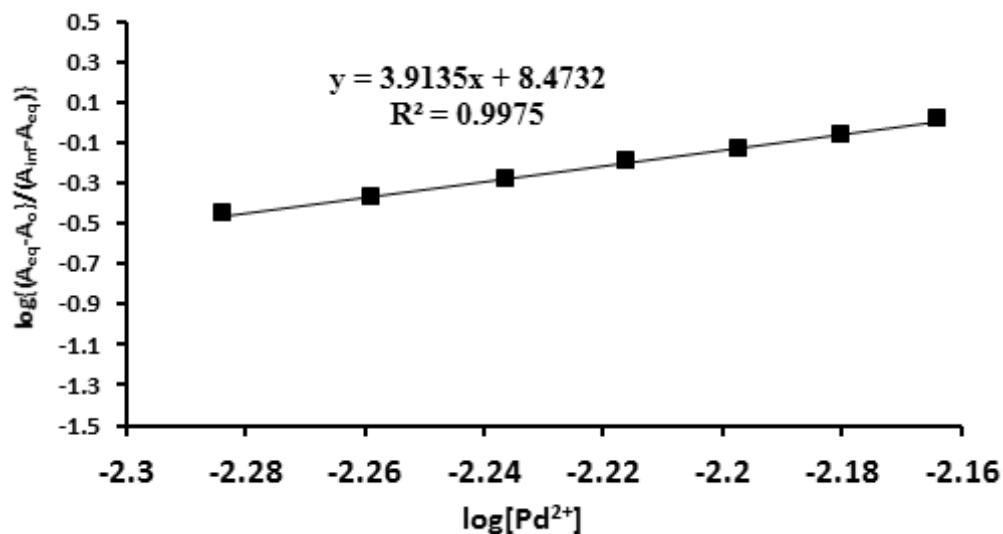
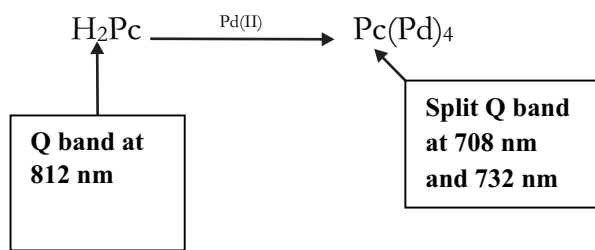


Figure 6: A plot of  $\log\left[\frac{(A_{\text{eq}} - A_o)}{(A_{\infty} - A_{\text{eq}})}\right]$  versus  $\log[\text{Pd}^{2+}]$  for **3b**



Scheme 3: Processes involved in Pd(II) coordination to **3b**

The implication of this is that the coordination in the case of **3b** was complete after the coordination of the Pd(II) ions to the sulphur of the peripheral dodecylthio substituents giving spectrum **4** shown in the highlights of the spectral changes in Figure 7 as the

final spectrum. The insertion of Pd(II) ions into the cavity which was observed in the case of the pentylthio and octylthio-derivatised phthalocyanines (spectrum **5** in Figure 7) did not happen (Ogunbayo and Nyokong, 2009).

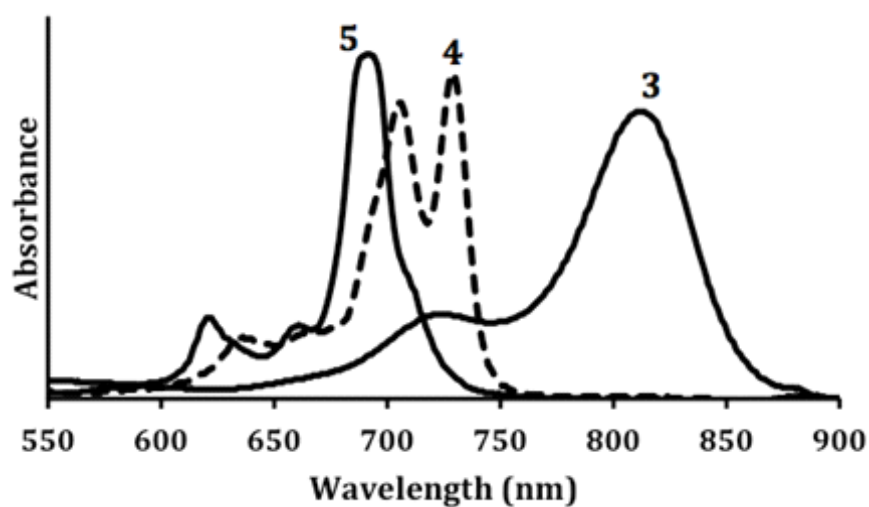


Figure 7: Highlights of the Spectra changes for **3a** and **3b**

This observation is consistent with the equilibrium constant of  $3.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$ , which is lower than  $1.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$  and  $1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$  for **3a** and the pentythio-derivatized respectively (Ogunbayo and Nyokong, 2009). The equilibrium constant of **3b** shows that the reaction is less towards the product, compared to the shorter chain  $\text{H}_2\text{Pcs}$ . This might be the reason for the termination of the reaction after the four Palladium ions were coordinated to the periphery of the phthalocyanines. This clearly demonstrates the impact of chain length on the binding process, with the shorter chain showing a more robust binding process than the longer chain molecule.

## CONCLUSION

Two metal-free octylthio-derivatised phthalocyanines ( $\text{H}_2\text{Pc}$ ) of different chain length were successfully synthesized and characterized. The inclusion of the results obtained from an earlier work on five carbon-chain thio-substituent  $\text{H}_2\text{Pc}$ ,  $\alpha$ -Octasubstituted pentylthio-derivatised Phthalocyanine, allowed a trend to be charted on the effect of chain lengths on the binding sequence and equilibrium constants. There was a correlation among chain length, equilibrium constants and the number of coordinated Pd(II) ions with increasing chain length leading to decreasing equilibrium constant. This shows that the uses of this  $\alpha$ -substituted macrocycles in the extraction and dosimetry of Palladium ions require long chain alkylthio substituents. However, the room temperature synthesis of stable multinuclear Palladium complexes from this procedure will be better carried out with Phthalocyanines with short chain alkylthio substituents since the formation of those products are better favored with decreasing chain length.

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