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Synthesis, *H*- or *J*-type aggregations, electrochemistry and *in situ* spectroelectrochemistry of metal ion sensing lead(II) phthalocyanines

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ABSTRACT

We report, in this study, peripherally 3- and 4-substituted functionalized ionophore ligands (1–3) and their α - and β -tetra polyalcohol substituted lead(II) phthalocyanines M{Pc[S-CH(C₃H₇)(C₂H₅OH)]₄} (7, 9 and 11) and M{Pc[S-C₆H₁₂(OH)]₄} (8, 10 and 12) which are a mixture of different isomers. The complexes have been fully characterized by elemental analysis, FT-IR, ¹H NMR, ¹³C NMR, MS (MALDI-TOF) and UV–Vis spectral data. These complexes induced *H*-type (face-to-face fashion) or *J*-aggregate (edgeto-edge) dimers when titrated with AgNO₃ or Na₂PdCl₄ in a THF-MeOH solution. Cyclic and square wave voltammetry studies showed that the complexes gave three one-electron ligand-based reductions and two one-electron oxidation couples having diffusion controlled mass transfer character. Assignments of these redox couples were confirmed by spectroelectrochemical measurements. The observation of split Q bands, which are characteristic spectral behavior of metal-free phthalocyanines, indicates demetallization of the complexes during the spectroelectrochemical measurement under the applied potentials. The types of the substituents on the ring of the phthalocyanines affect the demetallization process of the complexes.

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1. Introduction

Phthalocyanines are currently of great technological interest due to their excellent optical and electronic properties as well as their chemical and thermal stabilities [1–4]. The spectroscopic properties of phthalocyanines (Pcs) complexes are influenced strongly by the metal ion in the cavity or moieties on the periphery of the phthalocyanines. The metal ion binding capability of the Pcs on the periphery, based on molecular design, is also of great importance in terms of changing the photophysical, electrochemical and optoelectronic properties, causing higher potential utility [5-7]. The peripheral coordination of MPc with various metal ions will result in the alteration of the molecular conformation. Several conformations are known in phthalocyanine chemistry [8–10]. Among them, the planar conformation of Pcs can be distorted by some metal ions, such as Pb^{II}, Ti^{IV}, Sn^{II}, through conformational stress [11–13]. MPcs metalized with Pb^{II} or Sn^{II} metals show a domed conformation [14]. The radius of the Pb^{II} ion (1.75 Å) is greater than the radius of the inner core. Therefore, the Pb^{II} ion does not fit inside the core cavity and becomes pushed up at the center core of the phthalocyanine plane [1]. So, its structure becomes non-planar with a domed conformation, which can give rise to demetallization in a redox reaction [10,15].

Phthalocyanines show, on the other hand, a propensity to aggregate through coplanar association of the MPc rings in solution, which may negatively impact their solubility and photochemical properties [16–19]. Peripheral substitutions and some metal ions in the core are used for enhancing the solubility and changing the aggregation behavior of MPcs [20]. Also, there has been keen interest in phthalocyanine derivatives (Pcs) which bear specially designed peripheral substituents that coordinate with alkaline or transition metal ions [21–23].

In this study, in order to tune the molecular properties of lead(II) phthalocyanines, different functional groups have been introduced to the peripheral or non-peripheral position of the precursors. Although a significant number of reports on PbPcs are already available in the literature, to the best of our knowledge PbPcs having peripheral functionality have not been investigated [8–10,13,14,20]. We, therefore, have synthesized, characterized and examined metal ion sensing, voltammetric and spectroelectrochemical properties of lead(II) phthalocyanines.





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2.1. Materials and equipments

Pb(O₂Me)₂·H₂O was purchased from Aldrich. All other reagents were obtained from Merck and Fluka and used without purification. 3-Nitrophthalonitrile, 4-nitrophthalonitrile, 4'-(1-hy droxyhexan-3ylthio)-phthalonitrile (4), 3'-(6-hydroxyhexylthio)phthalonitrile (5) and 4'-(6-hydroxyl hexylthio)-phthalonitrile (6) were prepared according to the literature procedure [18,24– 26]. All reactions were carried out under dry N₂ atmosphere. Mass spectra were acquired on a Voyager-DETM PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. MS spectra were recorded in the reflectron mode with an average of 50 shots. An α -cyano 4-hydroxycinnamic acid (CHCA, 20 mg mL⁻¹ in THF or DMF) matrix for all compounds was prepared. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300 spectrometer instrument. Multiplities are given as s (singlet), d doublet), t (triplet). FT-IR spectra (KBr) were recorded on an ATI UNICOM-Mattson 1000 spectrophotometer. Routine UV-Vis spectra were obtained in a quartz cuvette on an Agilent Model 8453 diode array spectrophotometer. Chromatography was performed with silica gel (Merck grade 60) from Aldrich. The homogeneity of the products was tested in each step by TLC (SiO₂, CHCl₃ and MeOH).

Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm². The surface of the working electrode was polished with a diamond suspension before each run. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and was separated from the bulk of the solution by a double bridge. Ferrocene was used as an internal reference. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.1×10^{-3} mol cm⁻³. High purity N₂ was used for deoxygenating for at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements. Throughout the process, the reference electrode tip was moved as close as possible to the working electrode so that the uncompensated resistance of the solution was a smaller fraction of the total resistance, and therefore the potential control error was low. Moreover, IR (current \times resistance) compensation was applied to the CV and SWV scans to further minimize the potential control error.

In situ spectroelectrochemical measurements were carried out with an Ocean-optics QE65000 diode array spectrophotometer equipped with a potentiostat/galvanostat utilizing a three-electrode configuration of a thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was a Pt tulle. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. In situ electrocolorimetric measurements, under potentiostatic control, were obtained using an Ocean Optics QE65000 diode array spectrophotometer in the color measurement mode by utilizing a three-electrode configuration of a thin-layer quartz spectroelectrochemical cell. The standard illuminant A with a 2° observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (x, y and z values) were taken at open-circuit, using the electrolyte solution without MPc. During the measurements, readings were taken as a function of time under kinetic control.

