

Available online at www.sciencedirect.com





Polyhedron 26 (2007) 2638-2646

Novel phthalocyanines bearing four 4-phenyloxyacetic acid functionalities

Meryem Çamur, Ali Rıza Özkaya, Mustafa Bulut *

Marmara University, Department of Chemistry, 34722 Istanbul, Turkey

Received 27 October 2006; accepted 10 January 2007 Available online 21 January 2007

Abstract

Metal-free (2) and Co(II), Zn(II), Ni(II), Cu(II) metallophthalocyanines (2a–d) with four 4-phenyloxyacetic acid groups on the periphery were prepared by cyclotetramerization of new p-(3,4-dicyanophenoxy)phenylacetic acid (1) and the corresponding divalent metal salts. Further reactions of these products with thionylchloride and then benzylamine in tetrahydrofuran, and octanol in pyridine gave amide (3, 3a–d) and ester (4, 4a–d) derivatives, respectively. The new compounds have been characterized by elemental analyses, IR, UV–Vis, mass and ¹H NMR spectroscopy. The redox properties of compounds 2 and 2a–d were identified by cyclic voltammetry. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Phthalocyanines; 4-Hydroxyphenylacetic acid; Esterification; Metallophthalocyanines; Electrochemistry; Cyclic voltammetry

1. Introduction

Phthalocyanines (Pcs) form an important class of macrocyclic compounds which do not occur in nature [1]. Following the first synthesis in 1907, they have been established as blue and green dyestuffs, and their recent use as the photoconducting agent in photocopying machines has provoked research in various fields, including electrochromism, photovoltaic cell elements for electricity generation, electrophotography, application to optical computer read/write discs, low-dimensional metals, non-linear optics, electrocatalysis, liquid crystals, Langmuir-Blodgett films [2-8], chemical sensors [9] and photodynamic reagents for cancer therapy and other medical applications [10,11]. The two variables are the central metal ion and peripheral substituents: the possibility of inserting a great number of different metal ions into the phthalocyanine core is combined with the unlimited number and type of substituents, the variety of novel products is infinite. The introduction of bulky substituents on the peripheral position of the macrocycle increases drastically their solubility in organic solvents. In addition to the solubility, the spectral properties of phthalocyanines are also strongly influenced by the peripheral substituents on the macrocycles [12,13].

The phthalocyanine unit with an 18π electron aromatic system and its metal center in some cases is capable of oxidation or reduction. These redox processes depend on various factors such as the type of the central metal, solvent, axial ligands and substituents. The redox properties of phthalocyanines are critically related to most of their industrial applications. Cyclic voltammetry is the most widely used method to determine electrochemical properties in solution.

The present paper reports for the first time the synthesis and characterization of p-(3,4-dicyanophenoxy)phenylacetic acid from a single step reaction and its conversion into metal-free and metallophthalocyanines [M = Co(II), Zn(II), Ni(II) and Cu(II)] containing tetrakis(4-phenyloxyacetic acid) moieties at the periphery. Cyclic voltammetry of these compounds is also presented. The reactivity of the phenyloxyacetic acid substituents has been demonstrated by the preparation of better soluble esters than these pcs.

^{*} Corresponding author. Tel.: +90 216 3479641/1370; fax: +90 216 3478783.

E-mail addresses: mbulut@marmara.edu.tr, mustafabulut50@gmail.com (M. Bulut).

^{0277-5387/\$ -} see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.01.010

2. Experimental

2.1. Synthesis

IR spectra were recorded on a Shimadzu FTIR-8300 Fourier Transform Infrared spectrophotometer using KBr pellets, UV-VIS spectra on a Shimadzu UV-1601 UV-Vis spectrophotometer, and ¹H and ¹³C NMR spectra on a Varian UNITY INOVA 500 MHz spectrometer. Elemental analysis were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. Mass spectra were recorded on a Varian 711 spectrometer. 4-Nitrophthalonitrile was synthesized according to the reported procedure [14] and 4-hydroxyphenylacetic acid was purchased from Fluka Chemical Company, and was used as purchased. All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified. The solvents were stored over molecular sieves (4 Å). The homogeneity of the products were tested in each step by TLC (SiO₂).

