Synthesis and Pd(II) binding studies of octasubstituted alkyl thio derivatised phthalocyanines

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Abstract

Synthesis and characterization of non-peripherally (4,5) and peripherally (6,7) substituted metal free and Pd octapentylthiophthalocyanine and coordination of palladium ions to these Pcs are reported. The unmetalated complexes (4 and 6) show Pd coordination at the central metal and at the ring. The number of Pd ions bound to complex 4 were found to be five and to complex 6 were three. The equilibrium constant for the binding of Pd to complexes 4 was lower ($K = 1.2 \times 10^9$ dm^3 mol^{-1}) than for complex 6 ($K = 5.7 \times 10^{10}$ dm^3 mol^{-1}).

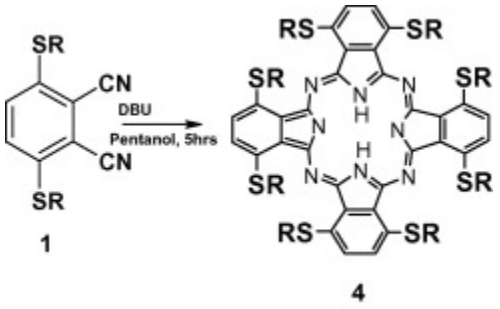
Graphical abstract

Unmetalated octapentylthiophthalocyanine show Pd coordination at the central metal and at the ring, however the nature of the complexes form depends on the point of substitution, peripheral versus non peripheral.

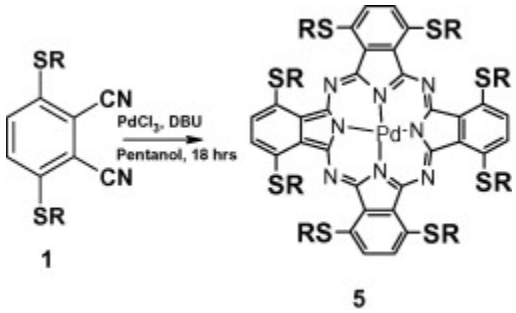
1. Introduction

The study of phthalocyanines has been carried out quite extensively over the past decades. Metallophthalocyanines (MPcs) have diverse applications in many fields of science and as a result they have captivated widespread attention in research. These complexes have been exploited as dyes and pigments and have potential as sensors, in electronic devices, in non-linear optics, Langmuir–Blodgett films and as photosensitizers in photodynamic therapy (PDT) [1], [2], [3], [4], [5], [6] and [7]. Phthalocyanines are generally known to be insoluble in common organic solvents. The solubility of these complexes is improved by introduction of substituents onto the phthalocyanine ring [8], [9] and [10]. The study of the chemistry of palladium phthalocyanines (PdPc) is still limited [11], [12], [13] and [14], hence in this work we report on the interaction of

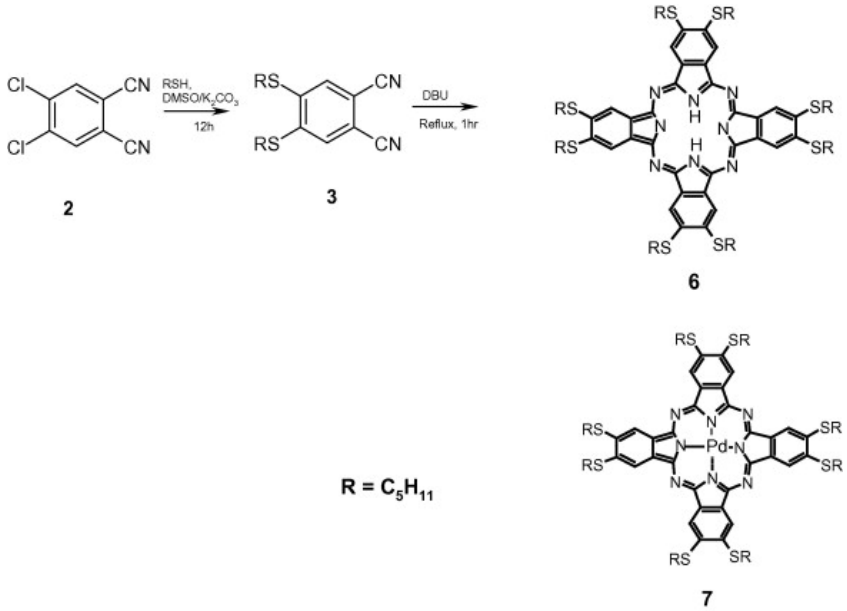
Pd(II) ions with of PdPc derivatives and their unmetalated counterparts (complexes 4–7, Scheme 1, Scheme 2 and Scheme 3).



Scheme 1. Synthesis of metal-free 1,4,8,11,15,18,22,25,-octapentylthiophthalocyanine (4).



Scheme 2. Synthesis of palladium 1,4,8,11,15,18,22,25,-octapentylthiophthalocyanine (5).



Scheme 3. Synthesis of metal-free 2,3,9,10,16,17,23,24,-octapentylthiophthalocyanine (6) and the structure of 7 reported before [24].

Investigation of coordination of various metal ions, including the platinum group metals, by a range of ligands has had extensive attention because of the significance of these reactions in some vital biochemical and chemical processes and various techniques such as linear-dichroic (IR-LD) infrared spectroscopy, nuclear magnetic resonance (^{1}H and ^{13}C NMR), thermogravimetry and differential scanning calorimetry among others were used for structural elucidation [15], [16], [17], [18], [19] and [20]. Metal ion binding studies have also been conducted using various MPcs as ligands, especially those bearing the thio functionality; and the chemical changes accompanying such binding monitored spectrophotometrically. This is due to the optical sensitivity of thio substituted Pcs and MPcs to some metal ions [21], [22] and [23]. The sulfur atoms in thio substituents of MPc can bind metals such as silver(I) and palladium(II). Platinum-group metals are of great economic and environmental concern; they are ranked as priority candidates among metal ions that deserve serious attention in the area of design of effective separation and efficient micro-sensing techniques. Hence the ability of substituted phthalocyanines to chelate palladium deserves exploration. Tetra substituted alkylthio-derivatised MPcs have been investigated in this respect, but such investigations have been hampered by aggregation, which accompanies the metal binding [21], [22] and [23].

The molecular architecture of the phthalocyanines also plays a significant role in the binding process. The point of attachment of the substituents to the ring (α or β) and their relative orientation in space should influence the ease of metal chelation because of the differences in intersubstituent distances. The central metal in the Pc cavity could also have an effect because of its influence on the Pcs symmetry and consequently intersubstituent distances. Reports on the synthesis of alkyl substituted PdPc is still limited and this work reports on the new peripherally and non-peripherally substituted PdPc complexes, their unmetallated conterparts and their use in coordinating Pd ions. The Pc complexes studied are: non-peripherally (5) and peripherally (7) substituted Pd octapentylthiophthalocyanines, and their corresponding unmetallated derivatives (4 and 6). The syntheses of complexes 4 to 6 are reported in this work, complex 7 has been reported before [24]. Even though studies of coordination Ag(II) and Pd (II) ions to alkylthio Pcs has been reported, no data on number of these ions which bind to Pcs is available. Such a study could help in comparing the efficiencies of MPcs in accumulating the metal ions.