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2.2.1. 3'-(2,3-Dihydroxypropylthio)-phthalonitrile (1) and 4'-(2,3-dihydroxypropylthio)-phthalonitrile (2)

3-Mercapto-1,2-propanediol (1.25 g, 11.57 mmol) was dissolved in 10 cm³ dry DMF and then finely ground anhydrous K_2CO_3 (~2.00 g, excess) was added to this mixture. Then 3nitrophthalonitrile or 4-nitrophthalonitrile (2.00 g, 11.56 mmol) was added to this mixture dropwise at 313 K, stirring effectively under an N₂ atmosphere. The reaction mixture was monitored by TLC (CHCl₃) under the N₂ atmosphere at ca. 313 K for 3 day. After the reaction mixture was cooled to room temperature, it was poured into ca. 200 cm³ ice-water media. The creamy precipitate that formed was filtered and then washed with ca. 100 cm³ water until the washings became neutral. The crude product was dissolved in ca. 20 cm³ THF and filtered again. The final product was chromatographed over a silica gel column using a mixture of CHCl₃ and MeOH (5/1) as eluent, giving a hydroscopic oily solid. Finally the pure powder was dried in vacuo.

Yield of **1**: 1.12 g (41.34%); m.p.: 387 K; FT-IR (KBr, v_{max}/cm^{-1}): 3363, 3226 (CH₂CH(R)–OH, CH₂–OH), 3067, 2927, 2879 (Aliph-CH₂), 2231 (–CN), 1720, 1705 (w, H–O···H), 1568 (st), 1454, 1423, 1406, 1352, 1292, 1210, 1197, 1155, 1099, 1068, 1033, 1014, 879, 856, 735; ¹H NMR (DMSO-d₆) δ , ppm: 7.88–7.72 (dd, t, dd 3H, Ar–H, H4, H5 and H6 (1/1/1)), 5.21 (d, –CHOH), 4.80 (t, –CH₂–OH, D₂O exchangeable; shift 5.0 and 5.35), 3.65 (m, –CH), 3.34 (t, 2H, –CH₂OH), 3.05 (t, 2H, CH–CH₂–S–); ¹³C NMR (DMSO-d₆) δ , ppm: 146.34 (Ar–C–S), 134.40, 132.20, 130.64, 116.53, 116.48, 115.09, 115.07, 112.95, 7069 (–CH₂OH), 65.03 (–CH₂OH), 40.42 (DMSO), 36.87 (S–CH₂); Anal. Calc. for C₁₁H₁₀N₂O₂S (234 g/mol): C, 56.40; H, 4.30; N, 11.96; Found: C, 56.14; H, 4.35; N, 11.48%. MS (MALDI-TOF): m/z: 234.3 [M]⁺, 235.3 [M]⁺.

Yield of **2**: 1.45 g (53.60%); m.p.: 383 K; FT-IR (KBr, v_{max}/cm^{-1}): 3336 (br, CH₂CH(R)–OH, CH₂–OH), 3011, 3059, 2937, 2888 (Aliph-CH₂), 2230 (–C=N), 1737, 1705 (w, H–O···H), 1565 (st), 1477, 1402, 1388, 1345, 1278, 1220, 1192, 1126, 1097, 1068, 1050, 885, 866, 835; ¹H NMR (DMSO-d₆) δ , ppm: 7.96–7.70 (s, dd, dd, 3H, Ar–H, H2, H5 and H6 (1/1/1)), 5.18 (d, –CHOH), 4.80 (t, –CH₂–OH, D₂O exchangeable), 3.63 (m, –CH), 3.54 (t, 2H, – CH₂OH), 3.03 (t, 2H, CH–CH₂–S–); ¹³C NMR (DMSO-d₆) δ , ppm: 148.26 (Ar–C–S), 134.21, 131.01, 130.90, 116.89, 116.43, 115.62, 110.00, 119.99, 70.72 (–CH₂OH), 65.09 (–CH₂OH), 40.42 (DMSO), 36.74 (S–CH₂); Anal. Calc. for C₁₁H₁₀N₂O₂S (234 g/mol): C, 56.40; H, 4.30; N, 11.96. Found: C, 56.22; H, 4.28; N, 11.52%. MS (MAL– DI-TOF): *m/z*: 234.5 [M]⁺.

2.2.2. 3'-(1-Hydroxyhexan-3ylthio)-phthalonitrile (3)

3-Mercapto-1-hexanol (0.77 g, 5.78 mmol) and 3-nitrophthalonitrile (1.00 g, 5.78 mmol) were dissolved in 10 cm^3 dry DMF and heated at 318 K in an N₂ atmosphere for 1 h. Then finely ground anhydrous K₂CO₃ (~1.20 g, 8.67 mmol) was added portionwise to the solution mixture over 0.5 h. The reaction mixture was stirred effectively under N₂ at 313-318 K for 3 days. After the reaction mixture was cooled to the room temperature, it was poured into ca. 150 cm³ ice-water media. The creamy precipitate that formed was filtered and then washed with water until the washings became neutral. The crude product was dissolved in ca. 30 cm³ CHCl₃ and washed again with ca. 50 cm³ 5% NaHCO₃ to remove any unreacted starting compounds. The creamy solution was dried using anhydrous Na₂SO₄, and then filtered. The solvent, CHCl₃, was removed under reduced pressure, giving a creamy powder. It was chromatographed in a silica gel column using a mixture of CHCl₃ and MeOH (100/5) as the eluent, giving the hydroscopic solid, 3'-(1-hydroxyhexan-3-ylthio)-phthalonitrile (3). Finally the pure powder was dried in vacuo.

Yield: 1.26 g (83.8%); m.p.: oily; FT-IR (KBr, ν_{max}/cm^{-1}): 2231 (-CN), 3420, 3246 (CH₂-OH), 3054, 3021 (Ar-H), 2928, 2876, 2855 (Aliph-CH₂) 1715 (H-O···H, weak), 1585 (st), 1540, 1476, 1388, 1275, 1199, 1120, 1075, 988, 856, 744, 570; ¹H NMR (DMSO-d₆) δ , ppm: 7.74 (dd, 1H, ortho to SR, phenyl H5), 7.67 (s, isomer, 1H, meta to CN and SR, phenyl H5), 7.60 (dd, 1H, ortho to Ar-H, phenyl H6), 4.58 (s, t, br, -CH₂-OH, D₂O exchangeable), 3.60 (t, 2H, -CH₂OH), 2.62 (-CH(R)-S-), 1.78 (m, 2H, -CH₂-CH₂OH), 1.58 (m, 2H, *CH*₂CH₂-CH₃), 1.35 (m, *CH*₂CH₃), 0.96 (t, CH₃); ¹³C NMR (DMSO-d₆) δ , ppm: 142.1, 134.8, 131.8, 130.4, 116.3, 114.8, 115.9, 115.8, 59.9 (-CH₂OH), 40.44 (DMSO), 39.8 (-CH₂), 39.3 (*CH*₂CH₂OH), 39.5 (*CH*₂CH₂CH₃), 14.0 (CH₃); *Anal.* Calc. for C₁₄H₁₆N₂OS: C, 64.62; H, 6.15; N, 10.77. Found: C, 64.11; H, 6.12; N, 10.38%. MS (ESI-MS): m/z (45%): 261.4 [M]⁺.

