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Synthesis and characterization of tetra-substituted palladium phthalocyanine complexes

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ABSTRACT

Tetra-substituted palladium phthalocyanine complexes with different electron withdrawing and electron donating substituents (–H, –NO_2, –NH_2, –Cl, –COOH, aryl thio) have been synthesized with a good yield. The synthesized complexes were characterized using XPS, UV–Vis, IR, Raman, XRD, TGA and electrochemistry. The XPS spectra show that the central metal ion is in the +2 state, while the UV–Vis spectra demonstrate split absorption peaks in the Q-band region 600–700 nm due to the presence of dimeric and oligomeric molecules in addition to the monomeric species. The UV–Vis and Raman spectra demonstrate a shift in the peaks/bands which is a result of the electron withdrawing and electron donating substituents at the periphery of the benzene ring compared to the parent palladium phthalocyanine. The thermogravimetic stability studies show that these complexes undergo two separate decomposition processes. The thermal stability for different complexes are in the order: PdPc < PdTPSPc < PdTClPc < PdTAPc < PdTCAPc = PdTNPc, indicating that the substituents at the periphery have an effect on the thermal stability. The cyclic voltammetric data in DMSO show that the central metal ion Pd does not undergo a redox process and the redox behaviour observed is mainly due to the macrocyclic ring reduction process.

1. Introduction

Phthalocyanines are a class of N_4-macrocycles known for their very interesting industrial applications due to their high stability, architectural flexibility, diverse coordination properties, good spectroscopic characteristics, rich and reversible redox chemistry. They are extensively used in the field of dyes, semiconductors, catalysis, linear optics, electrochromics, photovoltaic cells, liquid crystals, etc [1–3].

The functions of phthalocyanine derivatives are almost all based on their electron transfer reactions, because of their π-electron conjugated ring system. The physicochemical properties of the phthalocyanines can be fine-tuned by changing the central metal ion and also by changing the substituents at the periphery of the benzene rings. The substitution of functional groups at the periphery of benzene ring is advantageous because it gives flexibility in solubility and also efficiently tunes the colour of the material. Substitution of functional groups also changes the electron density of the macrocycle and finds its use in various fields. Tetra-substituted phthalocyanines tend to be more soluble and stable corresponding to their respective octa and higher-substituted complexes due to the possible formation of constitutional isomers and the dipole moment results from the unsymmetrical arrangement of the substituents [4–6].

Phthalocyanines can be tailored such that they consist of certain properties which are required for different methodologies such as electrodeposition, electropolymerization, Langmuir–Blodgett, self assembly, stabilizing of nanoparticles which finds numerous applications in catalysis, sensing and molecular electronics [1–3]. The stability and electron transfer abilities are the main key factors to determine the functionality of a material. The majority of literature on phthalocyanines includes studies on the central metal ion as first-row transition metal and lanthanide ion [1–6]. There is no systematic study on the synthesis of phthalocyanines with different electron withdrawing and electron donating substituents and characterization with third-row transition elements.

Palladium and its complexes are known to be very good catalysts in homogeneous and heterogeneous catalysis [7–10]. It can be believed that the combined effect of the metal ion palladium and the phthalocyanine macrocycle, the catalytic and sensing activity of palladium phthalocyanine complexes will be enhanced to a larger extent. Information about the synthesis of palladium phthalocyanine complexes, however, is very meagre in the literature [11,12]. Research has been focused on the electrochemical characterization

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of some palladium phthalocyanine complexes [13–16], however, to our best knowledge there is no literature available for the synthesis of palladium phthalocyanine complexes with different electron donor and acceptor substituents.

This paper deals with a spectroscopic, thermal and electrochemical characterization of newly synthesized palladium phthalocyanine complexes, which contain different electron withdrawing and electron donating substituents, including nitro, amine, chloro, carboxyl and thio aryl compounds. An effort has been made to discuss the effect of substituents on the optical, thermal and electrochemical behaviour of these complexes.

2. Experimental section

2.1. Materials

Precursors phthalonitrile ($C_6H_4(CN)_2$) (99%), 4-nitrophthalonitrile ($C_6H_4(CN)_2(NO_2)$) (99%) and trimellitic anhydride ($C_9H_4O_5$) (98%) were purchased from Sigma Aldrich and used as such without any purification. Palladium chloride ($PdCl_2$), sodium sulphide nonahydrate ($Na_2S\cdot 9H_2O$), sodium nitrite ($NaNO_2$), cuprous chloride (CuCl), urea ($CO(NH_2)_2$), ammonium chloride (NH_4Cl), ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), thiophenol ($C_6H_5SH$), potassium carbonate ($K_2CO_3$), nitrobenzene ($C_6H_5NO_2$), methanol ($CH_3OH$), ethanol ($C_2H_5OH$), tetrahydrofuran (THF), acetone (CH_3COCH_3), dimethyl sulphoxide (DMSO, 98%) and hydrochloric acid (HCl) were also purchased from Sigma–Aldrich.

Inlaid glassy carbon disk electrodes with a geometric area 0.071 cm^2 (BASi) were used for the electrochemical characterization. The electrodes were polished using polishing cloth (MicroCloth, Buehler) using sequentially 1.0 μm and 0.5 μm alumina. The electrodes were sequentially washed in water and later on in ethanol while being sonicated for 10 min in an ultrasonic bath.

2.2. Methods

Elemental analysis for carbon, hydrogen and nitrogen were done using Vario EL-III CHNS Element Analyzer (Elementar Analysensysteme GmbH). The metal contents of the metal complexes were determined by decomposing a known amount of the complex using a H_2SO_4–HNO_3 mixture, followed by careful evaporation and calcinations [17].

IR spectra were recorded using a Perkin Elmer spectrum 100 FT-IR spectrometer attached to Spot light 400-Perkin Elmer FT-IR imaging system in the ATR mode with germanium crystal.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a S-Probe mono-chromatized XPS spectrometer from Surface Science Instruments (VG) with an Al Kα X-ray (1486.6 eV) monochromatic source. The take off angle was 45° with the voltage and power of the source 10 kV and 200 W respectively. A base pressure of 2×10^{-9} mbar was obtained in the measuring chamber and the pass energy spectra was 157.7 eV (resolution stand 4: 0.15 eV). The analysis surface was 250×1000 μm^2 with a flood gun (neutralizer) setting of 0.2 eV. The accumulation time was about 30 min for Pd 3d, N 1s and C1s spectra.