2. Experimental

2.1. Materials and equipment

1-Pentanol, dimethylformamide (DMF), pentanethiol, dimethylsulfoxide (DMSO) 1.8-diazabicyclo[5, 4, 0] undec-7-ene (DBU), cerium chloride, potassium carbonates, dichloromethane (DCM), 1-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). 1,2-Dichloro-4,5-dicyanobenzene (2) [25] and [26], 3,6-bis(pentathio)-4,5-dicyanobenzene (1) and 1,2-bis(pentylthiol)-4,5-dicyanobenzene (3) [24] and [27], were synthesised as reported in literature. The synthesis of palladium-2,3,9,10,16,17,23,24,-octakis(pentylthio)phthalocyanine (7) has been reported before [24]. UV–Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer, ^{1}H 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.

2.2. Binding and kinetic studies

For all binding studies, $PdCl_2$ was dissolved in ethanol and the H_2Pc or PdPc complexes in DCM. In order to minimize dilution effects, very small volumes (μl) of the $PdCl_2$ stock solution were added to 2 mL of the Pc solution, and changes were monitored spectroscopically. For kinetic studies, varying concentrations of $PdCl_2$ (0–1×10^{-2} M) in ethanol were added to a fixed concentration (5×10^{-6} M) of the H_2Pc or PdPc derivatives, and the absorbance changes accompanying each addition monitored with time.

For equilibrium studies, the steady increase in absorbance of the Q band of the Pc product formed with increase in Pd (II) ion concentration was noted and used in the determination of the binding constants as well as number of bound Pd (II) ions, according to Eq. (1):

(1)

$$\mathrm{Log}\frac{}{} = \log K + n \log[\mathrm{Pd}]$$

where A_{eq} is the equilibrium absorbance of the Pd-bound Pc (product); A_o, the initial absorbance before the addition of $PdCl_2$, and A_∞, the maximum attainable absorbance of the product. K is the binding constant, and n is the number of bound Pd(II) ions.

The complexes formed by the interaction between Pd(II) and unmetallated complexes 4 and 6 could be isolated by evaporating the solvents (ethanol/DCM) and recrystalyzing in ethanol. Elemental analyses for the complex between Pd and 4:

Anal. Calc. for $C_{72}H_{98}N_8S_8(PdCl_2)_4$): C, 41.81; H, 4.80; N, 5.48. Found: C, 40.90; H, 4.92; N, 5.57%.

Elemental analyses for complex between Pd and 6:

Anal. Calc. for $C_{72}H_{98}N_8S_8(PdCl_2)$: C, 52.79; H, 5.86; N, 7.04. Found: C, 52.07; H, 5.94; N, 6.93%.

2.3. Synthesis

2.3.1. Metal-free1,4,8,11,15,18,22,25,-octakis(pentylthio)phthalocyanine (4), Scheme 1

In refluxing pentanol (10 ml), 3,6-bis(pentathio)-4,5-dicyanobenzene (1) (0.5 g, 1.5 mmol) and DBU (1.70 g, 11.17 mmol) were added. The solution was heated to reflux for 5 h. 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 4. Yield: 0.18 g (37%), UV/Vis [(CNP, λ_{max}/nm, (log ε)] 813 (5.05), 719 (3.5). *Anal.* Calc. for $C_{72}H_{98}N_8S_8$: C, 64.80; H, 6.87 N, 8.01, S, 20.32. Found: C, 64.87; H, 7.47, N, 7.71, S, 20.44%. ^{1}H NMR (400 mHz); δ ppm; ($CDCl_3$), 8.00 (8H, s, H_{arom}), 3.32–3.35 (16H, t, Ar–SCH_2–), 2.15–2.00 (16H, m, Ar–SCH_2–CH_2–), 1.65–1.2 (32H, m, $H_{aliphatic}$), 1.00–0.80 (24H, t, CH_3); [IR (KBr pellets) ν_{max}/cm^{-1}]; 1320, 1278, 1217, 1186, 1142, 1077, 939, 808, 736, 668 (C–S–C), 577, 499, 418; 3057 (N–H), 2953 (C–H), 2922 (C–H), 2358, 2336, 1865, 1791, 1730, 1652(C═N), 1556, 1538,1505, 1456.

2.3.2. Palladium-1,4,8,11,15,18,22,25,-octakis(pentylthio)phthalocyanine (5), Scheme 2

In refluxing pentanol (10 ml), 3,6-bis(pentathio)-4,5-dicyanobenzene (1) (0.5 g, 1.5 mmol), $PdCl_2$ (0.12 g, 0.75 mmol) and DBU (1.70 g, 11.17 mmol) were added. Reflux was continued for a further 18 h. Reaction was then cooled down 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 5. Yield: 0.12 g (40%), UV/Vis [CNP, λ_{max}/nm, (log ε)] 750 (4.5), 679 (4.11). *Anal.* Calc. $C_{72}H_{96}N_8PdS_8$: C, 60.20; H, 6.74; N, 7.80. Found: C, 59.63; H, 6.87; N, 7.51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.71 (8H, s, Ar–H), 4.10 (16H, s, S–CH_2), 1.52–1.21 (48H, m, –$(CH_2)_3$), 1.21–0.92 (24H, m, –CH_3);[IR (KBr pellets) ν_{max}: 2929, 2859, 1732, 1650(C═N), 1572, 1466, 1338, 1293, 1236, 1163, 941, 799, 750, 650(C–S–C).

2.3.3. Metal-free 2,3,9,10,16,17,23,24,-octakis(pentylthio)phthalocyanine (6)

Compound 3 (0.5 g, 0.95 mmol) was heated in pentanol (5 ml) in the presence of DBU (1.66 ml, 1 mmol) with stirring and heated under reflux for 1 h in a nitrogen atmosphere. After cooling, the dark green product was precipitated with methanol, filtered and then purified using silica gel packed column chromatography with DCM as eluent. Yield: 0.37 g (74%), UV/Vis [(CNP, λ_{max}/nm, (log ε)] 737 (5.12), 710 (5.04), 673 (4.51), 640 (4.40), 457 (4.43). *Anal.* Calc. for $C_{72}H_{98}N_8S_8$: C, 64.80; H, 6.87 N,8.01, S, 20.32. Found: C, 65.93; H, 7.75, N, 6.16, S,19.91%. ^{1}H NMR (400 mHz); δ ppm ($CDCl_3$) 8.37 (8H, s, H_{arom}), 3.44–3.40 (16H, s, Ar–SCH_2–), 2.14–2.09 (16H, q, Ar–SCH_2–CH_2–), 1.82–1.78 (16H, q, $H_{aliphatic}$), 1.66–1.60 (16H, q, $H_{aliphatic}$), 1.31–1.22 (24H, t, CH_3–);

[IR (KBr pellets) ν_{max}/cm^{-1}]; 3449 (N–H), 2957, 2926, 2858 (C–H), 1648(C═N), 1592, 1507, 1461, 1400, 1325, 1325, 1073, 1026, 935, 868, 749, 681 (C–S–C).