2.2.3. 1(4),8(11),15(18),22(25)-Tetrakis-(2,3-dihydroxypropylthio)lead(II)phthalocyanine (**7**); 2(3),9(10),16(17),23(24)-tetrakis {2,3-dihydroxypropylthio)-lead(II) phthalocyanine (**8**)

3'-(2,3-Dihydroxypropyl)-phthalonitrile (1) (0.25 g, 1.07 mmol) or 4'-(2,3-dihydroxypropyl)-phthalonitrile (2) (0.25 g, 1.07 mmol) and anhydrous Pb(O₂CMe)₂ (0.035 g, 1.07 mmol), in the presence of 0.5 cm³ N,N-dimethylaminoethanol (NNDMAE) and without 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 0.05 cm³) as a strong base, were heated to reflux temperature in a sealed tube under an N₂ atmosphere for 5 h. The color of the mixture turned green during 0.5 h heating, and the heating was continued for an additional 4 h. The green product was then cooled to room temperature. The crude product was washed several times successively, first with ca. 30 cm³ i-PrOH, acetone and then with CH₃CN to remove impurities. The lead(II) phthalocyanines were purified by flash-chromatography using CHCl₃. Finally, they were dried in vacuo. While product 7 is soluble in DMF, DMSO and pyridine, compound 8 is slightly soluble in MeOH, THF, and shows excellent solubility in DMF and DMSO.

Yield of **7**: 0.045 g (14.73%); *Anal.* Calc. for C₄₄H₄₀N₈O₈S₄Pb (1142 g/mol): C, 46.23; H, 3.50; N, 9.81. Found: C, 46.04; H, 3.57; N, 9.26%. FT-IR (KBr, v_{max}/cm^{-1}): 3290, 3240 (br, H-bonded), 3045 (Ar–H), 2966, 2916, 2874, 1715, 1705 (w, H–O···H), 1651, 1564, 1534, 1398 (st), 1252, 1194, 1102, 1052, 889, 845, 744; ¹H NMR (DMSO-d₆) δ , ppm: 7.78–7.22 (m, superimposed 12H, phenyl H4, H5 and H6), 5.20 (d, very broad, 4H, –CH–*OH*), 4.74 (t, 4H, very broad, –CH₂–*OH*, D₂O exchangeable), 3.68 (m, 4H, –CH), 3.54 (t, 8H, –CH₂OH), 2.85 (d, 8H, CH₂–*CH*₂–S–); UV–Vis (THF) λ_{max} nm (log ε): 743 (π–π^{*}), 707 (agg), 687 (*n*–π^{*}), 466 (CT), 341 (deeper, π–π^{*}); MALDI-TOF-MS *m/z* (as matrix; α-cyano 4-hydroxycinnamic acid; CHCA): 1143.

Yield of **8**: 0.051 g (16.69%); *Anal.* Calc. for C₄₄H₄₀N₈O₈S₄Pb (1142 g/mol): C, 46.23; H, 3.50; N, 9.81. Found: C, 46.11; H, 3.55; N, 9.28%. FT-IR (KBr v_{max}/cm^{-1}): 3290, 3240 (br, H-bonded), 3045 (Ar–H), 2966, 2916, 2874, 1713, 1703 (w, H–O···H), 1645, 1562, 1531, 1395, 1317, 1232, 1184, 1161, 889, 869, 812, 794; ¹H NMR (DMSO-d₆) δ , ppm: 7.75–6.95 (m, superimposed 12H, phenyl H4, H5 and H6), 5.15 (d, very broad, 4H, –CH–*OH*), 4.63 (t, 4H, very broad, –CH₂–*OH*, D₂O exchangeable), 3.65 (m, 4H, –CH), 3.55 (t, 8H, –CH₂OH), 2.80 (d, 8H, CH₂–*CH*₂–S–); UV–Vis (THF) λ_{max} nm (log ε): 724 (π–π^{*}), 690 (agg), 655 (*n*–π^{*}), 404 (CT), 354 (deeper, π–π^{*}); MALDI-TOF-MS *m/z* (as matrix; α-cyano 4-hydroxycinnamic acid; CHCA): 1144.3 [M+H]⁺.

2.2.4. 1(4),8(11),15(18),22(25)-Tetrakis-(1-hydroxyhexan-3ylthio)phthalocyaninatolead(II) (**9**) 2(3),9(10),16(17),23(24)-tetrakis-(1-hydroxyhexan-3-ylthio)phthalocyaninatolead(II) (**10**)

The same procedure as described for the preparation of **7** and **8**, were used to prepare compounds **9** and **10**, except the purification steps started with **3** (0.15 g, 0.576 mmol) and Pb(O_2CMe)₂ (0.19 g, 0.576 mmol). The crude product was washed several times

successively with first ca. 50 cm^3 hexane, and then ca. 50 cm^3 CH₃CN to remove unreacted impurities. The main compound was extracted with CH₂Cl₂. The solvent, CH₂Cl₂, was removed under reduced pressure giving green oily compound. The pure phthalocyanines were purified by flash-chromatography using CH₂Cl₂. Both compounds are soluble in CH₂Cl₂, CHCl₃, MeOH, EtOH, THF, DMF, DMSO and pyridine and slightly soluble in CH₃CN.

