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Electrochemical and spectroelectrochemical properties of new metal free, nickel(II), lead(II) and zinc(II) phthalocyanines

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ABSTRACT

The new metal free, nickel(II), lead(II) and zinc(II) phthalocyanines containing 2-[2-(4-allyl-2-methoxyphenoxy)ethoxy]ethoxy groups were synthesized and structurally characterized by using IR, ^{1}H NMR, ^{13}C NMR, UV–vis and elemental analysis spectral data. Redox properties of the complexes were determined with voltammetric and in situ spectroelectrochemical measurements in different electrolytic systems, tetrabutylammonium perchlorate (TBAP) dissolved dichloromethane (DCM) and dimethylsulfoxide (DMSO). All complexes gave two reversible reduction couples in the cathodic sides of the voltammograms in TBAP/DCM. While two oxidation processes were observed for all complexes in DCM, these processes were recorded as broad and split waves. All of the redox processes of the complexes shifted to the negative potentials and behaved more reversible in TBAP/DMSO electrolyte. Due to the narrow anodic potential window of DMSO, only one oxidation process was recorded in DMSO, while third reduction processes could be observed at more negative potentials for all complexes. Changing of the metal center of the complexes caused to shifting of the redox processes due to the different effective nuclear charge on the metal ions of the complexes. It can be easily concluded that the results of the voltammetric and in situ spectroelectrochemical supported the proposed structure of the complexes.

1. Introduction

Metallophthalocyanine (MPc) complexes have become very important during recent years due to their unique optical, electronic, catalytic and structural properties [1–3]. These unique properties lead to many applications in different scientific and technological areas such as photoconducting agents in photocopying devices, chemical sensors, catalysis, liquid crystals, photodynamic therapy of cancer, solar energy conversion, nonlinear optics, semiconductors, and optical data storage [4–12].

The applicability especially in some of these areas including electrocatalysis, electrochromism, and energy producing devices such as fuel cells and some optoelectronic devices is closely related to their unique electron transfer properties. Therefore, the identification of the redox properties of newly synthesized metallophthalocyanine (MPc) compounds has vital importance in determining the possibility of the usage in these technological applications. Some MPcs, especially iron, cobalt and manganese Pcs have been used in catalytic reactions because of their central metal based redox activity [13–18].

Owing to low solubility of phthalocyanines in common organic solvents and water, application of phthalocyanines is limited. For this reason, one of the main aims of research on the phthalocyanines is to increase their solubility in common organic solvents. Low solubility of phthalocyanines in common organic solvents can be overcome by introducing different kinds of substituents such as alkyl, alkoxy, phenoxy, macrocyclic groups [19,20] in common organic solvents and amino, sulfo or carboxyl groups in water [21,22]. In this work, we have synthesized metal free, nickel(II), lead(II) and zinc(II) phthalocyanines with 2-[2-(4-allyl-2-methoxyphenoxy)ethoxy]ethoxy functionalized groups. Thanks to these functionalized groups, metal free, nickel(II), lead(II) and zinc(II) phthalocyanines complexes **2–5** can readily dissolve in organic solvents [23]. In this paper, effects of the 2-[2-(4-allyl-2-methoxyphenoxy)ethoxy]ethoxy substituents to the redox activity of the metal free, nickel(II), lead(II) and zinc(II) phthalocyanines complexes **2–5** were examined with different voltammetric

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techniques and in situ spectroelectrochemical measurements in different electrolytic systems.

2. Experimental

2.1. Materials

4-Nitrophthalonitrile were prepared according to the literature [24], all reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [25].

2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer, using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometers in $CDCl_3$ and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Optical spectra in the UV–vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected. GC Agilent Technologies 7820A equipment (30 m × 0.32 mm × 0.50 μm DB Wax capillary column, FID detector) was used GC measurements. Elementel analysis were recorded on Costech ECS 4010 Spectrometer.