3. Results

3.1. Synthesis and characterization

The syntheses of complexes 4–6 were achieved by treating the corresponding phthalonitriles (1 or 3) with palladium chloride in 1-pentanol for complex 5, Scheme 2 or with DBU only for unmetalated complexes 4 and 6, Scheme 1 and Scheme 3, respectively. Column chromatography with silica gel was employed to obtain the pure products. The MPc derivatives were characterized by UV–Vis, IR and NMR spectroscopies, and elemental analyses. The analyses were consistent with the predicted structures. The sharp peak for the C≡N vibrations in the IR spectra of phthalonitriles 1 or 3 at ~2200 cm^{-1} disappeared after conversion into phthalocyanines and there was appearance of a C═N band at 1652, 1650 and 1645 cm^{-1} for 4, 5 and 6, respectively. The phthalocyanines showed vibrations due to C–S–C group between 650 and 688 cm^{-1}.

The ^1H NMR spectra of MPc derivatives in $CDCl_3$ showed all the substituent and Pc ring protons in their respective regions, Fig. 1. A singlet, assigned to Pc aromatic ring protons, appeared in the range 8.00–8.71 (integrating for 8 protons) in the ^1H NMR spectra of 4–6. The S–CH_2 protons were observed between 3.32 and 4.10, integrating for a total of 16 protons for each complex (4–6). The rest of the aliphatic protons were observed between 1.2 and 2.15 intergrading for 48 protons for each complex (4–6). The methyl protons occurred between 0.8 and 1.31 intergrading for 24 protons. The cavity protons of the unmetalatted phthalocyanines [4 and 6] were not observed due to aggregation of the molecules in $CDCl_3$.

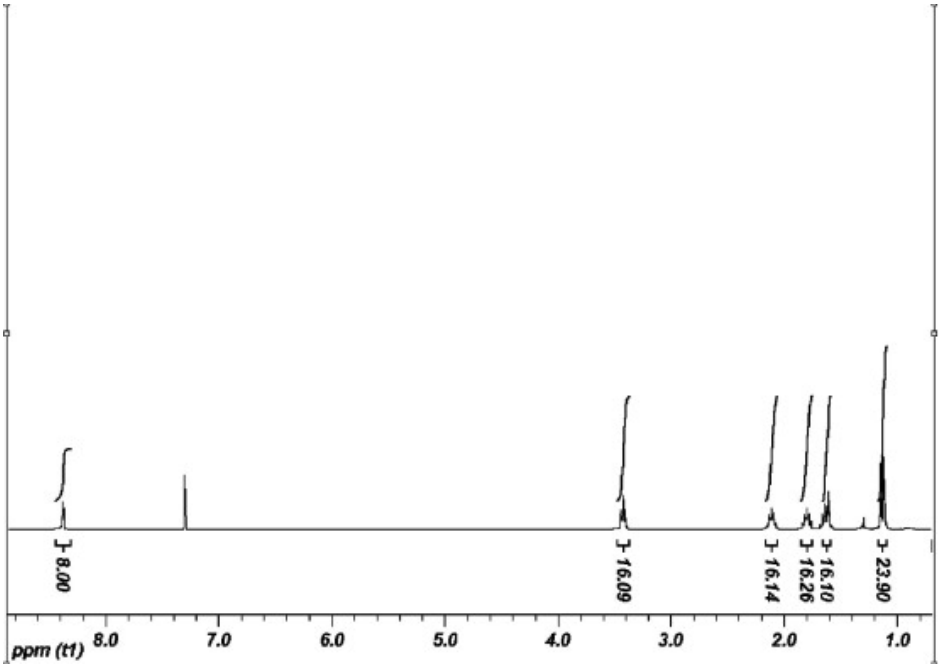


Fig. 1. ^{1}H NMR spectrum of 6 in $CDCl_3$.

Pcs exhibit limited solubility in most solvents but substitution at the peripheral (β) and non-peripheral (α) positions allows for improved solubility [28]. Non-peripheral substitution in Pcs has been reported to result in higher solubility in comparison with peripheral substitution [29]. Fig. 2a shows the ground state electronic absorption spectra of 4 and 6 in DCM, while the spectra of 5 and 7 in the same solvent are shown in Fig 3a. It can be observed from these figures that the spectra of the non-peripherally substituted complexes: 4 and 5, are significantly red-shifted relative to those of their peripherally substituted counterparts, as expected. The red shifting for non-peripherally substituted derivatives is attributed to greater electron density enhancement caused by substitution at the non-peripheral substitution compared with that at the peripheral position. The Q band for 4 is observed at 801 nm in DCM. For 6, the components of the split Q band are observed at 698 and 730 nm in DCM. The spectrum of 4 does not show the typical split Q band expected for unmetalated phthalocyanines; it is known that the resolution of the split of the Q band decreases with increasing wavelength [30], hence for 4, the large red shift must have resulted in an unsplit Q band. The Q bands for the metallated derivatives 5 and 7 are observed at 747 and 693 nm, respectively in DCM (Fig. 3a). The spectra for all complexes are broad in DCM, suggesting aggregation in this solvent. DCM is a non-coordinating solvent; hence it lacks the capacity to prevent π–π stacking of the PdPc units. Fig. 2 and Fig. 3b, respectively show the ground state absorption spectra of 4 and 6, and 5 and 7 in CNP. The spectra in CNP are narrower than those in DCM for both the metallated (5,7) and unmetalated (4,6) derivatives, which is ascribed to the lower tendencies of the complexes to aggregate in CNP. However, complex 5 still shows broad spectrum in CNP. Aggregation in Pcs is usually depicted by broadening

and/or splitting of Q band, indicating the presence of additional electronic levels of aggregates. Beer–Lambert law was obeyed for the complexes in CNP, even for concentrations less than 1×10^{-5} mol dm^{-3} (Fig. 4a). However in DCM, Beer–Lambert law was obeyed only at lower concentrations (>1×10^{-6} mol dm^{-3}), confirming the presence of aggregates. The Q band maxima of the Pcs are red shifted in CNP compared to DCM. In CNP, the Q band for 4 was at 813 nm compared to 801 nm in DCM, while the split Q band of 6 appeared at 707 and 736 nm in CNP compared to 693 and 731 nm in DCM. The Q band for 5 appears at 750 nm while that of 7 appears at 699 nm in CNP. Aromatic solvents have been known to result in red shift of the Q band in phthalocyanine complexes [31], hence the observed red shift in CNP. The observed spectral red-shifts in CNP relative to those in DCM could also be interpreted in terms of the higher refractive index of CNP [31].