Yield of **9**: 0.055 g (30.65%). *Anal.* Calc. for $C_{56}H_{64}N_8O_4S_4Pb$ (1246 g/mol): C, 53.93; H, 5.14; N, 8.99. Found: C, 53.33; H, 5.15; N, 8.78%. FT-IR [KBr ν_{max}/cm^{-1}]: 3278 (br, H-bonded), 2954, 2927, 2883, 1722 (w, H–O···H), 1653, 1600, 1525, 1463, 1377, 1315, 1273, 1212, 1092, 1034, 874, 856, 795; ¹H NMR (DMSO-d₆): δ , ppm 8.12–7.75 (m, 12H, br, phenyl H3, H5, H6), 5.23 (s, t, br, -CH₂–OH, D₂O exchangeable), 4.14 (t, br, 8H, –*CH*₂OH), 3.42 (m, br, 4H CH₂*CH*(–S–)CH₂), 3.30 (DMSO), 1.80–1.70 (m, 8H, CH₂*CH*₂CH), 1.60–1.45 (q, 8H, CH₂*CH*₂CH–), 1.45–1.35 (m, 8H CH₂*CH*₂CH₃), 0.98 (t, 12H, *CH*₃). UV–Vis (DMF): λ_{max} nm (log ε): 738 (π – π^*), 701 (agg), 668 (n– π^*), 453 (CT), 339 (deeper, π – π^*); MALDI-TOF-MS *m*/*z* (as matrix; α-cyano 4-hydroxycinnamicacid; CHCA): 1247 [M+H]⁺.

Yield of **10**: 0.82 g (32.32%). C₅₆H₆₄N₈O₄S₄Pb (1246 g/mol): C, 53.93; H, 5.14; N, 8.99. Found: C, 53.85; H, 5.18; N, 8.88%. FT-IR [KBr ν_{max}/cm^{-1}]: 3290 (vb), 3065, 2954, 2929, 2870, 1768 (w, H–O···H), 1712 (st), 1660 (w), 1598, 1519, 1481, 1454, 1417, 1359, 1313, 1232, 1134, 1066, 1033, 904, 821; ¹H NMR (DMSO-d₆): δ , ppm 8.07–7.73 (m, br, 12H, phenyl H3, H5, H6), 5.02 (s, t, br, 4H, -CH₂–OH, D₂O exchangeable), 3.84 (t, br, 8H, -CH₂OH), 3.44 (m, br, 4H, CH₂CH(-S–) CH₂), 3.30 (DMSO), 1.79–1.72 (m, 8H, CH₂CH₂CH), 1.58–1.47 (q, 8H, CH₂CH₂CH–), 1.43–1.36 (m, 8H, CH₂CH₂CH₃), 0.96 (t, 12H, CH₃). UV–Vis (THF): λ_{max} nm (log ε): 732 (π–π^{*}), 696 (agg) 670 (*n*–π^{*}), 413 (CT), 349 (deeper, π–π^{*}); MALDI-TOF-MS *m/z* (as matrix; α-cyano 4-hydroxycinnamicacid; CHCA): 1247 [M+H]⁺.

2.2.5. 1(4),8(11),15(18),22(25)-Tetrakis-(6-hydroxyhexylthio)phthalocyaninatolead(II) (**11**) 2(3),9(10),16(17),23(24)-tetrakis-(6-hydroxyhexylthio)phthalocyaninatolead(II) (**12**)

The same procedures as described for the preparation of **7** and **8** were used to prepare compounds **11** and **12**, except the purification steps started with **5** and **6** (0.15 g, 0.576 mmol) and Pb(O₂CMe)₂ (0.19 g, 0.576 mmol). The crude product was washed several times successively, with first 20 cm³ hexane, and then 20 cm³ CH₃CN to remove impurities. The main compound was extracted with ca. 50 cm³ CH₂Cl₂, then the phthalocyanines (**11** and **12**) were purified by flash-chromatography using CH₂Cl₂. The solvent, CH₂Cl₂, was removed under reduced pressure giving green oily compounds. Both compounds are soluble in CH₂Cl₂, CHCl₃, MeOH, EtOH, THF, DMF, DMSO and pyridine, and are slightly soluble in CH₃CN.

Yield of **11**: 0.055 g (30.65%); *Anal.* Calc. for C₅₆H₆₄N₈O₄S₄Pb (1246 g/mol): C, 53.93; H, 5.14; N, 8.99. Found: C, 53.33; H, 5.15; N, 8.78%. FT-IR (KBr v_{max}/cm^{-1}): 3278 (br, H-bonded), 2954, 2927, 2883, 1722 (w, H–O···H), 1653, 1600, 1525, 1463, 1377, 1315, 1273, 1212, 1092, 1034, 874, 856, 795; ¹H NMR (DMSO-d₆) δ , ppm: 7.85–7.60 (m, 12H, phenyl H4, H5 and H6), 4.20 (t, br, 4H, –CH₂–OH, D₂O exchangeable), 3.58 (t, 8H, –*CH*₂OH), 2.92 (8H, CH₂–*CH*₂–S–), 1.68 (m, 8H, –*CH*₂CH₂–S–Ar), 1.50 (m, 8H, CH₂CH₂CH₂–OH), 1.37 (m, 16 H, 2×*CH*₂CH₂OH). UV–Vis (DMF) λ_{max} nm (log ε): 757 (π–π^{*}), 702 (agg), 680 (*n*–π^{*}), 457 (CT), 340 (deeper, π–π^{*}); MALDI-TOF-MS *m*/*z* (as matrix; α-cyano 4-hydroxycinnamic acid; CHCA): 1248.1 [M+H]⁺.

Yield of **12**: 0.82 g (32.32%); C₅₆H₆₄N₈O₄S₄Pb (1246 g/mol): C, 53.93; H, 5.14; N, 8.99. Found: C, 53.85; H, 5.18; N, 8.88%. FT-IR (KBr v_{max}/cm^{-1}): 3290 (vb), 3065, 2954, 2929, 2870, 1768 (w, H–O···H), 1712 (st), 1660 (w), 1598, 1519, 1481, 1454, 1417, 1359, 1313, 1232, 1134, 1066, 1033, 904, 821; ¹H NMR (DMSO-d₆) δ ,



Scheme 1. Synthetic route of 3'-(2,3-dihydroxypropylthio)-phthalonitrile (1); 4'-(2,3-dihydroxypropylthio)-phthalonitrile (2), 3'-(1-hydroxyhexan-3ylthio)-phthalonitrile (3) and their α - and β -lead(II)phthalocyanines{M[Pc(S-CH₃CH₂(OH)CH₂(OH))]₄} (M = Pb^{II} (7–12). (i) K₂CO₃, 3-mercapto-1,2-propanediol, DMF, 303 K, 3 days; 3-mercapto-1-hexanol, DMF, 303 K, 3 days for **3**; (ii) anhydrous Pb(acac)₂, NNDMEA.