2.1.1. p-(3,4-Dicyanophenoxy)phenylacetic acid (1)

4-Hydroxyphenylacetic acid (0.88 g, 5.78 mmol) and 4-nitrophthalonitrile (1.0 g, 5.78 mmol) were dissolved in dry DMF (100 ml) under nitrogen and anhyd. K₂CO₃ (1.60 g, 11.56 mmol) was added. After stirring for 24 h at 50-60 °C, the reaction mixture was treated with diluted HCl under ice cooling. The pure precipitate was filtered, washed with water to neutralize, and dried. Yield: 0.812 g (50.73%). M.p. 177–180 °C. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3500 (carboxylic acid OH), 3067-3050 (Ar-CH), 2930-2918 (aliphatic CH), 2231 (C=N), 1703 (C=O), 1588-1488 (Ar C=C), 1246 (Ar-O-Ar), 1205, 1161, 1079, 942, 842, 801, 664 and 523. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 12.36 (s, 1H, COOH), 8.09 (d, 1H, Ar-H), 7.77 (d, 1H, Ar-H), 7.39 (d, 1H, Ar-H), 7.35 (dd, 2H, Ar-H), 7.15 (dd, 2H, Ar-H), 3.63 (s, 2H, CH₂). ¹³C NMR (d-DMSO 500 MHz, δ ppm): 173.20 (acid C=O), 161.83 (Ar-C), 153.17 (Ar-C), 137.02 (Ar-C), 133.38 (Ar-C), 132.28 (Ar-C), 123.38 (Ar-C), 122.58 (Ar-C), 120.81 (Ar-C), 117.40 (Ar-C), 116.61 (C≡N), 116.09 (C≡N), 108.80 (Ar–C). MS (LC–MS, Scan ES⁺) m/z: 278 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in CHCl₃: 306 (3.73).

2.1.2. 2,9,16,23-Tetrakis(4-phenyloxyacetic acid)phthalocyanine (2)

Compound 1 (0.5 g, 1.80 mmol) and lithium metal (0.2 g, 28.6 mmol) were heated and stirred at 170 °C for 3 h under nitrogen in a mixture of 1,2-dichlorobenzene (4 ml) and pentanol (4 ml). After cooling to room temperature, acetonitrile was added in order to precipitate the product. The green precipitate was filtered and then washed with water and acetonitrile. It was dissolved in a small amount of methanol and precipitated by diluted HCl. In this mixture, the Li₂pcs formed was converted into H_2pcs . The green precipitate was filtered and washed with

water, hot acetonitrile, hot methanol, chloroform and diethyl ether, and dried. It is soluble in DMF, DMSO and pyridine. Yield: 0.255 g (51%). M.p. >300 °C. *Anal.* Calc. for C₆₄H₄₂N₈O₁₂: C, 68.94; H, 3.77; N, 10.05. Found: C, 68.89; H, 3.68; N, 10.11%. FT-IR (KBr), $\nu_{max}/(cm^{-1})$: 3410 (carboxylic acid OH), 3290 (NH), 3037 (Ar–CH), 2955–2866 (aliphatic CH), 1715 (C=O), 1603–1474 (Ar C=C), 1232 (Ar–O–Ar), 1165, 1090, 1013, 932, 831, 745, 644 and 608. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 12.40 (br s, 4H, COOH), 7.24–6.02 (m, 28H, Ar–H), 3.97 (s, 8H, CH₂), -7.22 (br s, 2H, NH). MS (LC-MS, Scan ES⁺) *m/z*: 1114 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 287 (4.82), 340 (4.87), 638 (4.74), 667 (4.79), 699 (4.69).