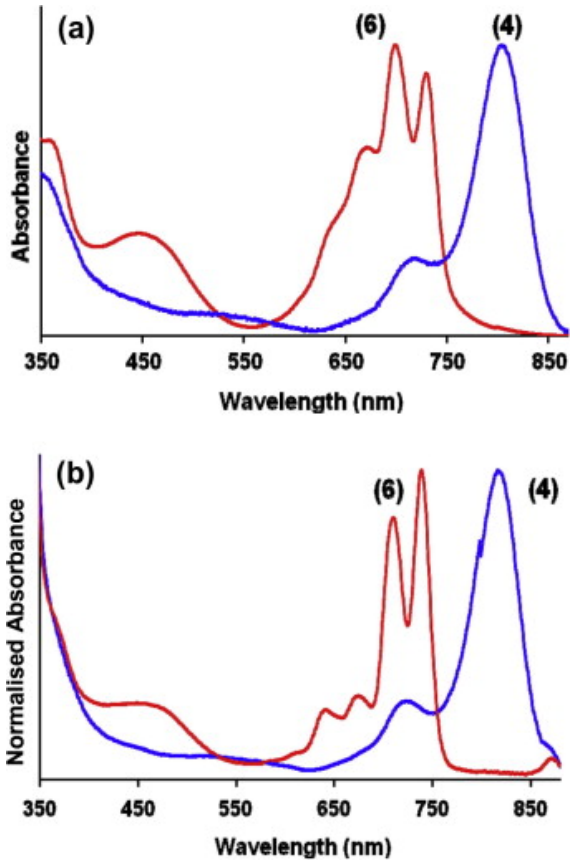


Fig. 2. Electronic absorption spectra of 4 and 6 in (a) DCM and (b) CNP. Concentration ~1×10^{-5} M.

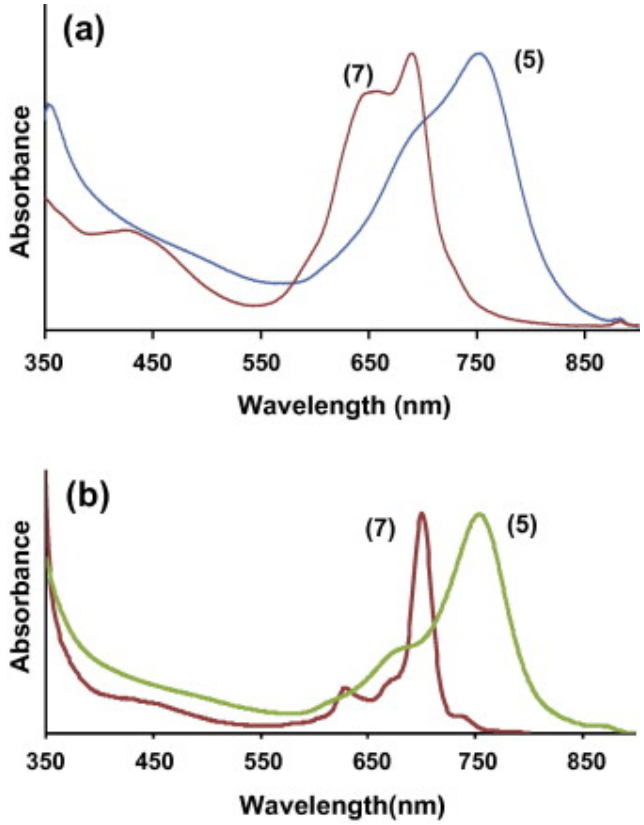


Fig. 3. Electronic absorption spectra of 5 and 7 in (a) DCM (b) CNP. Concentration ~1 × 10^{-5} M.

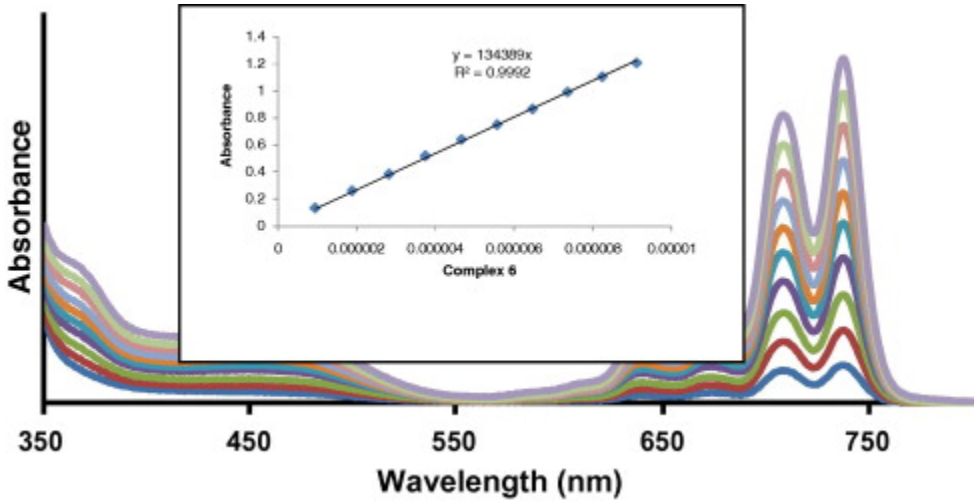


Fig. 4. (a)Absorption spectra of compound 6 in CNP at different concentrations. Inset: Beer–Lambert Plot.

3.2. Pd(II) binding to Pcs

3.2.1. Metal-free 1,4,8,11,15,18,22,25,-octapentylthiophthalocyanine (4)

It is possible that binding of Pd(II) to complex 4 and 6 will occur at the thio groups or at the central core of the Pc skeleton. On addition of Pd(II) to a solution of 4, spectral changes shown in Fig. 5 were observed. The first part shown in Fig. 5a consists of a decrease in the Q band intensity (at 801 nm in DCM) accompanied by broadening and the shift of the band to high energy (754 nm). These spectral changes are consistent with formation of aggregates observed on metal binding in thio substituted MPc complexes [21]. The lack of clear isosbestic points, suggests that there may be more than two species in solution. Higher aggregates could also be present in solution. Further addition of Pd(II) resulted in spectral changes shown in Fig. 5b, which consist of the decrease in the broad peak at 754 nm and the formation of a split peak with maxima at 708 and 732 nm. The observed split in Q band suggests that a PdPc complex has not formed yet and the complex is still H_2Pc with Pd(II) ions coordinated to the pentylthio groups or the PdPc complex has formed with unsymmetrical substitution of Pd ions on the ring. Further addition of $PdCl_2$ resulted in the formation of a new band at 693 nm and the gradual disappearance of the split Q band (Fig. 5c and d). Elemental analysis confirmed to binding of four Pd(II) ions at this stage, see Section 2 for the data. The ^1H NMR spectra of the complex isolated at this stage showed a change in chemical shift of the protons relative to what obtained in the original ligand (4), the most conspicuous shift being the macrocyle protons indicating a change in electron distribution [15], [18] and [20]. The singlet peak shifted downfield from 8.00 to 8.30 ppm which indicated higher resonance of the ring protons due to desheilding effect that resulted from reduced mesomeric effect of the sulfur lone pairs of electrons on the ring when part of those lone pairs were used in coordination with Pd ions. The IR spectrum of this complex also showed a dramatic change compared with that of 4. The bands between 1000 and 600 cm^{-1} showed conspicuous split, especially at 939, 808, and 736 cm^{-1}.