Fig. 1. (a) Simulated and (b) experimental isotopic patterns of the MALDI-TOF spectrum of complex 7.

ppm: 7.80–7.55 (br, 12H, phenyl H3, H5 and H6), 4.18 (s, t, br, –CH₂–*OH*, D₂O exchangeable), 3.58 (t, 12H, –*CH*₂OH), 2.96 (CH₂– S–), 1.62 (m, 2H, CH₂–S–Ar), 1.45 (m, 2H, *CH*₂CH₂CH₂–OH), 1.37 (m, 2×*CH*₂–CH₂CH₂). UV–Vis (THF) λ_{max} nm (log ε): 734 (π – π^*), 688 (agg), 664 (n– π^*), 412 (CT), 349 (deeper, π – π^*); MALDI-TOF-MS *m*/*z* (as matrix; α-cyano 4-hydroxycinnamic acid; CHCA): 1248.4 [M+H]⁺.

3. Results and discussion

3.1. Synthesis and characterization

The α and β tetra substituted functional lead phthalocyanines, $M{Pc[S-CH (C_{3}H_{7})(C_{2}H_{5}OH)]_{4}}$ (7, 9 and 11) and $M{Pc[S-CH (C_{3}H_{7})(C_{2}H_{5}OH)]_{4}}$ $C_6H_{12}(OH)]_4$ (**8**, **10** and **12**), as a mixture of different isomers, have been synthesized by the cyclotetramerization of the corresponding phthalonitriles carrying 3'-(2,3-dihydroxypropyl) (1), 4'-(2,3dihydroxypropyl) (2), 3'-(1-hydroxyhexan-3ylthio) (3), 4'-(1hydroxyhexan-3ylthio) (4) [25], 4'-(6-hydroxyhexylthio) (6) [21] and 3'-(6-hydroxyhexylthio) (5) [26] functional moieties in the presence of anhydrous Pb(O₂CMe)₂ and NNDMAE solvent (Scheme 1). The phthalocyanines were purified by flash-chromatography using CHCl₃ and CH₂Cl₂. The functional substituents and pyramidal geometry of the lead(II) complexes (7–12) confer better solubility than expected in a number of organic solvents, including CHCl₃, CH₂Cl₂, THF, EtOH, DMF, DMSO and DMAA. The purification steps were tedious owing to the functional substituents on the periphery of the Pcs and possible demetallization at



Fig. 2. UV-Vis spectra of (a) 8 and (b) 10 in THF/MeOH during titration with Ag^{I} (in MeOH).

the core of all PbPcs. The demetallization process occurs because the metal ion does not fit inside the central cavity and becomes pushed up above the Pc plane.

3.2. Spectroscopic characterization

Lead(II) phthalocyanine complexes **7–12** were characterized by FT-IR, UV–Vis, MALDI-TOF and ¹H NMR spectroscopy, as well as by



Fig. 3. UV-Vis spectra of 11 in THF/MeOH during titration with Pd^{II} (in MeOH).



Fig. 4. UV-Vis spectra of 12 in THF/MeOH during titration with (a) Pd^{II} (in MeOH) and (b) Ag^{I} (in MeOH).

elemental analysis. In the FT-IR spectra of the complexes, the most pronounced bands were the diagnostic –OH absorptions between 3400 and 3200 cm⁻¹, antisymmetric C–H stretching vibrations of CH₂ and CH₃ between 2975 and 2850 cm⁻¹ and S–CH₂ stretching at ca. 1220–1240 cm⁻¹ [10,13,18]. The most significant indicators for the formation of Pb^{II}Pc complexes **7–12** are the disappearance of the deuterium exchangeable signals belonging to peripheral – OH protons in the middle of the ¹H NMR spectra (δ = 5.5– 4.5 ppm) [18,25]. The shifts and changes in intensity of certain peaks in the ¹H NMR spectra of **7–12** are consistent with the precursors. The electronic spectra of Pb^{II}Pcs **7–12** were recorded in DMF solvent in the range 300–900 nm. UV–Vis spectral measurements indicated that the Q-band assigned to the π – π * transitions for all the PbPcs is particularly sensitive to the presence of both substituents on the benzene ring and the metal atom in phthalocy-anine core [10,15,27]. The B-bands of the complexes, assigned to the deeper π – π * transitions, were observed between 330 and 370 nm. Incorporation of the electron acceptor Pb^{II} ion in the core of the Pc molecule caused a bathochromic shift of the Q band to a pronounced extent in comparison to the ones observed in the spectra of H₂Pc and H₂Pz [10,13,15]. The isotopic mass distribution of the protonated molecular ion peak of complex **7** (Fig. 1) and **8** were

 Table 1

 Voltammetric data of the lead(II) phthalocyanines.

Complex		Redox processe	s					$^{d}\Delta E_{1/2}$
		Oxidation 2	Oxidation 1	Reduction 1	Reduction 2	Reduction 3	Reduction 4	
8	$E_{1/2}$ (V vs. SCE)		0.72	-0.66	-0.90	-1.43		1.38
	$\Delta E_{\rm p} ({\rm mV})$		65	62	68			
	$I_{\rm pa}/I_{\rm pc}$		0.80	0.91	0.78			
10	$E_{1/2}$ (V vs. SCE)		0.81	-0.67	-1.01	-1.34	-1.83 ^e	1.48
	$\Delta E_{\rm p} ({\rm mV})$		140	172	197			
	I_{pa}/I_{pc}		0.66	0.73	0.85			
11	${}^{a}E_{1/2}$ (V vs. SCE)		0.72	-0.63	-0.94	-1.50	-1.82 ^e	1.35
	$^{b}\Delta E_{\rm p}~(\rm mV)$		100	60	75	100		
	^c I _{pa} /I _{pc}		0.55	0.45	0.85	0.92		
12	$E_{1/2}$ (V vs. SCE)	1.09 ^e	0.75	-0.64	-0.94	-1.25	-1.86 ^e	1.38
	$\Delta E_{\rm p} ({\rm mV})$		80	55	57	130		
	$I_{\rm pa}/I_{\rm pc}$		0.75	0.90	0.85	0.72		

^a $E_{1/2} = (E_{pa} + E_{pc})/2$ at 100 mV s⁻¹ (E_{pc} for reduction, E_{pa} for oxidation for irreversible processes).

^b $E_{\rm p} = E_{\rm pa} - E_{\rm pc}$ at 0.100 Vs⁻¹ scan rate.

^c I_{pa}/I_{pc} for reduction, I_{pc}/I_{pa} for oxidation processes at 0.100 Vs⁻¹ scan rate.