UV–VIS spectra were recorded using a Cary 50 from VARIAN with DMSO as a blank. A total of 0.5 mM of the complex in DMSO was used for recording the spectra in the region of 280–800 nm.

Raman spectra were recorded with a confocal Raman spectrometer Senterra R200-L (Bruker) using a 785 nm diode laser with a power of 300 mW at the source. An Olympus microscope, coupled to the spectrometer was used for the visualization of the sample and for the microanalysis with an objective lens of 50× magnification. The spectrometer is equipped with a thermo-electrically cooled CCD detector (1024 × 256 pixels). Raman spectra were recorded in the wave number region of 100–1800 cm^{-1} as bulk powder samples. For each spectrum 15 accumulations of 30 s were recorded.

XRD spectra were recorded using model ARL X-TRA from ThermoFisher Scientific in the range 10–60° at 25 °C with a scan rate of 1°/min at a step of 0.020° and integration time of 1.2 s. XRD spectra were obtained using Cu Kα radiation ($k = 1.934$ Å).

Thermogravimetric analyses were carried out using the SDT 2960 of TA instruments. Five to 10 mg of the sample was used for the analysis at a heating rate of 10 °C/min in dry air atmosphere with a flow rate of 100 mL/min.

Cyclic voltammetric experiments were used to examine the redox behaviour of the palladium phthalocyanine complexes. Experiments were performed using an Autolab potentiostat (PGSTAT 100) with GPES software, in a three electrode cell system with saturated calomel electrode as reference, a glassy carbon (GC) electrode as working electrode and carbon as counter electrode. The electrochemical experiments were performed in 0.01 M tetrabutyl ammonium perchlorate (TBAP) in dry DMSO at a scan rate of 50 mV/s in an inert atmosphere by purging with nitrogen gas for 20 min before each electrochemical measurement. A total of 2 mM of the complexes were used for the electrochemical characterization in solution.

2.3. Synthesis procedures

2.3.1. Synthesis of palladium(II) phthalocyanine (PdPc)

Palladium(II) phthalocyanine (PdPc) was synthesized by modifying slightly the procedure described for the synthesis of other metal phthalocyanines [11,18]. A total of 5 g (0.039 mol) phthalonitrile and 1.77 g (0.01 mol) palladium chloride were mixed well and heated slowly under reflux to 140 °C while stirring over an oil bath, at which point the phthalonitrile melts and forms a brownish slurry. The reaction mixture was then heated to 180 °C and maintained at 180 °C for 2 h with constant stirring. The crude product was cooled to room temperature and the solid mass was finely ground and washed with methanol, hot alcohol and water to remove the intermediates and unreacted components. The product was dried in the oven for 1 h to obtain 5.6 g of a bluish green solid. Anal. for palladium(II) phthalocyanine, $C_{32}H_{16}N_8Pd$: Calc. (%) C, 62.09; H, 2.59; N, 18.11; Pd, 17.21. Found C, 61.73; H, 2.79; N, 18.45, Pd, 17.03. Electronic absorption, λ_{max} (nm): 328, 436, 617,661. IR absorption bands (cm^{-1}): 754(w), 871(s), 913(m), 950(w), 1069(w), 1093(m), 1114(s), 1164(s), 1287, 1326(s), 1361(m), 1415(w), 1463(m), 1504(w), 1556(s), 1605(w).

2.3.2. Synthesis of palladium(II) tetranitrophthalocyanine (PdTNPc)

Palladium(II) tetranitrophthalocyanine (PdTNPc) was prepared by mixing a total of 6.5 g (0.039 mol) 4-nitrophthalonitrile and 1.77 g (0.01 mol) palladium chloride. The mixture was heated slowly to 140 °C while stirring to form a slurry [18]. The reaction mixture was maintained at 160 °C with constant stirring for 3 h under reflux. The solid crude product was cooled to room temperature and the crude was purified using the procedure as explained for PdPc (see above) to afford 6.05 g of a bluish green product. Anal. for palladium(II) tetranitrophthalocyanine, $C_{32}H_{12}N_{12}O_8Pd$: Calc. (%) C, 48.1; H, 1.50; N, 21.04; O, 16.03; Pd, 13.33. Found; C, 48.49; H, 1.34; N, 20.79; Pd, 13.56. Electronic absorption, λ_{max} (nm): 346, 431, 620, 684. IR absorption bands (cm^{-1}): 755(w), 815(w), 845(s), 909(w), 1048(w), 1104(m), 1143(s), 1256 (s), 1330(s), 1405(m), 1437(w), 1523(s), 1605(m).

2.3.3. Synthesis of palladium(II) tetraaminephthalocyanine (PdTAPc)

Palladium(II) tetraaminophthalocyanine was prepared by the reduction of the nitro derivative using sodium sulphide [18,19]. A total of 2.0 g of PdTNPc was placed in 50 mL water. To this slurry 10 g of sodium sulphide nonahydrate was added and stirred at 50 °C for 5 h. The product was allowed to settle down and washed with 0.5 M hydrochloric acid and 1 M sodium hydroxide solution, sequentially 3 times. Finally, the compound was washed with water until the filtrate is neutral to litmus paper. The crude product was dried in the oven at 70 °C for 3 h to obtain 1.4 g of a dark bluish solid. Anal. for palladium tetraaminephthalocyanine, $C_{32}H_{20}N_{12}Pd$: Calc. (%) C, 56.59; H, 2.95; N, 24.74; Pd, 15.72. Found; C, 56.16; H, 3.24; N, 24.79; Pd, 15.84. Electronic absorption, λ_{max} (nm): 313, 432, 648, 724. IR absorption bands (cm^{-1}): 754(w), 817(m), 868(s), 909(s), 946(w), 1052(w), 1105(m), 1143(s), 1255(w), 1334(s), 1408(w), 1516(s), 3215(w), 3334(s).