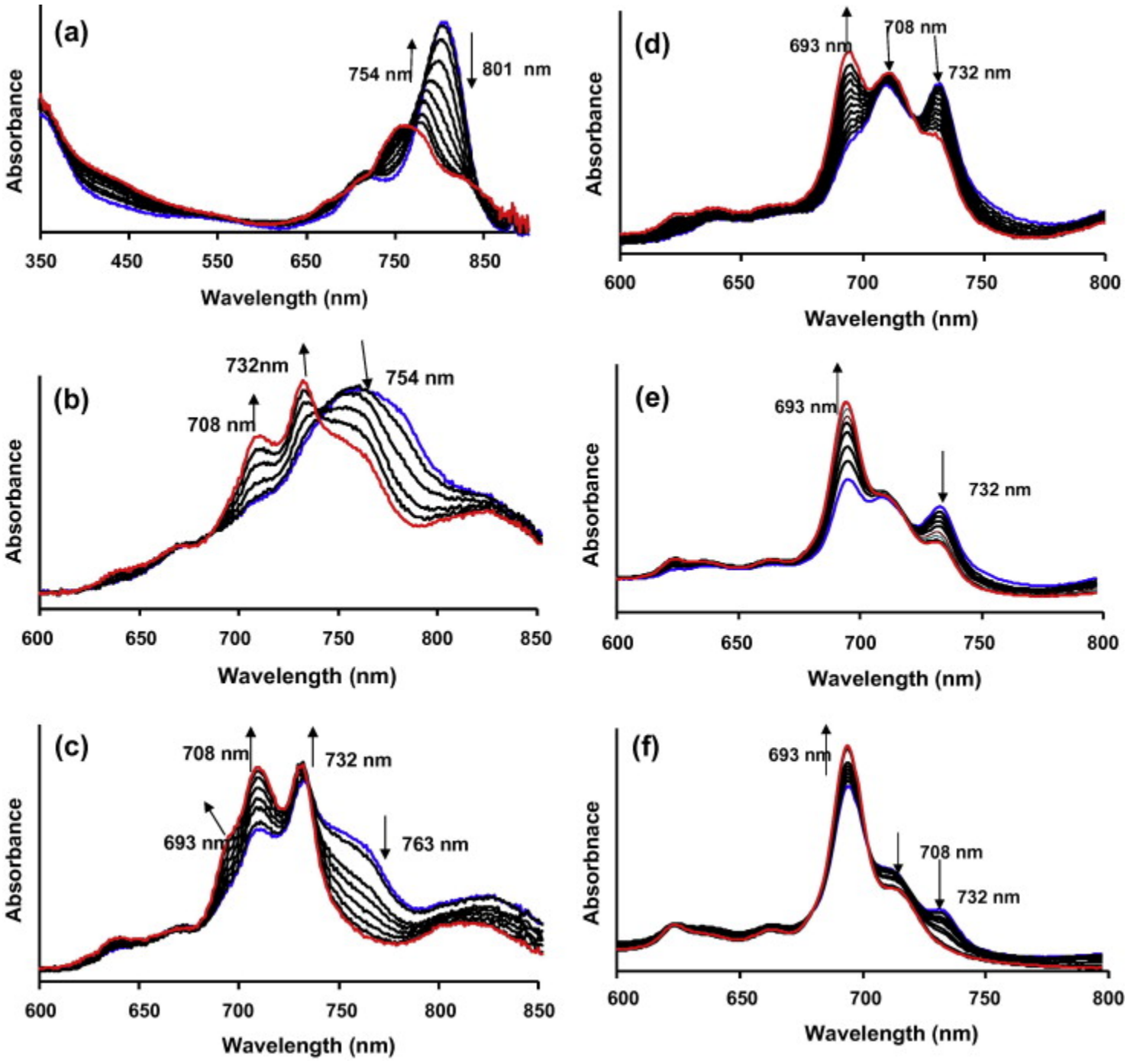


Fig. 5. UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to complex 4 (concentration = 5×10^{-6} M) in DCM. Concentration of $PdCl_2$ (a) 6.5×10^{-4}–3.05×10^{-3} M (b) $3.05\ 10^{-3}$–7.20×10^{-3} M (c) 7.20×10^{-3}–1.0×10^{-2} M (d) 1.0×10^{-2}–1.18×10^{-2} M (e) 1.18×10^{-2}–1.32×10^{-2} M (f) 1.32×10^{-2}–1.5×10^{-2} M. 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.

A gradual disappearance of the split Q band and the appearance of a new single Q band that was blue shifted compared to the original split Q band were observed on further addition of Pd(II) ions, Fig. 5e. The final spectrum in Fig. 5f is typical of a metallated phthalocyanine complex [32], and suggests the formation of a symmetrically substituted PdPc complex. No further spectral changes were observed on addition of more Pd ions.

The equilibrium studies for the binding of Pd(II) ions to complex 4, were carried out for using Eq. (1). A plot $\log[(A_{eq}-A_o)/(A_\infty-A_{eq})]$ versus $\log[Pd^{II}]$ (Fig. 6), gave an equilibrium constant of $K = 1.2 \times 10^9$ dm^3 mol^{-1} and n of 5, thus showing that five Pd(II) ions are coordinated to the to the Pc at the end of the reaction.

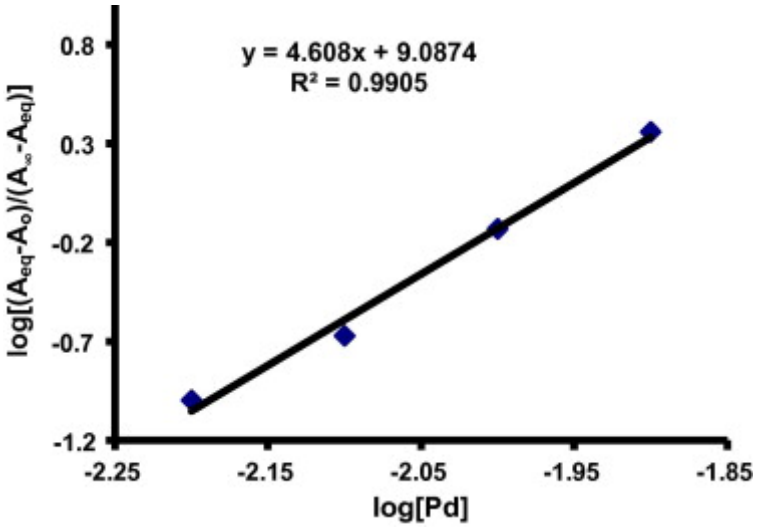


Fig. 6. Plot of $\log[(A_{eq}-A_o)/(A_\infty-A_{eq})]$ versus $\log[Pd^{II}]$ for complex 4 in DCM.