^d $E_{1/2} = E_{1/2}$ (first oxidation) – $E_{1/2}$ (first reduction).

^e Recorded by SWV.



Fig. 5. (a) CVs of **11** $(5.0 \times 10^{-7} \text{ mol cm}^{-3})$ at various scan rates on Pt in DCM/TBAP (inset SWV of **11**; SWV parameters: pulse size = 100 mV; frequency: 25 Hz) (b) CVs of **11** recorded with different switching potentials at 0.100 Vs⁻¹ scan rate (inset: repetitive CVs of the first reduction process of **11**).

observed between 1143 and 1149 Da, with 1 Da mass increments. Complexes **9** and **10** gave isotopic mass distributions of the protonated molecular ion peak between 1247 and 1253 Da with 1 Da mass increments.

3.3. Metal ion binding titrations

Generally, Pc compounds tend to interact with each other by attractive π - π * stacking due to their extended flat aromatic surface, leading to aggregation [16–19,25,26]. The aggregation of Pb[Pc(α -SR)₄] and Pb[Pc(β -SR)₄] (R: functional group) complexes were detected using UV–Vis spectroscopy (Fig. 1). The shape of the Q-band is known to be a sensitive probe in determining the types of Pc aggregation. Blue-shifting, broadening and a decrease of the Q-band in intensity, and formation of the Q-band of the MPc dimer in the higher energy region are indicative of face-to-face conformations [16–19].

It is well known that sulfur atoms on the periphery of the metallo or metal-free phthalocyanine complexes (MPcs) are optically sensitive to soft metal ions, such as Ag^I and Pd^{II}. Therefore, we have employed UV–Vis spectroscopy to monitor the metalion binding capability of the MPc. Each titration experiment was carried out using a MeOH/thf solution of the MPcs (10/90, v/v) to ensure complete dissolution of the analyte salt in MeOH. The



Fig. 6. (a) CVs of **12** $(5.0 \times 10^{-7} \text{ mol cm}^{-3})$ at various scan rates on Pt in DCM/TBAP. (b) CVs of **12** recorded with different switching potentials during positive potential scan at 0.100 Vs⁻¹ scan rate. (c) SWV of **12** recorded with different initial potentials; SWV parameters: pulse size = 100 mV; frequency: 25 Hz.

concentration of the metal salt (ca. 10^{-6} mol cm⁻³) was kept higher than those of the MPc (ca. 10^{-8} mol cm⁻³) to diminish the absorption decreases of the bands due to dilution. Gradual addition of Ag^I to the solutions of **7–12** at room temperature caused a gradual color change, from green to light-green, which suggests that the complexes coordinate with Ag^I to form aggregated species. Interaction of Ag^I with these complexes decreases the solubility of the complexes formed, which results in the observation of an intractable product at the end of the titration. As shown in Fig. 2a and b (8 and 10) and Fig. 4b (11), Ag^I binding to the donor atoms of the complexes results in pronounced effects on the Q, B and shoulder band absorptions ($n-\pi^*$ transitions: attributed to the non-bonding sulfur electron (*n*) to the π^* phthalocyanine orbital) [16–19,27]. While Ag^I is added gradually to **7–12**, the Q band absorption intensities of the monomeric species (743, 724, 738, 732, 757, 734 nm respectively) decrease gradually and the band intensities assigned to the dimer aggregated species (at 693, 690, 694, 693, 740 and 687 nm respectively) are enhanced simultaneously. The B-bands of the complexes shift at the same time to the higher energy side by about 15-25 nm with a slight change in intensity. As shown in Figs. 2-4, the spectral changes during the titrations of the complexes with Ag^I and Pd^{II} give clear isosbestic points which demonstrate that the titrations give one type of aggregated species. This type may a mixture of different isomers, however these different isomers do not affect the spectral changes of the proposed aggregated species. The relation between the absorbance band molar extinction coefficients of the monomeric and aggregated species indicate dimer formation of the aggregated species [28,29]. While blue shifts of the Q bands are observed during the titration with Ag^I, the Q bands of the non-peripherally substituted phthalocyanines (7, 9 and 11) shift to longer wavelengths during titration with Pd^{II}. These different spectroscopic changes indicate different types of aggregates (*H*- and *J*-types) and the existence of Pd^{II} coordination to the sulfur donor atoms of the complexes with a square-planar type of formation. This means that the complexation of the α - or β -substituted complexes with Pd^{II} decreases the concentration of the monomeric units to some degree, but do not increase the dimeric band to the same extent due to the formation of slightly less soluble aggregated units. Consequently, the interaction of the Pd^{II} ion with the peripheral moieties of the complexes causes decomposition of the aggregates of the planar phthalocyanine molecules to some degree in solution. As known, spectral shifts due to chromophoric packing can generally be explained by the molecular exciton model proposed by Kandaz and co-workers [18,25] which suggests that the



Fig. 7. (A) Cyclic voltammograms of **8** $(5.0 \times 10^{-7} \text{ mol cm}^{-3})$ with different switching potentials at 0.100 Vs^{-1} scan rate on Pt in DCM/TBAP (inset SWV of **8**; SWV parameters: pulse size = 100 mV; frequency: 25 Hz).

bathochromic and hypsochromic shifts correspond to edge-toedge (*J*-aggregates) and face-to-face (*H*-aggregates) aggregations respectively. When the angle α lies within the range 54.7° < α < 90°, the aggregate is defined as the *H*-aggregate, from which a blue-shifted absorption with broadening could be detected. However, when α is a close to the critical angle, i.e., $\alpha \approx 54.7^{\circ}$, the absorption maximum remains almost unshifted or is bathochromically shifted with broadening when the 3-substituted phthalocyanines interact with Pd^{II} [25]. These uncommon changes may result from the formation of a Pd^{II}–Pc complex exhibiting a different geometry, the decomposition of the aggregates and the formation of square planar type complexes [16–19]. The results of the titration with Ag^I or Pd^{II} ions are in harmony with those obtained in previous works [16–19,25,26,30].