2.1.3. General procedure for the 2,9,16,23-tetrakis

(4-phenyloxyacetic acid) phthalocyaninatometal derivatives (2a-d)

A mixture of compound **2** (0.05 g, 0.045 mmol) and 0.45 mmol metal salts $[CoCl_2 \cdot 6H_2O \ 0.11 \text{ g}, \text{Zn-}(AcO)_2 \cdot 2H_2O \ 0.10 \text{ g}, \text{NiCl}_2 \cdot 6H_2O \ 0.11 \text{ g}$ or $CuCl_2 \ 0.06 \text{ g}]$ in dry DMF (1.5 ml) was heated and stirred at 155 °C for 24 h under N₂ in a sealed glass tube. After cooling to room temperature, the reaction mixture was treated with diluted HCl. After that, the precipitated green-blue solid was filtered off. The product was washed with water, hot methanol, hot acetonitrile and diethyl ether, and dried.

2.1.3.1. 2,9,16,23-Tetrakis(4-phenyloxyacetic acid)phthalocyaninatocobalt (II) (2a). This is soluble in THF, DMF, DMSO and pyridine. Yield: 0.029 g (55%). M.p. >300 °C. Anal. Calc. for C₆₄H₄₀N₈O₁₂Co: C, 65.58; H, 3.42; N, 9.56. Found: C, 65.86; H, 3.39; N, 9.73%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3396 (carboxylic acid OH), 3045 (Ar– CH), 2925–2866 (aliphatic CH), 1728 (C=O), 1603–1474 (Ar C=C), 1232 (Ar–O–Ar), 1161, 1094, 1057, 1016, 953, 880, 824, 745, 671 and 579. MS (LC-MS, Scan ES⁺) m/z: 1171 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 328 (4.90), 662 (5.03).

2.1.3.2. 2,9,16,23-Tetrakis(4-phenyloxyacetic acid)phthalocyaninatozinc (II) (**2b**). This is soluble in THF, DMF, DMSO and pyridine. Yield: 0.038 g (72%). M.p. >300 °C. Anal. Calc. for C₆₄H₄₀N₈O₁₂Zn: C, 65.25; H, 3.40; N, 9.53. Found: C, 65.16; H, 3.47; N, 9.65%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3402 (carboxylic acid OH), 3067–3030 (Ar– CH), 2925–2866 (aliphatic CH), 1728 (C=O), 1603–1470 (Ar C=C), 1232 (Ar–O–Ar), 1161, 1090, 1045, 1016, 941, 889,864, 824, 745 and 664. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 12.40 (br s, 4H, COOH), 8.00–7.20 (b, 28H, Ar–H), 3.31 (s, 8H, CH₂). MS (LC-MS, Scan ES⁺) m/z: 1177 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 356 (4.77), 612 (4.44), 679 (5.13).

2.1.3.3. 2,9,16,23-Tetrakis(4-phenyloxyacetic acid)phthalocyaninatonickel (II) (2c). This is soluble in THF, DMF, DMSO and pyridine. Yield: 0.045 g (85.6%). M.p. >300 °C. Anal. Calc. for C₆₄H₄₀N₈O₁₂Ni: C, 65.58; H, 3.42; N, 9.56. Found: C, 65.06; H, 3.37; N, 9.45%. FT-IR (KBr), $v_{max}/$ (cm⁻¹): 3425 (carboxylic acid OH), 3067–3038 (Ar–CH), 2926–2918 (aliphatic CH), 1722 (C=O), 1599–1410 (Ar C=C), 1234 (Ar–O–Ar), 1161, 1121, 1086, 1057, 953, 883, 824, 748, 671 and 644. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 12.80 (br s, 4H, COOH), 7.74–7.23 (b, 28H, Ar–H), 3.24 (s, 8H, CH₂). UV–Vis λ_{max} (nm) (log ε) in DMF: 333 (4.48), 609 (4.58), 672 (4.40).