When a large excess of $PdCl_2$ was added to 4, spectral changes shown in Fig. 7 were observed, these consisted of direct formation of the final spectrum in Fig. 5f. These changes occurred with time allowing for the calculation of rate constants assuming first order kinetics since Pd(II) is in excess. The rate constants were obtained by first plotting absorbance versus time for each concentration of Pd(II) (ranging from 1.5×10^{-3} to 5.0×10^{-3}) to obtain initial rates, the latter were then plotted against [Pd(II)] (Fig. 7 inset) to get the rate constant from the slope using least square analysis. The value of the rate constant was 1.38×10^{-5} dm^3 mol^{-1} s^{-1}. When low concentrations ($<1 \times 10^{-4}$ M) of Pd(II) ions were employed for complex 4, changes with time observed in Fig. 7 were not observed probably due to the slow nature of the spectral changes.

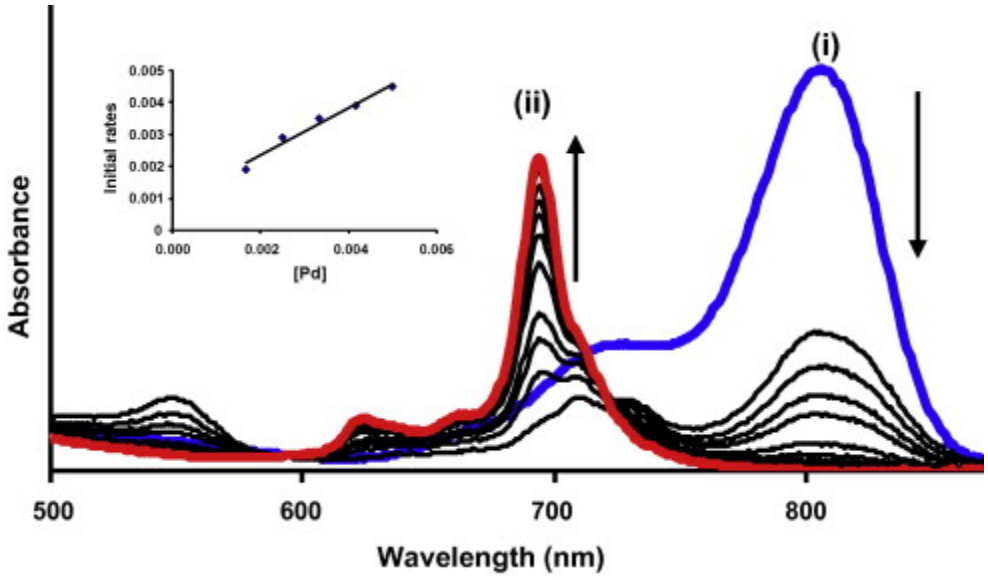


Fig. 7. UV–Vis spectral changes observed on addition of excess $PdCl_2$ in ethanol (concentration = 3×10^{-3} M) to a solution of complex 4 (1×10^{-5} M) in DCM. (i) before and (ii) after addition of $PdCl_2$. Inset: Plot of initial rates versus the concentration Pd.

.2.2. Metal-free 2,3,9,10,16,17,23, 24,-octapentylthiophthalocyanine (6)

The spectra generated on the addition of Pd(II) ions to complex 6 are shown in Fig. 8. For 6, The Q band is split since this complex is blue shifted compared to 4. Non-peripherally substituted MPc complexes show more red shifting compared to peripherally substituted. The absorption spectrum of the Pc before the addition of Pd(II) ions is shown in Fig. 8a(i). With the addition of Pd(II) ions the intensity of the peaks at 693 and 731 nm decreased and a new single peak appeared at 714 nm (Fig. 8a(ii)). This spectrum resembles that of MPc suggesting the insertion of the metal into the center of the Pc ring. The spectral changes could not be due to symmetric substitution of the Pd ions on the ring since a split Q band would still be observed. The ^{1}H NMR spectra of the complex formed here also show change in chemical shift of some of the peaks due to change in electronic distribution of the complex on coordination with Pd ions. The aromatic and S–CH_2 protons did not show significant shift while the aliphatic and methyl protons were observed as mutiplets and triplets at 1.24–1.19 ppm and 1.08–0.91 ppm integrating to 48 and 24 protons respectively. Elemental analysis of the complex at this stage confirmed the coordination of one Pd(II) ion, most probably into the center of the ring hence no splitting in the Q band. The same type of spliting that was observed in the IR spectrum of 4 was also noticed in the spectrum of 6 at 935, 868 and 749 cm^{-1}.