3.4. Electrochemical measurements

The solution redox properties of the complexes were studied using CV and SWV techniques in DCM on a platinum electrode. Table 1 lists the assignments of the couples recorded and the estimated electrochemical parameters, which included the half-wave peak potentials ($E_{1/2}$), the ratio of anodic to cathodic peak currents (I_{pa}/I_{pc}), peak potential separations (ΔE_p) and HOMO–LUMO gaps ($\Delta E_{1/2}$). The CV and SWV studies reveal that all the complexes give three well-defined ring-based reductions and two oxidation couples. The separation between the first and second ring reductions was found to be in the range 0.33–0.40 V for all the complexes. These peak separations and the HOMO–LUMO gap values are in agreement with the reported separation for redox processes in lead(II) phthalocyanine complexes [10,31–35].

Fig. 5 shows the CV and SWV of **11** in the DCM/TBAP electrolyte system. Complex **11** gives four reduction processes at -0.63, -0.94, -1.50 and -1.82 V and one oxidation processes at 0.72 V versus SCE at 0.100 Vs⁻¹ scan rate. The assignments of the redox couples are proposed below using spectroelectrochemistry measurements. The anodic to cathodic peak separations ($\Delta E_{\rm p}$) changed from 60 to 120 mV with a change in the scan rate from 10 to 500 mV s⁻¹ ($\Delta E_{\rm p}$ changing from 60 to 110 mV was obtained for the ferrocene reference), indicating the reversible electron transfer character of the complex (Fig. 5a). Reversibility is also illustrated by the similarity in the forward and reverse SWV scans (Fig. 5a inset). However, while the I_{pa}/I_{pc} values of the couples are less than unity at slow scan rates, the values of I_{pa}/I_{pc} increases towards unity with increasing scan rates, suggesting the existence of an irreversible chemical reaction succeeding the first reduction and oxidation processes [34]. This kind of chemical reaction might be the demetallization of the complex assigned by spectroelectrochemical measurements, given below. A change of the peak character with different switching potentials supports the existence of this chemical reaction (Fig. 5b). Repetitive cycles between 0 and -0.80 V cause a change from reversible to irreversible behavior for the first reduction process (inset in Fig. 5b). These behaviors indicate demetallization of the complex after the first reduction process. Changing from reversible to irreversible character and the observation of a new wave at 0.37 V indicate that the complex was also demetallized after the first oxidation process when the vertex potential goes to more positive potentials, step by step.

Fig. 6 shows the CV and SWV of **12** in the DCM/TBAP electrolyte system. Changing the substituents from the α position to the β position affects the CV and SWV responses of the complex



Fig. 8. *In situ* UV–Vis spectral changes of **11**. (a) (inset: at the beginning of the first reduction process during the potential application at $E_{app} = -0.75$ V.) Second part of the spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -1.05$ V (the second reduction process). (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (b) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes during the potential application at $E_{app} = -0.75$ V. (c) The spectral changes dur

considerably. For complex 12, four reduction and two oxidation processes are recorded at -0.64, -0.94, -1.25, -1.86, 0.75 and 1.09 V versus SCE at 0.100 Vs⁻¹ scan rate. While the peak character of complex **11** is affected by the scan rates, switching potentials and repetitive potential scans, complex 12 is not considerably affected by these stresses. The anodic to cathodic peak separations $(\Delta E_{\rm p})$ indicate reversible character of the electron transfer reactions for the reduction processes. The values of I_{pa}/I_{pc} for the reduction couples are unity for the first and second reductions and ca. 0.60 for the third reduction at all scan rates (Fig. 6a). The peak characters of the reduction processes do not change with the different switching potentials and repetitive CV cycles. However, the oxidation behavior of the complex changes with the different switching potentials, as shown in the CV and SWV in Fig. 6b and c. When the potential is switched before the second oxidation process, the complex gives a quasi-reversible oxidation process $(\Delta E_{\rm p} = 130 \text{ mV} \text{ and } I_{\rm pa}/I_{\rm pc} = 0.80)$, whereas when the potential is switched after the second oxidation process, the first quasi-reversible oxidation process becomes irreversible and a new couple is observed at 0.26 V. This new peak shifts to 0.35 V when the potential was switched from more positive potentials. These behaviors indicate the existence of a chemical reaction after the first oxidation reaction, which may be demetallization of the complex.

Complex **10** showed very similar CV and SWV responses to **12**, with a small potential shift due to the different electron releasing ability of the substituents. However, complex **8** gave completely different CV and SWV responses to the other complexes. It gives two common ring reduction processes and a very intense uncommon peak at -1.20 V, which may be due to dinitrile benzene groups of the products formed after decomposition. This means that the complex is stable during first two reduction processes, but decomposes immediately after the second reduction process. It does not demetallize during the oxidation process, and so gives a clear reversible oxidation process (Fig 7).

3.5. In situ spectroelectrochemical and in situ electrocolorimetric measurements

Spectroelectrochemical studies were employed to confirm the assignments of the redox couples recorded in the CVs and SWVs of the complexes. The spectroelectrochemical studies indicate different spectroscopic changes to the common ring based redox processes because of the demetallization of the complexes. Demetallization of the Pb^{II}Pc complexes was also observed by Kandaz et al. [30] during the potential application at just negative of the first reduction process over a period of a few minutes. In our previous studies [13,31,35] we also indicated the demetallization of the PbPcs before or after the first reduction processes and during the positive potential scans, depending on the substituents. Similarly in this study, demetallization of complexes (10-12) is observed simultaneously with or just after the first reduction and/ or first oxidation of the phthalocyanine rings. In contrast, complex 8 is stable until the second reduction potential and the during oxidation process.

Fig. 8 shows the *in situ* UV–Vis spectral changes and color changes of **11** under the applied potential of the redox processes. During the controlled potential reduction of the complex at -0.75 V, two distinct spectral changes are recorded at the same potential application continuously (Fig 8a). At the beginning of the process, a new band is enhanced at 668 nm while the remaining spectrum does not change considerably (inset in Fig 8a). These changes give a split Q band, which indicates the formation of the metal free phthalocyanine (H₂Pc). Then the Q-band at 732 nm, $n-\pi^*$ transition band at 622 nm and the B bands at 346 and 405 nm decrease in intensity, while the band at 668 nm remains unchanged. These changes are typical for a ring-based reduction for

a metal free phthalocyanine [10,31,35]. The green color of the solution (point \Box *x* = 0.3249, *y* = 0.4492) changes to greenish yellow (point \bigcirc *x* = 0.3358, *y* = 0.409) during the process (Fig. 8d). Further potential application at -1.05 V (Fig. 8b) causes a decrease in