2.1.3.4. 2,9,16,23-Tetrakis(4-phenyloxyacetic acid)phthalocyaninatocopper (II) (2d). This is soluble in THF, DMF, DMSO and pyridine. Yield: 0.029 g (55%). M.p. >300 °C. Anal. Calc. for $C_{64}H_{40}N_8O_{12}Cu$: C, 65.33; H, 3.40; N, 9.53. Found: C, 65.63; H, 3.36; N, 9.85%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3410 (carboxylic acid OH), 3074– 3030 (Ar–CH), 2918-2850 (aliphatic CH), 1715 (C=O), 1603–1466 (Ar C=C), 1232 (Ar–O–Ar), 1165, 1094, 1049, 1016, 953, 872, 824, 741, 671 and 648. UV–Vis λ_{max} (nm) (log ε) in DMF: 342 (4.63), 626 (4.56), 678 (4.71).

2.1.4. General procedure for the N-benzylamide derivatives of phthalocyanine (3, 3a–d)

The phthalocyanine derivatives (2, 2a-d) (0.02 g) were refluxed for 4 h in thionylchloride (2 ml). At the end of the reaction, thionylchloride was removed under reduced pressure. The resulting solid was dissolved in dry THF (1 ml). Dry benzylamine (0.5 ml, 4.58 mmol) was dissolved in dry THF (1 ml) and dropped into the acid chloride at 10 °C. The mixture was stirred at room temperature for 15–16 h. After the reaction, THF was removed under reduced pressure. The reaction mixture was treated with water to precipitate the product, and filtered. The products were washed with water, methanol, acetonitrile and diethyl ether, and dried.

2.1.4.1. 2,9,16,23-Tetrakis(N-benzyl-4-phenyloxyacetamide) phthalocyanine (3). This is soluble in DMF, DMSO and pyridine. Yield: 0.014 g (53.4%). M.p. >300 °C. Anal. Calc. for C₉₂H₇₀N₁₂O₈: C, 75.10; H, 4.76; N, 11.43. Found: C, 75.16; H, 4.47; N, 11.12%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3290 (NH), 3059–3030 (Ar–CH), 2918–2850 (aliphatic CH), 1728 (C=O), 1655 (amide NH), 1603–1462 (Ar C=C), 1250 (Ar–O–Ar), 1165, 1132, 1094, 1028, 949, 827, 745, 696, 599 and 507. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 8.65 (s, 4H, –CONH), 7.63–7.11 (b, 48H, Ar–H), 4.31 (d, 8H, –NH<u>CH</u>₂Ar), –8.00 (br s, 2H, NH). MS (LC-MS, Scan ES⁺) *m*/*z*: 1470 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMSO: 302 (4.28), 330 (4.28), 646 (4.17), 682 (4.36), 704 (4.30).

2.1.4.2. 2,9,16,23-Tetrakis(N-benzyl-4-phenyloxyacetamide) phthalocyaninatocobalt (II) (3a). This is soluble in THF, DMF, DMSO and pyridine. Yield: 0.022 g (84.3%). M.p. >300 °C. Anal. Calc. for C₉₂H₆₈N₁₂O₈Co: C, 72.29; H, 4.45; N, 11.00. Found: C, 72.34; H, 4.62; N, 11.12%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3290 (NH), 3074–3030 (Ar–CH), 2926–2858 (aliphatic CH), 1726 (C=O), 1651 (amide NH), 1603–1462 (Ar C=C), 1254 (Ar–O–Ar), 1198,1161, 1117, 1020, 984,916, 824, 748, 696, 604 and 503. MS (LC-MS, Scan ES⁺) m/z: 1527 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 330 (4.79), 667 (4.75).