2.3.4. Synthesis of palladium(II) tetrachlorophthalocyanine (PdTClPc)

Palladium(II) tetrachlorophthalocyanine, PdTClPc, was synthesized through an intermediate step involving the formation of a diazonium salt intermediate from PdTAPc [20].

2.3.4.1. Preparation of palladium(II) phthalocyaninetetradiazonium salt ($PdPcTN_2^+Cl^-$). Palladium(II) phthalocyaninetetradiazonium salt ($PdPcTN_2^+Cl^-$) was prepared by adding finely ground palladium(II) tetraaminophthalocyanine (1.0 g) to 20 mL of a 1.0 N hydrochloric acid solution. The mixture was kept in a bath of crushed ice with constant stirring until the temperature of the solution fell below 5 °C. To this cold solution, a chilled aqueous solution of sodium nitrite (0.65 g/5 mL) was added in small portions (0.5 mL at a time) while constantly stirring. Heat was evolved by the reaction. The temperature was kept below 10 °C using ice cubes and then this solution was used in the next step.

2.3.4.2. Preparation of palladium(II) tetrachlorophthalocyanine (PdTClPc). In order to prepare palladium(II) tetrachlorophthalocyanine (PdTClPc), a clear, chilled (<10 °C) solution of palladium phthalocyaninetetradiazoniumchloride was added with constant stirring to a freshly prepared chilled cuprous chloride solution in concentrated HCl (5.3 g/8 mL). The mixture was allowed to attain room temperature, after which it was warmed in a water bath to about 60 °C until the evolution of nitrogen gas ceased. The green product was filtered and washed with sodium hydroxide (1.0 N), hydrochloric acid (1.0 N) and finally with distilled water till the filtrate was neutral. The complex was dried at 100 °C for 30 min to obtain 0.9 g of a black to green solid. Anal. for palladium tetrachlorophthalocyanine, $C_{32}H_{12}N_8Cl_4Pd$: Calc. (%) C, 50.79; H, 1.59; N, 14.82; Cl, 18.73; Pd, 14.07. Found; C, 50.91; H, 1.24; N, 14.49; Pd, 14.40. Electronic absorption, λ_{max} (nm): 349, 443, 624, 673. IR absorption bands (cm^{-1}): 754(w), 817(s), 840(s), 910(w), 1049(w), 1103(m), 1143(s), 1201(w), 1329(s), 1402(m), 1437(w), 1520(s).

2.3.5. Synthesis of palladium(II) phthalocyaninetetracarboxylic acid (PdTCAPc)

Palladium(II) phthalocyaninetetracarboxylic acid (PdTCAPc) was prepared by mixing 2.0 g (0.01 mol) trimellitic anhydride, 0.53 g (0.003 mol) palladium chloride, 4.0 g urea, 0.25 g ammonium chloride and 0.05 g ammonium molybdate into 10 mL nitrobenzene. The mixture was gradually heated and maintained at 180 °C for 4 h with stirring under reflux [21]. The deep bluish black solid was cooled to room temperature and washed with methanol and water. Then the crude product was stirred at 90 °C with aqueous solutions saturated with sodium chloride consecutively with sodium hydroxide (1.0 M) and then with hydrochloric acid (1.0 N) till the evaporation of ammonia completely ceased. The product was finally washed with distilled water till the filtrate was neutral to the litmus paper. The complex was dried at 100 °C for 30 min to afford 1.72 g of a black to green product. Anal. for palladium(II) phthalocyaninetetracarboxylic acid, $C_{36}H_{16}N_8O_8Pd$: Calc. (%) C, 54.38; H, 2.01; N, 14.10; O, 16.11; Pd, 13.40. Found; C, 54.63; H, 2.24; N, 13.79; Pd, 13. 69. Electronic absorption, λ_{max} (nm): 332, 441, 617, 664. IR absorption bands (cm^{-1}): 776(w), 848(s), 942(w), 1105(s), 1152(s), 1247(w), 1319(s), 1380(m), 1512(s), 1667(w), 3182(b).

2.3.6. Synthesis of palladium(II) tetra(thiophenyl)phthalocyanine (PdTPSPc)

Palladium(II) tetra(thiophenyl)phthalocyanine (PdTPSPc) was synthesized from phenylthiophthalonitrile. Phenylthiophthalonitrile [22] was synthesized from thiophenol and then used for the synthesis of PdTPSPc.

2.3.6.1. 4-(thiophenyl)phthalonitrile. Thiophenol (2.32 g, 0.021 mol) and 4-nitrophthalonitrile (3.00 g, 0.018 mmol) were dissolved in DMSO (20 mL) and stirred at room temperature in a nitrogen atmosphere for 15 min. Finely ground K_2CO_3 (7.5 g, 0.058 mol) was added slowly over a period of 2 h and the reaction mixture was stirred continuously for 12 h. The mixture was added to water (100 mL) and stirred for another 30 min. The precipitate was filtered, washed thoroughly with water and dried. The product was re-crystallized from hot ethanol. Anal. For 4-(thiophenyl)phthalonitrile, $C_{14}H_8N_2S$: Calc. (%) C, 71.16; H, 3.39; N, 11.86; S, 13.59. Found. C, 71.53; H, 3.24; N, 11.39; S, 13.98.

2.3.6.2. Palladium(II) tetra(thiophenyl)phthalocyanine. Mixture of 4-(phenylthio)phthalonitrile (0.52 g, 0.002 mol), palladium chloride (0.12 g, 0.7 mmol) and urea (0.25 g) were stirred at 190 °C for 12 h. The crude product was filtered, and the resulting solid sequentially washed with methanol and water. Then the product was purified by column chromatography, using THF as the eluting solvent. After evaporation of the solvent, the product was further purified by washing with acetone and then with ethanol in a Soxhlet apparatus to afford 0.38 g of the title compound as a black to green solid. Anal. for palladium tetra(thiophenyl)phthalocyanine, $C_{56}H_{37}N_8S_4Pd$: Calc. (%) C, 63.63; H, 3.50; N, 10.60; S, 12.15; Pd, 10.08. Found. C, 64.23; H, 3.24; N, 10.29; S, 12.8; Pd, 10.63. Electronic absorption, λ_{max} (nm): 331, 428, 632, 675. IR absorption bands (cm^{-1}): 776(w), 820(s), 881(w) 928(w), 1037(s), 1064(w), 1112(s), 1152(s), 1247(w), 1306(s), 1342(m), 1389(w), 1437(s), 1510(s).