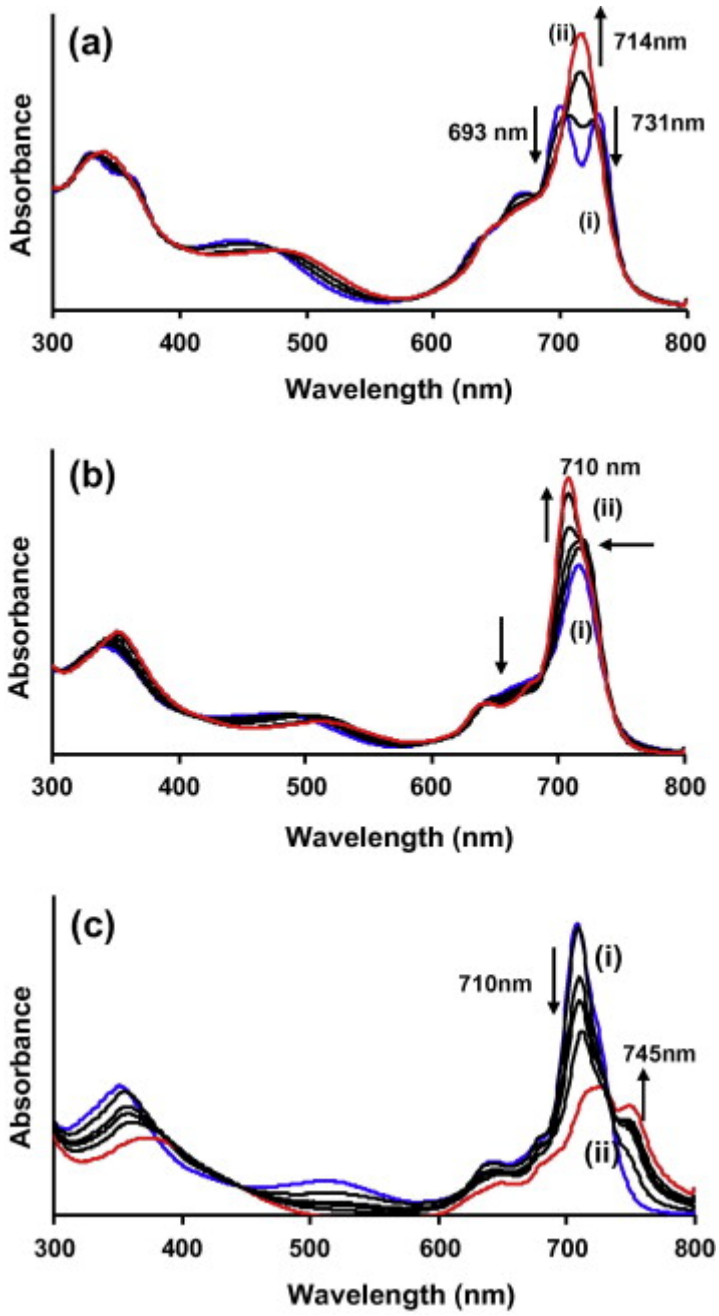


Fig. 8. UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to complex 6 (concentration = 5×10^{-6} M) in DCM. Concentration of $PdCl_2$ (a) 4.00×10^{-4}–4.61×10^{-4} M, (b) 4.61×10^{-4}–5.06×10^{-4} M, (c) 5.06×10^{-4}–5.5×10^{-4} M. The first spectrum in (b) is the same as the last spectrum in (a), the first spectrum in (c) is the same as the last spectrum in (b).

Further addition of Pd(II) ions resulted in increase in the intensity accompanied by blue-shifting of the peak at 714 nm (Fig. 8b) to 710 nm. The blue shifting is as a result of the binding of Pd(II) ions to the peripheral sulfur, which engages the lone pair of electrons on sulfur and therefore cancels their mesomeric contribution to the ring electron density. As the addition of Pd(II) ions continued the broad peak around 710 nm started disappearing and

a split band emerged at 720 and 745 nm as shown in Fig. 8c. This spectroscopic response might be due to unsymmetric substitution of Pd(II) ions. As was the case with complex 4, no further spectral changes were observed on addition of more Pd ions. The number of Pd(II) ions bound to the Pc and equilibrium constant was determined for complex 6 using Eq. (1) and Fig. 9.

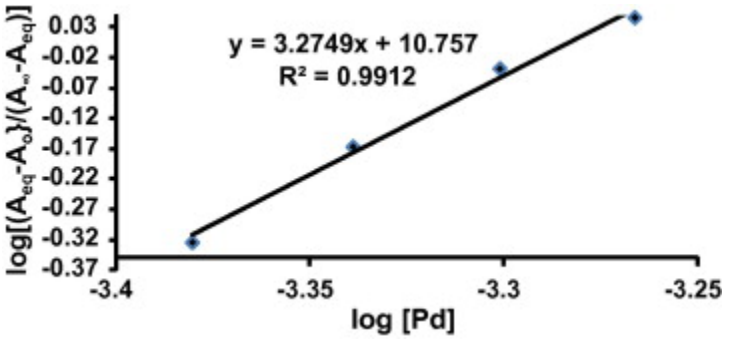
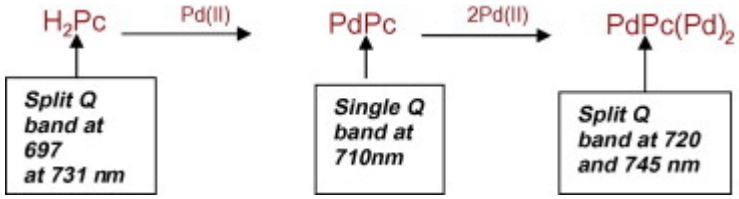


Fig. 9. Plot of $\log[(A_{eq}-A_o)/(A_\infty-A_{eq})]$ versus $\log[Pd^{II}]$ for complex 6 in DCM.

plot $\log[(A_{eq}-A_o)/(A_\infty-A_{eq})]$ versus $\log[Pd^{II}]$ (Fig. 9), gave an equilibrium constant of $K = 5.7 \times 10^{10}$ dm^3 mol^{-1} and n of 3 for complex 6, thus showing that three Pd(II) ions are coordinated to the to the Pc at the end of the reaction. Probably the two at the periphery coordinated to adjacent sulfur instead of opposite ones giving rise to the loss of symmetry. The possible processes occurring during the addition of Pd ion to solutions of complex 6 are shown by Scheme 4.The nature of Pd(II) binding differ between complexes 4 and 6 in that in 4, five Pd ions are coordinated, while for complex 6 three Pd ions are coordinated. The differences in the binding abilities of the two compounds (4 and 6) could be due to accessibility of binding sites. Also the modes of coordination of Pd(II) ions may be different for peripherally (6) and non-peripherally (4) substituted complexes since in the latter there is a possibility of coordination between pentylthio groups on adjacent benzene groups.



Scheme 4. Possible processes involved in Pd(II) coordination to 6.

3.2.3. Palladium octapentylthiophthalocyanine complexes 5 and 7

Both 4 and 5 are non-peripherally substituted, however 5 has a central Pd(II) ion unlike 4 which is unmetalated. The same applies to 6 and 7, which are both peripherally substituted, but the latter has a central Pd(II) ion and the former is unmetalated.

Fig. 10a(i) shows the spectra of 5 before and after addition of Pd(II) ions. On addition of Pd(II) ions, reduction in intensity coupled with blue shifting from 750 to 718 nm of the Q band was observed (Fig. 10a(ii)). Effect of

further addition of Pd(II) ions is depicted in Fig. 10(b), and consists of continued blue-shifting of the Q band from 718 to 695 nm and there is narrowing of the Q band and its increase in its intensity. The continuous shift towards the blue is consistent with the engagement of S lone pairs in the substituents, thereby reducing the ring electron density and consequently causing the blue shift. The Q band maximum at 695 nm is similar to the final spectrum obtained for 4 following addition of Pd(II) ions (Q band at 693 nm), suggesting that the final complexes are the same.

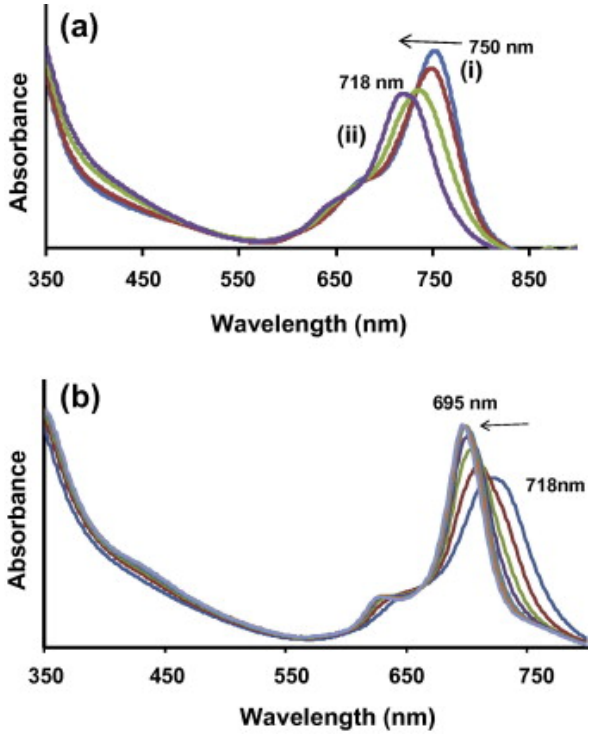


Fig. 10. UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to complex 5 (concentration = 5×10^{-6} M) in 1-chloronaphthalene. Concentration of $PdCl_2$ (a) 9.00×10^{-5}–4.00×10^{-4} M (b) 4.00×10^{-4}–1.5×10^{-3} M. The first spectrum in (b) is the same as the last spectrum in (a).