2.1.4.3. 2,9,16,23-Tetrakis(N-benzyl-4-phenyloxyacetamide) phthalocyaninatozinc (II) (**3b**). This is soluble in THF, DMF, DMSO and pyridine. Yield: 0.016 g (60.2%). M.p. >300 °C. Anal. Calc. for C₉₂H₆₈N₁₂O₈Zn: C, 72.02; H, 4.44; N, 10.96. Found: C, 72.16; H, 4.62; N, 10.72%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3290 (NH), 3067–3022 (Ar–CH), 2918–2858 (aliphatic CH), 1728 (C=O), 1651 (amide NH), 1603–1462 (Ar C=C), 1250 (Ar–O–Ar), 1161, 1094, 1016, 976,897, 831, 764, 696, 596 and 507. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 8.70 (s, 4H, –CONH), 7.78–7.01 (b, 48H, Ar–H), 4.42 (d, 8H, –NH<u>CH2</u>Ar),. UV–Vis λ_{max} (nm) (log ε) in DMF: 360 (4.77), 614 (4.49), 683 (5.15).

2.1.4.4. 2,9,16,23-Tetrakis(N-benzyl-4-phenyloxyacetamide) phthalocyaninatonickel (II) (3c). This is soluble in DMF, DMSO and pyridine. Yield: 0.017 g (66%). M.p. >300 °C. Anal. Calc. for C₉₂H₆₈N₁₂O₈Ni: C, 72.29; H, 4.45; N, 11.00. Found: C, 72.56; H, 4.28; N, 10.84%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3388 (NH), 3059–3030 (Ar–CH), 2934–2851 (aliphatic CH), 1736 (C=O), 1647 (amide NH), 1595–1458 (Ar C=C), 1254 (Ar–O–Ar), 1202, 1165, 1109, 1016, 989, 920, 839, 745, 692, 596 and 511. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 8.67 (s, 4H, –CONH), 7.68–7.11 (b, 48H, Ar–H), 4.45 (d, 8H, –NH<u>CH2</u>Ar). UV–Vis λ_{max} (nm) (log ε) in DMSO: 287 (4.47), 621 (4.01), 672 (3.79).

2.1.4.5. 2,9,16,23-Tetrakis(N-benzyl-4-phenyloxyacetamide) phthalocyaninatocopper (II) (**3d**). This is soluble in DMF, DMSO and pyridine. Yield: 0.018 g (71%). M.p. >300 °C. Anal. Calc. for C₉₂H₆₈N₁₂O₈Cu: C, 72.09; H, 4.44; N, 10.97. Found: C, 72.27; H, 4.18; N, 10.62%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3396 (NH), 3067–3022 (Ar–CH), 2926–2858 (aliphatic CH), 1740 (C=O), 1647 (amide NH), 1595–1462 (Ar C=C), 1246 (Ar–O–Ar), 1161, 1109, 1016, 984, 905, 841, 745, 700, 599 and 515. (LC-MS, Scan ES⁺) *m/z*: 1531 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMSO: 344 (4.48), 627 (4.42), 679 (4.44).

2.1.5. General procedure for the synthesis of octylacetate derivatives of phthalocyanine (4, 4a–d)

A mixture of the phthalocyanine derivatives (2, 2a-d) (0.02 g) and thionylchloride (2 ml) were refluxed for 4 h. At the end of the reaction, thionylchloride was removed under reduced pressure. The resulting solid was dissolved in dry pyridine (0.5 ml, 3.17 mmol). Dry octanol (0.5 ml) was dissolved in dry pyridine (0.5 ml) and dropped into acid chloride at 0 °C. The mixture was stirred at 50–60 °C for 30 min at room temperature for 15–16 h, and poured into cold diluted HCl. The oily product was treated with diethyl ether to precipitate the ester. The crude

2641

product washed with water and dried, purified on silica gel column chromatography with chloroform as the eluent.