3. Results and discussion

Fig. 1 shows a brief schematic for the synthesis of tetra-substituted palladium phthalocyanine complexes with the different functional groups at the periphery of benzene ring. The 4-substituted precursors lead to the formation of 2,9,16, 23-tetrasubstituted complexes with four positional isomers (C4h, C2v, Cs, D2h) [23] and the composition of the isomers depends on the central metal ion and the structure of the peripheral substituent [24]. The formation of isomers is due to the symmetry involved in the condensation reaction used in phthalocyanine synthesis. Separation of the isomers is extremely difficult, and accordingly only a few pure tetrasubstituted isomers have been isolated hitherto. The use of highly pure precursors and the extreme care taken during the synthesis and purification leads to formation of complexes with higher composition of C4h isomer, 2,9,16,23-symmetrically substituted phthalocyanine. Even then, smaller amounts of other isomers will be formed which have not been separated here. Though the elemental analysis data was in agreement with the theoretical calculations, small discrepancies indicate that the complexes are not 100% pure. In addition it is also difficult to achieve complete conversion because of the extreme synthetic conditions employed and the insolubility of phthalocyanines in most of the aqueous and organic solvents.

The complexes are dark blue to bluish-green in colour and are soluble in dimethyl sulfoxide, dimethyl formamide, pyridine,

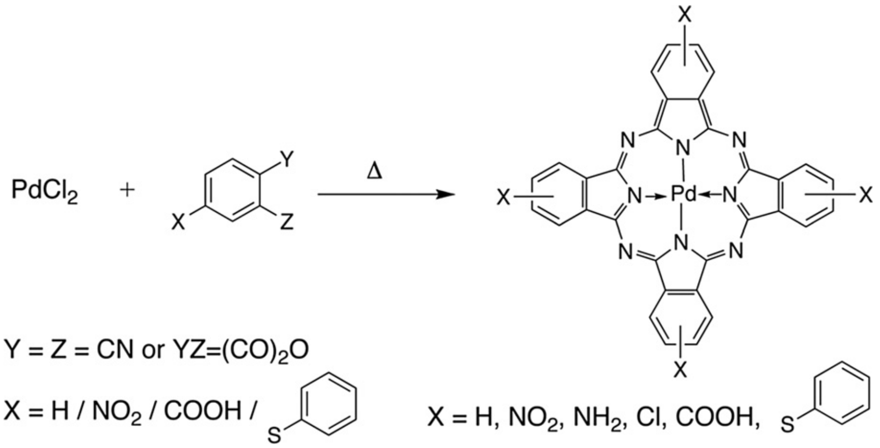

Fig. 1. Brief schematics for the synthesis of palladium phthalocyanine complexes.

chloronaphthalene and concentrated sulphuric acid. The solutions appear to be stable in these solvents for more than a week. But after some time, few of the molecules of these complexes become aggregated and slowly start settling down. The palladium phthalocyanine complexes were obtained with a good yield (75–90%). The ATR-IR spectra for all the complexes (spectra in supplementary information) showed absorption peaks around 750, 850, 940, 1060, 1110 and 1150 cm^{-1} which may be assigned to phthalocyanine skeletal vibrations [25]. Two absorption bands are observed at 3334 and 3215 cm^{-1} for the PdTAPc complex which are the characteristic asymmetric and symmetric stretching vibrations of the amino group. PdTCAPc showed a broad band at 3100–3600 cm^{-1} which can be assigned to the —OH of the carboxylic acid group. All the spectra showed absorption peaks in the range around 3060 cm^{-1} due to the aromatic C—H stretching.

The synthesized complexes were characterized by XPS to study the presence of different elements in the synthesized complexes and to study the effect of the substituents on the binding energy. Fig. 2 shows the XPS spectra of the C1s region for different complexes and the N1s, Pd3d regions for PdPc. The Pd 3d spectra