Fig. 9. *In situ* UV–Vis spectral changes of **12**. (a) (inset: at the beginning of the first reduction process during the potential application at $E_{app} = -0.80$ V.) Second part of the spectral changes during the potential application at $E_{app} = -0.80$ V. (b) The spectral changes during the potential application at $E_{app} = -0.80$ V. (b) The spectral changes during the potential application at $E_{app} = -0.80$ V. (b) The spectral changes during the potential application at $E_{app} = -0.80$ V. (c) Chromaticity diagram of **12** (each symbol represents the color of the electro-generated species; \Box : neutral **12**, Pb^{II}Pc⁻², \bigcirc : color of the solution after the solution after the solution after the first reduction, \preceq_{c1} : color of the solution after the second reduction, \preccurlyeq_{c1} : color of the solution.

intensity of all the bands, which confirms the decomposition of the species due to demetallization. The demetallization and then the decomposition of the complex were also confirmed by the spectral changes during the re-oxidation of the complex at this stage. Reoxidation of the complex at this stage does not result in the regeneration of the starting spectrum and color, which indicates that the second reduction process of the complex is irreversible in that applying 0.00 V did not result in the regeneration of the starting spectrum and color. Fig. 8c shows the spectral changes during the ring-based oxidation process under the applied potential at 0.85 V. During this process, while the absorption of the Q-band at 732 nm and the $n-\pi^*$ transition band at 622 nm decrease in intensity, new bands are observed at 552 and 890 nm which are assigned to a LMCT transition. At the same time, the B band at 415 nm decreases in intensity. The decrease in the O band without shift and the observation of new bands at 552 and 890 nm are characteristic of ring-based oxidation processes. The green color of the solution changes to orange (point $\leq x = 0.3676$, y = 0.3821) during this process. After this point, when a more positive potential was applied, all the bands in the spectra decrease in intensity due to decomposition of the complex.

Complexes **12** (Fig. 9) and **10** give very similar *in situ* UV–Vis spectroscopic changes during the potential applications corresponding to the relevant electron transfer processes. *In situ* UV–Vis spectroscopic changes of **12** during the potential application at -0.80 V (Fig. 9) show that the complex is demetallized during the first reduction process. At the beginning of the potential application at -0.80 V, a new band starts to appear at 677 nm, while the intensity of the Q-band at 717 nm does not change due to the demetallization of the complex. The process result in a split Q band

(Fig. 9a) corresponding to the formation of $[H_2Pc(-2)]$. Then, at the same potential application, one of the split Q bands decreases with a blue shift while the other one remains unchanged, then both bands decreases in intensity. This final process shows the reduction of the $[H_2Pc(-2)]$ species to $[H_2Pc(-3)]$, followed by the decomposition of the reduced species. As shown in Fig. 9b, the ring oxidation process occurs at 0.90 V potential application, then the oxidized species are demetallized and then decompose during the potential application at 1.30 V. Decomposition of the complex after the demetallization process also explains the CV behavior of the complex at higher concentrations. The waves recorded at 0.26 V in the CV of the complex may result from the species produced by the decomposition reaction. Complex 10 gave very similar spectroscopic changes to 12. The only difference is the ease of the demetallization process. During the potential application at -0.80 V, the O-band of complex **10** splits into two bands assigned to the formation of the metal free phthalocvanine. However in the case of 12, the complex starts to reduce and then demetallized. Complex **10** was demetallized at the beginning of the potential application at -0.80 V, while 12 shows spectroscopic changes corresponding to simultaneous ring reduction and demetallization processes.

Complex **8** gives completely different spectroscopic changes to the other complexes. As shown in Fig. 10, during the potential applications at -0.80 and -1.05 V, the spectral changes indicate a ligand-based reduction of the complex. A decrease of the Q band and the observation of a new band at around 600 nm indicate the ligand-based reduction and are easily assigned to the $[Pb^{II}Pc^{-2}]/[Pb^{II}Pc^{-3}]^-$ process (Fig. 10a). At -1.05 V potential application, the Q band decreases without shift and new bands are observed



Fig. 10. *In situ* UV–Vis spectral changes of **8**. (a) The spectral changes during the potential application at $E_{app} = -0.80$ V. (b) The spectral changes during the potential application at $E_{app} = -0.80$ V. (c) The spectral changes during the potential application at $E_{app} = -0.80$ V. (d) Chromaticity diagram of **8** (each symbol represents the color of the electro-generated species; \Box : neutral **8**, Pb^{II}Pc⁻², \odot : color of the solution after the first reduction, \triangle : color of the solution after the second reduction, $\frac{1}{\sqrt{2}}$: color of the solution after the first oxidation).

at 547 and 640 nm. These spectroscopic changes are indicators of the $[Pb^{II}Pc^{-3}]^{-}[Pb^{II}Pc^{-4}]^{2-}$ redox process (Fig. 10b). After the second reduction, the complex decomposed under the applied potential of -1.60 V. As shown in Fig. 10c, the ring oxidation process occurs at 0.85 V potential application and then the complex decomposed during the potential application at 1.30 V. Color changes of the complex during the electron transfer reactions are monitored by *in situ* electrocolorimetric measurements and a chromaticity diagram of the colors is given in Fig. 10d.

The CV, SWV and *in situ* spectroscopic responses of the complexes indicate that different substituents of the complexes and the positions of the substituents affect the voltammetric and spectroscopic changes. The ease of the demetallization process differs with the environment of the phthalocyanine ring. The order of the ease of demetallization is 11 > 12 = 10 > 8.

4. Conclusion

The synthesis, characterization, metal ion sensing, voltammetric and spectroelectrochemical properties of newly synthesized functional Pb^{II}Pc derivatives have been presented in this work for the first time. It has been shown that the hetero atoms on the periphery of the Pb^{II}Pc complexes are optically sensitive to soft metal ions such as Ag^I and Pd^{II}. A demetallization process was observed during the voltammetric and spectroelectrochemical measurements. Observation of the demetallization process of Pb^{II} in the Pc skeleton supports a different position to Pc carrying transition metal ions. The demetallization process occurred because the metal ion does not fit inside the central cavity and becomes puffed up above the Pc plane. Oxidation and reduction of the complexes change the symmetry of the complex, causing demetallization of the complex. After the demetallization process, the cavity of the ring cannot be loaded with proton ions due to the absence of any protons. This may cause the decomposition of the complexes. Different substituents of the complexes change the ease of the demetallization processes of the complexes. The substituent of complex 12 stabilizes the complex so it gives two ring based reduction processes and decomposes only after -1.30 V potential application.

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