2.3. Synthesis

2.3.1. Metal free phthalocyanine (2)

A mixture of 4-[2-(2-(4-allyl-2-methoxyphenoxy)ethoxy)ethoxy]phthalonitrile **1** (0.2 g, 0.53 mmol), four drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 3 mL of *n*-pentanol was taken in a reaction tube. The mixture was heated in the sealed glass tube for 24 h under dry inert atmosphere at 160 °C. The reaction mixture was precipitated by adding aqueous acetic acid. The precipitate was filtered, washed with hot ethanol, and acetonitrile. After drying under vacuum, the product was chromatographed on a basic alumina column with chloroform–methanol (99:1) solvent system as eluent. Yield: 100 mg (47%). FT-IR ν_{max}/cm $^{-1}$ (KBr pellet): 3291 (N—H), 3074–3007 (Ar—H), 2931–2837 (Aliph. C—H), 1613, 1504, 1417, 1339, 1321, 1264, 1214, 1150, 1120, 1091, 1008, 919, 818, 742. ^{1}H NMR. ($CDCl_3$), (d:ppm): 8.17–8.09 (m, 12H, Ar—H), 7.50–7.01 (m, 12H, Ar—H), 5.90 (m, 4H, —CH =), 5.26 (m, 8H, =CH_2), 4.32 (t, 16H, O—CH_2), 3.83 (s, 12H, —OCH_3), 3.29 (d, 8H, —CH_2), 2.02 (m, 16H, CH_2—O), −4.58 (s, 2H, NH). ^{13}C NMR. ($CDCl_3$), (d:ppm): 159.92, 151,67, 149.68, 146, 76, 143.36, 137.47, 133.39, 123.32, 122.14, 121.32, 120.56, 119.50, 110.40, 110.19, 103.48, 107.27, 70.10, 69.39, 68.89, 68.50, 68.00, 58.82, 55.76. UV–vis ($CHCl_3$): λ_{max}, nm (log ε): 702 (5.00), 672 (4.96), 609 (4.43), 342 (4.81).

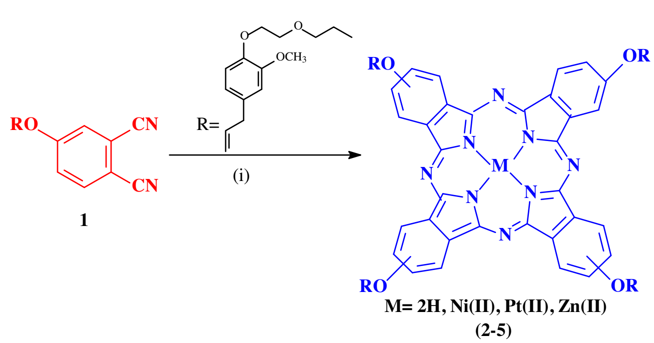

Fig. 1. The synthesis of new Metal free, Ni(II), Pb(II) and Zn(II) phthalocyanines. Reagent and condition: (i) *n*-pentanol, DBU, 160 °C, as metal salts $NiCl_2$, $PbCl_2$ and Zn $(CH_3COO)_2$ with 47%,47%, 45% and 40% yield.

Elemental Analysis $C_{88}H_{90}N_8O_{16}$: calcd. C 69.73; H 5.98; N 7.39, found: C 69.47; H 5.84; N 7.71.

2.3.2. General procedure of metal phthalocyanines ***(3–5)***

To give the metal phthalocyanines, the mixture of phthalonitrile compound **1** (0.2 g, 0.53 mmol), the related anhydrous metal salt $NiCl_2$ (33.7 mg, 0.26 mmol) for compound **3**, $PbCl_2$ (72.32 mg, 0.26 mmol) for compound **4,** $Zn(CH_3COO)_2$ (0.045 mg, 0.26 mmol) for compound **5** and four drops of DBU was heated at 160 °C in dry *n*-pentanol (3 mL) in a sealead tube, and stirred for 24 h. At the end of the reaction, green product was precipitated by addition of ethanol (20 mL) and filtered off. Along 2 h, the green solid product was refluxed with ethanol (30 mL), filtered off again and washed with hot ethanol, distilled water and diethyl ether. After drying under vacuum, the product was chromatographed on basic alumina column with chloroform–methanol (99:1) for compound **3**, (95:5) for compound **4,** (99:1) for compound **5** solvent system as eluent.