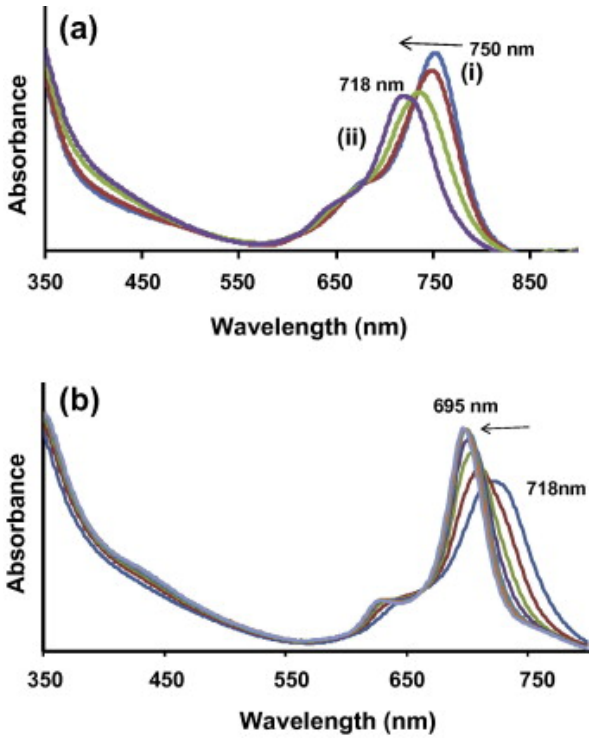
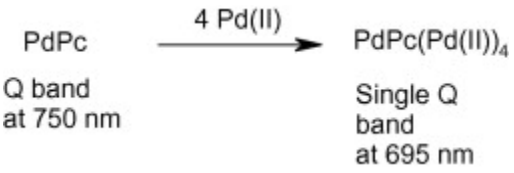


Fig. 10. UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to complex 5 (concentration = 5×10^{-6} M) in 1-chloronaphthalene. Concentration of $PdCl_2$ (a) 9.00×10^{-5}–4.00×10^{-4} M (b) 4.00×10^{-4}–1.5×10^{-3} M. The first spectrum in (b) is the same as the last spectrum in (a).

The possible processes occurring during the addition of Pd(II) ion to solutions of complex 5 are shown by Scheme 5.



Scheme 5. Possible processes involved in Pd(II) coordination to complex 5.

A plot $\log[(A_{eq}-A_o)/(A_\infty-A_{eq})]$ versus $\log[Pd^{II}]$ for 5 (Fig. 11), gave an equilibrium constant of $K = 1.66 \times 10^{13}$ dm^3 mol^{-1} and n of 4, thus showing that 4 Pd(II) ions are coordinated to the to the Pc at the end of the reaction, with the equilibrium favouring the formation of the complex with four Pd(II) ions coordinated all at the ring in a symmetrical fashion since the Q band of the final spectrum is not split.

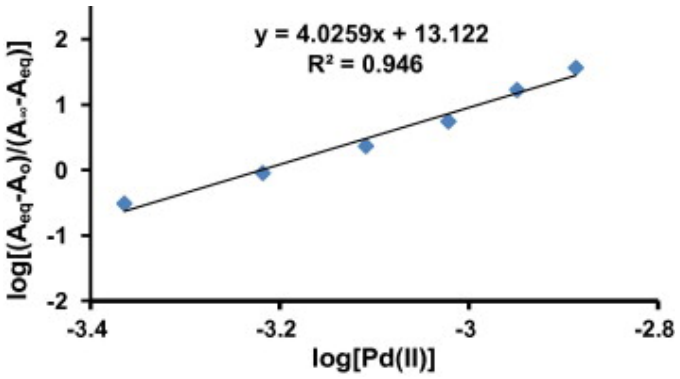


Fig. 11. Plot of $\log[(A_{eq}-A_o)/(A_\infty-A_{eq})]$ versus $\log[Pd^{II}]$ for complex 5 in CNP.

For complex 7 which is peripherally substituted, Fig. 12a and 12b show that on titration with Pd(II) ions, the final spectrum shows a split Q band, suggesting unsymmetrical substitution by the Pd(II) ions as was the case with 6, which is also peripherally substituted. Thus the point of substitution (peripheral or non-peripheral) determines the nature of binding (symmetrical or non-symmetrical) of Pd(II) ions to the MPc complexes.

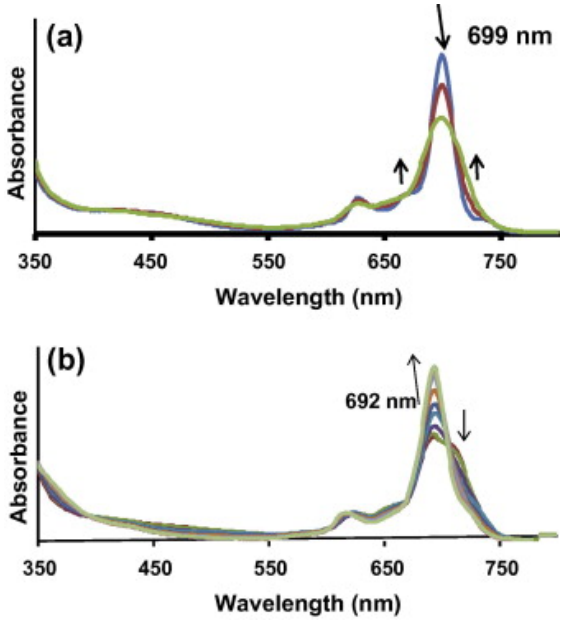


Fig. 12. UV–Vis spectral changes observed on addition of $PdCl_2$ in ethanol to complex 7 (concentration = 8×10^{-6} M) in 1-chloronaphthalene. Concentration of $PdCl_2$ (a) 3.00×10^{-5}–2.50×10^{-4} M (b) 2.50×10^{-4}–1.5×10^{-3} M. The first spectrum in (b) is the same as the last spectrum in (a).

4. Conclusions

Octasubstituted pentylthio derivatised phthalocyanines have been employed for the binding of Pd(II) binding. Each of the complexes gave a distinct spectroscopic response. Only three Pd ions could be bound to 6, while for 4

five Pd ions could be bound. The final spectra for Pd(II) binding to 4 is similar to the spectra for coordination of Pd(II) to the corresponding 5 showing that similar complexes are formed. For complexes 6 and 7, the final spectrum is split. The observed results show that the molecular architecture and symmetry play vital roles in the binding process and the nature of the final product.

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