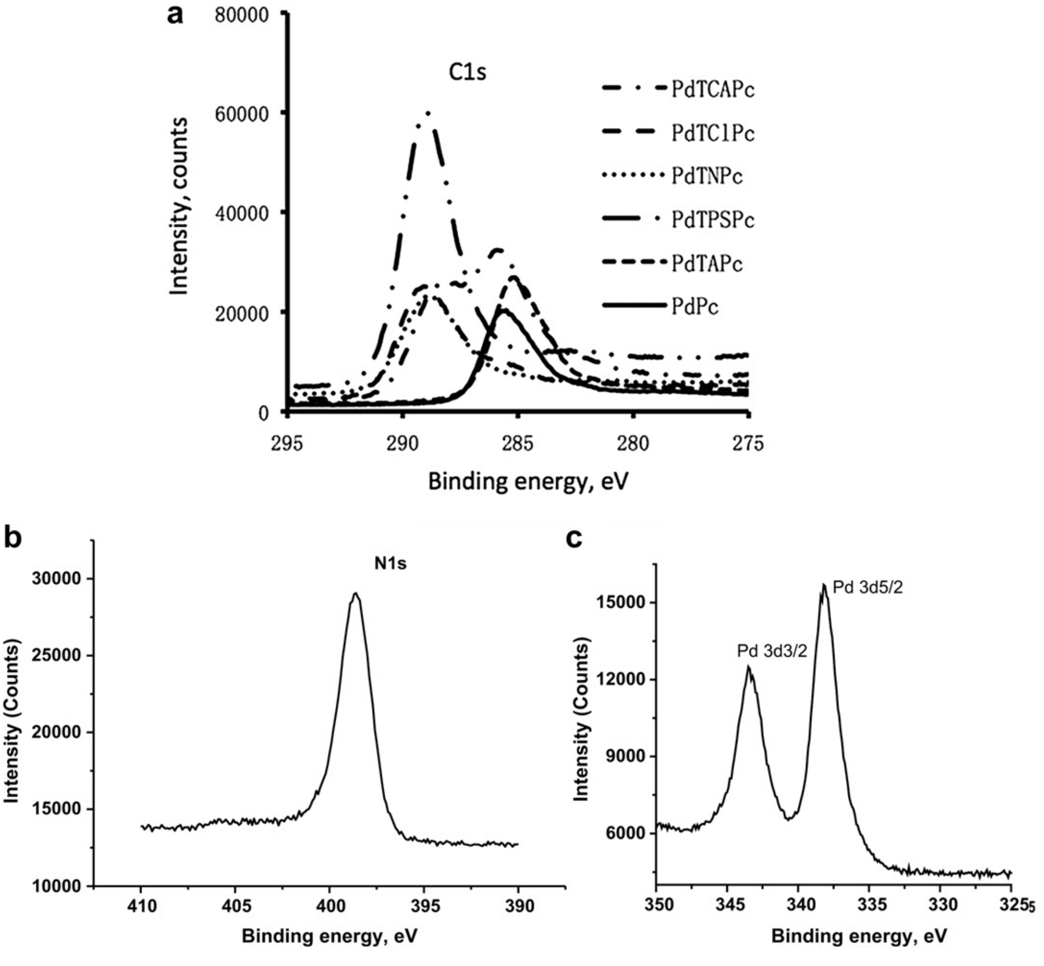

Fig. 2. X-ray photoelectron spectra of (a) carbon 1s for different complexes, (b) nitrogen 1s, (c) palladium 3d regions for the PdPc.

show two intense peaks at ~338.5 and 343.8 eV with a shift of around 0.1–0.5 eV for different complexes. The peak at lower binding energy can be attributed to 3d5/2 and the other peak at higher binding energy to 3d3/2. The Pd3d5/2 peak indicates the presence of Pd in +2 state in the phthalocyanine complexes. The complexes show a main N1s peak at ~398 eV. The main peak is associated with a shoulder and indicates that the phthalocyanine complexes have nitrogen atoms in two kinds of chemical environment: four nitrogen atoms only bond with two carbon atoms and form C–N=C bonds, while the other four nitrogen atoms not only bond with carbon atoms but also bond with the copper atom through a coordination bond [26]. The PdPc show a main C1s peak at 285 eV, whereas the electron donor amine phthalocyanine shows a peak at 284.5 eV and the electron withdrawing nitro, chloro and phenylthio groups show peaks at ~288.5 eV. The C1s region of all the complexes show one main peak with two shoulders which can be assigned to C1s (phenyl rings), C1s (pyrrole) and C1s (π–π^*) satellite, respectively [26]. The C1s spectra of carboxylic phthalocyanine show two peaks which may be due to the presence of monomeric and oligomeric units. PdTNPc and PdTCAPc show an O1s peak at ~531 eV. The Cl 2p spectra of PdTClPc show a peak at 196.6 eV whereas a S2p peak was observed for PdTPSPc at 160.2 eV. The shift in the binding energy for the different complexes is in accordance with the literature [27]. In general, substituents with more electronegative species tend to shift core electron binding energies upfield to a higher energy and vice versa.

UV–VIS experiments were performed in dimethyl sulphoxide solvent in the range 280–800 nm (the UV cut-off region for DMSO is 265 nm). The aim was to provide information about the electron density of the complexes, their aggregation and their spectral shifts. UV–Visible spectra for the complexes are presented in Fig. 3. The peaks observed in the Q-band region in the range 615–730 nm are responsible for the observed green colour of the complexes. These transitions may be assigned to the $\pi \rightarrow \pi^*$ transitions [28]. The peaks obtained in the B-band region are in the range 310–350 nm. The broad absorption peaks observed in the range 420–450 nm are probably due to C_{4V} symmetry of the complexes [29]. The UV–Vis spectra of metallic mono-Pcs in solution display a narrow Q-band [1], but the splitting or two bands observed in these complexes indicates the presence of both monomeric and dimeric forms of the complexes in solution. The shoulder or splitting of the peak observed in the Q-band region may also be due to the vibronic fine structure in addition to dimeric species in solution [30].

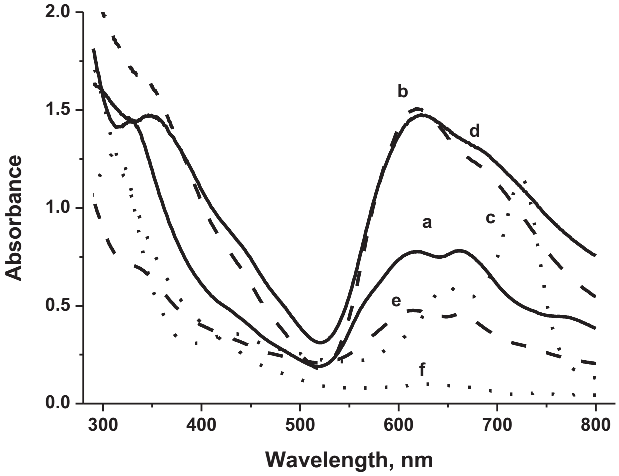

Fig. 3. UV–Visible spectra in DMSO for (a) PdPc, (b) PdTNPc, (c) PdTAPc, (d) PdTClPc, (e) PdTCAPc and (f) PdTPSPc.

Substitution of the electron donor $-NH_2$ group on the peripheral benzene ring of the PdPc structure shows a bathochromic shift to an extent of 60 nm. The substitution of the electron acceptor $-NO_2$ and –Cl groups also found to affect the bathochromic shift but to a smaller extent of 20 nm in comparison to the peak observed in the spectrum for PdPc complex. The presence of the –COOH substituent does not have any effect on the spectral shift, whereas the thiophenyl group also showed a bathochromic shift compared to the PdPc. The variation in the spectral shift of the peaks is due to the variation in the electron density of the macrocycle and the presence of various substituted functional groups. In general, an edge-to-edge configuration leads to the red shift or bathochromic effect, while a cofacial arrangement leads to the blue-shift or hypsochromic effect [14].

Raman analyses were performed to obtain information about the functional groups and the electron density associated with the macrocycle. The spectra for the different palladium phthalocyanine complexes as powder samples are given in Fig. 4. The Raman signals observed are in good agreement with the data documented in the literature for different phthalocyanine compounds [31–35]. The spectra are dominated by strong in-plane stretching and breathing modes of the phthalocyanine macrocycle. The bands observed are assigned based on the reported literature [31].