2.3.3. Synthesis of Nickel(II) phthalocyanine ***(3)***

Yield: 98 mg (47%). FT-IR ν_{max}/cm $^{-1}$ (KBr pellet): 3083 (Ar-H), 2977–2856 (Aliph. C—H), 1699, 1680, 1656, 1608, 1578, 1556, 1523, 1448, 1355, 1286, 1242, 1188, 1066, 998, 938, 903, 856, 788, 675, 542. ^{1}H NMR. ($CDCl_3$), (d:ppm): 7.45-7.02 (m, 12H, Ar-H), 6.95–6.67 (m, 12H, Ar-H), 6.25 (m, 4H, —CH =), 5.02 (m, 8H, =CH_2), 3.45 (m, 16H, O—CH_2), 3.39 (s, 12H, O—CH_3), 3.20 (d, 8H, —CH_2), 1.31 (m, 16H, CH_2—O). ^{13}C NMR. ($CDCl_3$), (d:ppm): 166.32, 150,89, 135.26, 134.88, 124,39, 124.23, 122.89, 122.64, 121.16, 120.85, 118.67, 118.22, 110.77, 110.34, 103.70, 111.34, 83.24, 78.60, 65.43, 62.76, 59.91, 55.82. UV–vis ($CHCl_3$): λ_{max}, nm (log ε): 675 (5.12), 612 (4.48), 331 (4.76). Elemental Analysis $C_{88}H_{88}N_8O_{16}Ni$: calcd. C 67.21; H 5.64; N 7.12, found: C 66.94; H 5.27; N 7.08.

2.3.4. Synthesis of lead(II) phthalocyanine ***(4)***

Yield: 102 mg (45%). FT-IR ν_{max}/cm $^{-1}$ (KBr pellet): 3078 (Ar—H), 2957–2876 (Aliph. C—H), 1818, 1786, 1663, 1600, 1515, 1422, 1403, 1386, 1295, 1254, 1199, 1168, 1096, 1071, 956, 921, 856, 818, 734, 703, 645, 582. ^{1}H NMR. ($CDCl_3$), (d:ppm): 7.12–6.68 (m, 12H, Ar—H), 6.56–6.27 (m, 12H, Ar—H), 6.14 (m, 4H, —CH=), 5.32 (m, 8H, =CH_2), 3.81 (m, 16H, O—CH_2), 3.69 (s, 12H, O—CH_3), 3.50 (d, 8H, –CH_2), 1.42 (m, 16H, CH_2—O). ^{13}C NMR. ($CDCl_3$), (d:ppm): 166.32, 155,12, 141.02, 138.72, 128,88, 125.61, 124.17, 122.34, 121.45, 120.61, 119.98, 118.45, 117.51, 110.67, 110.43, 110.30, 84.45, 78.78, 64.13, 60.45, 58.60, 54.01. UV–vis ($CHCl_3$): λ_{max}, nm (log ε): 669 (5.16), 616 (4.56), 338 (4.18). Elemental Analysis $C_{88}H_{88}N_8O_{16}Pb$: calcd. C 61.42; H 5.15; N 6.51, found: C 62.01; H 5.19; N 7.00.

2.3.5. Synthesis of zinc(II) phthalocyanine ***(5)***

Yield: 110 mg (40%). mp > 300 °C. FT-IR ν_{max}/cm $^{-1}$ (KBr pellet): 3063 (Ar—H), 2961–2826 (Aliph. C—H), 1768, 1716, 1637, 1603, 1505, 1446, 1417, 1336, 1265, 1216, 1149, 1119, 1086, 994, 911, 816, 742, 649, 597. ^{1}H NMR. ($CDCl_3$), (d:ppm): 7.25-6.99 (m, 12H, Ar—H), 6.80-6.77 (m, 12H, Ar—H), 6.01 (m, 4H, –CH =), 5.14 (m, 8H, =CH_2), 3.75 (m, 16H, O—CH_2), 3.69 (s, 12H, O—CH_3), 3.42 (d, 8H, —CH_2), 1.27 (m, 16H, CH_2—O). ^{13}C NMR. ($CDCl_3$), (d:ppm): 164.17, 151,32, 137.41, 136.82, 125,28, 124.40, 122.39, 121.54, 121.36, 120.45, 119.03, 119.40, 119.30, 110.90, 110.36, 110.18, 73.14, 72.50, 62.03, 61.56, 58.82, 54.42. UV–vis ($CHCl_3$): λ_{max}, nm (log ε): 678 (5.25), 610 (4.28), 332 (4.56). Elemental Analysis $C_{88}H_{88}N_8O_{16}Zn$: calcd. C 66.93; H 5.62; N 7.10, found: C 66.64; H 5.05; N 7.60.

2.4. Electrochemical and in situ spectroelectrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 ° C. The working electrode was a Pt disc with a surface