Table 1 gives an overview of the various bands and their corresponding assignments. The most intense band in the spectra of these complexes is the pyrrole stretching at around 1520 cm^{-1}, consistent with the data for other Pc, where the oxidation state of the central metal is presumed to be +2 [31–36]. The stretching vibration of the pyrrole ring on the phthalocyanine macrocycle is observed around 1340 cm^{-1}. The macrocyclic vibration observed around 1110 cm^{-1} can mainly be assigned to ν(C=C) and δ(C–H) vibrations. The peak at 1100 cm^{-1} shifted towards the higher wave number for the substituted complexes compared to the parent palladium phthalocyanine complex. In addition they show strong peaks in the region 700–1200 cm^{-1}. The spectral pattern in this region strongly depends on the molecular structure of the complexes and also on the chemical structure of the central metal. This can be clearly seen by the substituted phthalocyanines complexes show a shift in the peaks by 10–20 cm^{-1} compared to the parent palladium phthalocyanine. This is due to the electron with-drawing or electron-donating nature of the functional groups present on the periphery of the phthalocyanine macrocycle which alters the electron charge-density in the phthalocyanine macrocyclic ligand [1,2]. The pyrrole ring out-of-plane deformation is

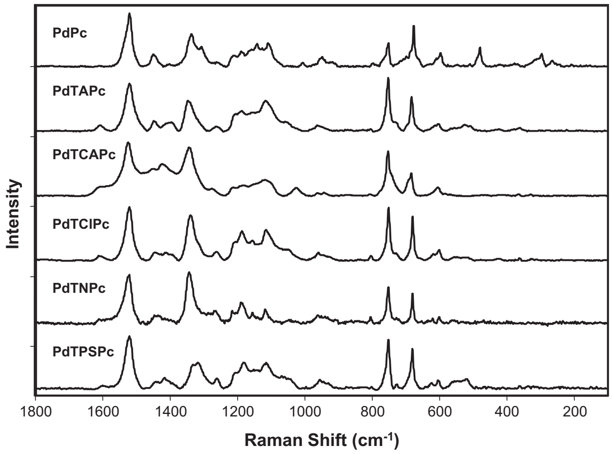

Fig. 4. Raman spectra of the six palladium phthalocyanine complexes as powder samples.

Table 1
Raman spectral bands for different palladium phthalocyanine complexes, with the respective assignments [28–33].

Assignment of peaks	Raman shift, cm^{-1}					
	PdPc	PdTNPc	PdTAPc	PdTClPc	PdTCAPc	PdTPSPc
ν(Benzene ring)		1610	1606	1605	1605	1592
νCαNα-pyrrole	1519	1522	1521	1520	1524	1521
ν(Isoindole ring)	1448	1438	1449	1444	1452	1444
νCαNβ, νCβCβ			1399	1409, 1388	1422	1416
Pyrrole stretch	1336	1343	1346	1340	1342	1345
δCH	1306					1313
	1257	1265	1260	1263	1274	1257
δCH	1206	1215	1207	1207	1212	1208
δCH	1190	1188	1189	1187	1183	1182
Pyrrole ring breathing	1141	1155	1157	1155		
νCC, δCH	1108	1116	1117	1114	1118	1115
ν(Isoindole)			1058	1048	1025	
	1006					996
	949.4	961.5	962.1	960.7	960.2	956.1
	918				943.5	
		802.7	805.1	803.4	804.4	
δCH, δCCC	752.6	751.8	751.3	749.7	752.5	752
		725.7	729.5	727.5		726.2
	698.1					
Macrocycle breathing	676.7	678.1	679.7	679.4	683.9	680.2
	609.5	624		618.3	604.2	603.3
Benzene ring deformation	597.3	599.5	604.1	597.9		
Out-of-plane ring deformation	576.7		522.7			518.8
Pyrrole ring deformation	480.5		421.3	418.3		

observed at 730 cm^{-1} and the out-of plane δ(C–H) bending vibration appears at 750 cm^{-1} [33].

Powder X-ray diffraction spectra for the different phthalocyanine complexes are shown in Fig. 5. The X-ray diffraction pattern of the complexes, except for PdTCAPc, shows many sharp peaks in the spectra, indicating the crystalline nature of the samples. The carboxylic acid substituted complex, PdTCAPc, shows a few peaks which are broader in nature indicating the formation of dimers and oligomers in the complex due to the condensation of carboxylic acid at high temperatures to give the oligomers [37]. PdTCAPc shows peaks at two-theta values 27.22, 32.96 and 40.17 whereas other complexes show peaks at 11.42, 13.82, 14.51, 16.92, 22.65, 25.62, 27.22, 32.96 and 40.17°. The d_{hkl} and 2theta values obtained were compared with the values reported in literature (ICDD-PDF Files) and found to be in good agreement for the related phthalocyanine complexes [38]. In general, XRD spectra indicate that the complexes are slightly crystalline in nature.

Thermal studies provide information about the thermal stability and the decomposition behaviour of the complexes at different temperatures. The TGA curves obtained are shown in Fig. 6. An overview of the decomposition temperatures of the synthesized complexes are given in Table 2. The thermogravimetric curve for PdTCAPc shows a mass loss below 100 °C due to the loss of water and moisture from the sample with an exothermic decomposition.

The phthalocyanine complexes do not show any sharp melting point but decompose at elevated temperatures. The onset of the decomposition is situated around 350 °C, indicating these complexes are highly stable in air even at high temperatures. The derivative of the mass signal clearly shows that there are two separate decomposition processes: the first with a maximum around 370 °C (±38 °C) and the second around 425 °C (±35 °C). The decomposition temperatures obtained from the derivative of the mass-signal is given in Table 2. The decomposition temperature for the different complexes increases in the following order.

$$\text{PdPc} < \text{PdTPSPc} < \text{PdTClPc} < \text{PdTAPc} < \text{PdTCAPc} = \text{PdTNPc}$$

This can be indicated in terms of functional groups

$$-\text{H} < -\text{S}-\text{C}_6\text{H}_5 < -\text{Cl} < -\text{NH}_2 < -\text{COOH} = -\text{NO}_2$$

The latter clearly indicates that the substitution of functional group at the periphery of the benzene ring leads to the higher thermal stability of the phthalocyanine macrocycle. The variation in thermal stability was also observed for phthalocyanine complexes with different central metal ions [39,40]. The higher stability of the complexes with carboxylic acid and nitro functional groups can be attributed to the extra stability achieved by the phthalocyanine macrocycle due to the extended aromaticity provided by the carboxylic and nitro groups.

If we assume that the mass at 200 °C is that of the dry complex and the end product formed after decomposition at 500 °C is PdO, then we can compare the end mass of the experimental sample with the predicted or theoretical end mass. Table 3 shows the mass residue at 700 °C. Column 6 and 7 in Table 3 show the experimentally determined PdO residue (compared to the mass at 200 °C) and the theoretical molecular mass of PdO for the synthesized samples (% mass difference between experimental and theoretical

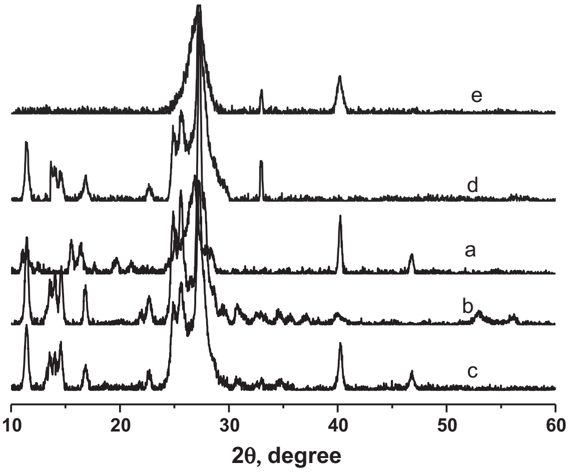

Fig. 5. XRD spectra of (a) PdPc, (b) PdTNPc, (c) PdTAPc, (d) PdTClPc and (e) PdTCAPc.

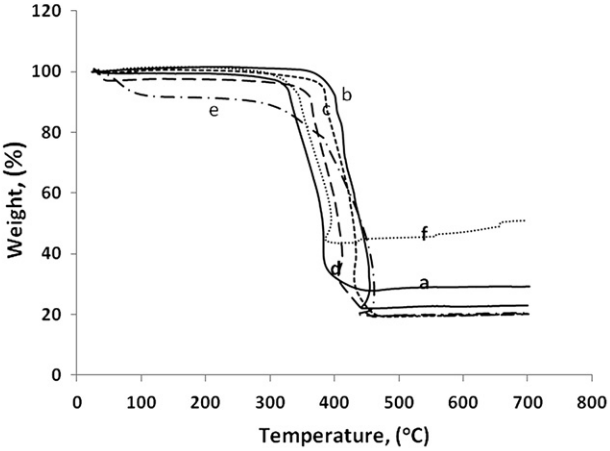

Fig. 6. Thermogravimetric curves for (a) PdPc, (b) PdTNPc, (c) PdTAPc, (d) PdTClPc, (e) PdTCAPc and (f) PdTPSPc.

Table 2
Decomposition temperature of the palladium complexes.

Complex	Functional group	Loss of water	First decomposition step (°C)	Second decomposition step (°C)
PdPc	–H	–	388	429
PdTNPc	$-NO_2$	–	401	430
PdTAPc	$-NH_2$	–	388	429
PdTClPc	–Cl		367	406
PdTCAPc	–COOH	Yes	389	456
PdTPSPc	$-S-C_6H_5$		333	380

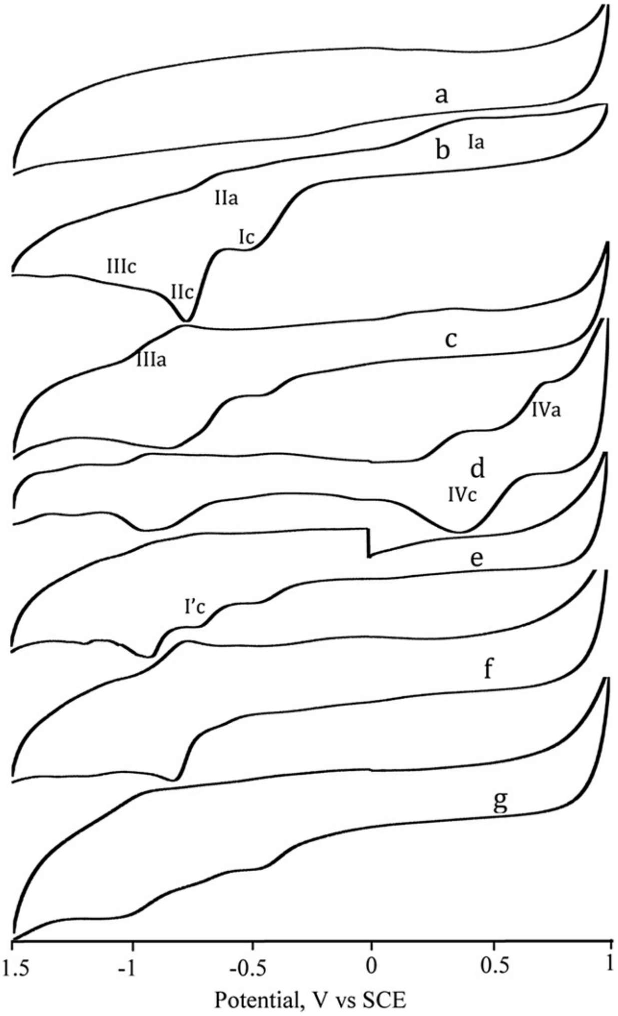

Fig. 7. Cyclic voltammetric curves with GC for (a) blank, 2 mM (b) PdPc, (c) PdTNPc, (d) PdTAPc, (e) PdTClPc, (f) PdTCAPc and (g) PdTPSPc in 10 mM TBAP in DMSO at 50 mV/s.

values are given in the bracket). The higher residue obtained in case of PdTPSPc indicates the formation of $PdSO_4$ instead of PdO in the temperature region we have studied. Overall thermogravimetric studies reveal that the complexes are highly stable in air (up to temperatures of 400 °C) and also reveal that the complexes are pure as the decomposition products at 700 °C are comparable to the expected PdO theoretical mass value.

The complexes were also studied for their electrochemical redox behaviour and the cyclic voltammograms are presented in Fig. 7. The bare glassy carbon electrode does not show any peaks in the experimental potential region 1.0 to −1.5 V. The palladium phthalocyanine complexes show three common redox peaks. These peaks can be attributed to the redox behaviour of the phthalocyanine macrocyclic ligand. PdPc complex showed reduction peaks at around −0.512 (Ic), −0.77 (IIc) and −1.079 (IIIc) V and oxidation peaks at 0.41 (Ia), −0.34 (IIa) and −0.6 (IIIa) V which were less intense compared to the reduction peaks indicating that the redox phenomena is quasi-reversible.

Since the Pd metal-ion has no accessible d-orbital levels lying within the l_al_u (HOMO) – l_{eg} (LUMO) gap of a phthalocyanine species, its redox chemistry will be similar to redox inactive metallophthalocyanines. In other words the Pd(II) metal centre does not undergo any redox process and the redox peaks observed are due to the phthalocyanine macrocyclic ligand [1,12–15]. The reduction peak at −0.512 V can be accounted for (Pc/Pc^{-1}), −0.77 to (Pc^{-1}/Pc^{-2}) and −1.1 to −1.2 V can be attributed to the phthalocyanine ring reduction (Pc^{-2}/Pc^{-3}) [41]. Almost the same peaks and the same behaviour were observed for PdTNPc, PdTClPc, PdTCAPc, PdTPSPc. The splitting of the peaks or shoulders observed for some of the complexes which is well documented in literature that splitting of a peak arises due to the aggregation of the electroactive species [1,16]. The shoulder got disappeared at higher scan rates which may be due to the disintegration of the aggregated molecules. This type of behaviour has been observed for palladium phthalocyanine complexes [15]. PdTAPc showed extra peaks at 0.38 and −0.05 V with their oxidation peaks at 0.73 and 0.41 V respectively. The peak at 0.71 V can be ascribed to the irreversible oxidation of the aromatic amino group as was observed for aniline in the electrochemical preparation of polyaniline [42]. The electron transfer abilities of phthalocyanines depend on the nature and number of substituents and are due to the interaction between the phthalocyanine ring and the metal centre which is influenced by conjugated π-electron current of the phthalocyanine ring [1,2]. The peak potentials for these phthalocyanine complexes were observed at considerably low negative potentials with respect to those of the common phthalocyanines reported in the literature [1,43–46], though the electrochemical measurement were carried out in polar solvent, DMSO which shifts the redox reactions towards more negative potentials. If the redox inactive metallophthalocyanines showed the redox peak at −0.8 V vs SCE, while these complexes showed redox peak

Table 3
Comparison of the mass residues of different complexes.

Complex (column 1)	Functional group (column 2)	Molecular mass (theoretical) g/mol (column 3)	% of dry mass			
			Experimental			% of dry mass theoretical (Column 7)
			Mass at 200 °C (mg) (column 4)	Mass at 500 °C (mg) (column 5)	% of dry mass experimental (column 6)	
PdPc	–H	618.8	6.857	1.873	23.77	19.7(−4)
PdTNPc	$-NO_2$	798.8	6.320	1.395	22.07	15.3(−6.7)
PdTAPc	$-NH_2$	678.8	5.543	1.066	19.23	18(−1.2)
PdTClPc	–Cl	756.6	6.409	1.300	13.82	16.2(2.4)
PdTCAPc	–COOH	794.8	8.817	1.908	21.64	15.4(−5.2)
PdTPSPc	$-S-C_6H_5$	1051.0	6.753	3.011	44.59	11.65(−32)

around −0.5 to −0.6 V. This is due to the substituted electron withdrawing and electron donating groups. The electron-withdrawing effect of the nitro, chloro, phenylthio groups at the periphery decreases the charge density in the phthalocyanine ring and thus shifts reduction potential to more positive values as compared to the PdPc which showed a macrocyclic ligand reduction peak at −0.48 V, while electron donating $-NH_2$ group which increases the charge density of the phthalocyanine ring and thus shifts the reduction potential towards more negative values (−0.54 V). The voltammograms could be repeatedly scanned without any change in the redox characteristics except for the PdTAPc complex which is expected to undergo electropolymerization. In summary, palladium phthalocyanine complexes do not show redox peaks for the palladium central metal ion and the redox peaks observed are due to the macrocyclic ring reduction. It is expected that these complexes find numerous application in modified electrodes for catalysis and sensing.

4. Conclusions

Tetra-substituted palladium phthalocyanine complexes of nitro, amine, chloro, carboxylic and aryl thio groups have been synthesized for the first time in a high yield. These complexes were characterized with XPS, UV–Vis, IR, Raman, XRD, TGA and electrochemistry. The XPS spectra showed a peak at 344 eV indicating that palladium is in +2 oxidation state. The Q-band in the UV–Vis region shows a splitting in the peak due to the presence of oligomeric species. The electronic absorption spectra and the Raman spectra show a shift in the peaks for the substituted phthalocyanines compared to the parent unsubstituted palladium phthalocyanine spectra. This is due to the variation in the electron density of the macrocycle due to the presence of various substituted functional groups. XRD spectra indicated that the complexes are slightly crystalline in nature. The synthesized complexes are found to be stable up to 350 °C and form PdO as the decomposition product except aryl thio substituted complex which forms $PdSO_4$ on decomposition. The cyclic voltammetric data show three pairs of redox peaks which can be attributed for the phthalocyanine macrocyclic ring reduction, indicating central metal ion palladium is electrochemically inactive and does not show a redox behaviour. The physicochemical data reveal that the electron-withdrawing and electron-donating substituents have a major effect on the spectroscopic, stability and electrochemical data. These complexes will be utilized in the formation of self assembled monolayers, electrodeposition and electropolymerization as they are very interesting materials for catalysis and sensing.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2012.08.018.

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