2.1.5.1. 2,9,16,23-Tetrakis(octyl 4-phenyloxyacetate)phthalocyanine (4). This is soluble in THF, CHCl₃, CH₂Cl₂, DMF, DMSO and pyridine. Yield: 0.016 g (57.8%). M.p. >300 °C. Anal. Calc. for C₉₆H₁₀₆N₈O₁₂: C, 73.75; H, 6.79; N, 7.17. Found: C, 73.13; H, 6.53; N, 7.42%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3290 (NH), 3074 (Ar–CH), 2926– 2858 (aliphatic CH), 1732 (C=O), 1595–1466 (Ar C=C), 1250 (Ar–O–Ar), 1165 (ester C–O), 1024, 941, 835, 748, 627 and 519.¹H NMR (*d*-DMSO 500 MHz, δ ppm): 8.21–6.75 (b, 28H, Ar–H), 4.11 (t, 8H, COOCH₂R), 1.72–1.08 (m, 48H, COOCH₂(<u>CH₂</u>)₆CH₃), 0.89 (t, 12H, CH₃), –7.8 (br s, 2H, NH). MS (LC-MS, Scan ES⁺) *m/z*: 1562 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 320 (4.19), 619 (3.94), 644 (3.94), 681 (4.27).

2.1.5.2. 2,9,16,23-Tetrakis(octyl 4-phenyloxyacetate)phthalocyaninatocobalt (II) (4a). This is soluble in THF, CHCl₃, CH₂Cl₂, DMF, DMSO and pyridine. Yield: 0.012 g (43%). M.p. >300 °C. Anal. Calc. for C₉₆H₁₀₄N₈O₁₂Co: C, 71.15; H, 6.42; N, 6.92. Found: C, 71.85; H, 6.69; N, 6.56%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3056 (Ar–CH), 2926–2858 (aliphatic CH), 1736 (C=O), 1595–1458 (Ar C=C), 1246 (Ar–O–Ar), 1157-1101 (ester C–O), 1020, 916, 835, 748, 667, 627 and 519. MS (LC-MS, Scan ES⁺) m/z: 1619 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 303 (4.83), 324 (4.82), 663 (4.75).

2.1.5.3. 2,9,16,23-Tetrakis(octyl 4-phenyloxyacetate)phthalocyaninatozinc (II) (4b). This is soluble in THF, CHCl₃, CH₂Cl₂, DMF, DMSO and pyridine. Yield: 0.015 g (53%). M.p. >300 °C. Anal. Calc. for C₉₆H₁₀₄N₈O₁₂Zn: C, 70.89; H, 6.40; N, 6.89. Found: C, 71.21; H, 6.54; N, 6.42%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3067 (Ar–CH), 2926– 2851 (aliphatic CH), 1728 (C=O), 1595–1462 (Ar C=C), 1250 (Ar–O–Ar), 1161–1101 (ester C–O), 1020, 972, 901, 839, 745, 683, 623 and 519. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 8.31–6.62 (b, 28H, Ar–H), 4.17 (t, 8H, COOCH₂R), 1.76–1.03 (m, 48H, COOCH₂(<u>CH₂)₆CH₃), 0.86 (t, 12H, CH₃). MS (LC-MS, Scan ES⁺) m/z: 1625 [M⁺]. UV–Vis λ_{max} (nm) (log ε) in DMF: 353 (4.70), 638 (4.59), 680 (4.92).</u>

2.1.5.4. 2,9,16,23-Tetrakis(octyl 4-phenyloxyacetate)phthalocyaninatonickel (II) (4c). This is soluble in THF, CHCl₃, CH₂Cl₂, DMF, DMSO and pyridine. Yield: 0.023 g (84%). M.p. >300 °C. Anal. Calc. for C₉₆H₁₀₄N₈O₁₂Ni: C, 71.15; H, 6.42; N, 6.92. Found: C, 71.68; H, 6.27; N, 7.11%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3074 (Ar–CH), 2926–2858 (aliphatic CH), 1732 (C=O), 1595–1462 (Ar C=C), 1250 (Ar– O–Ar), 1165–1113 (ester C–O), 1020, 988, 916, 845, 787, 748, 683, 627 and 527. ¹H NMR (*d*-DMSO 500 MHz, δ ppm): 8.12–6.73 (b, 28H, Ar–H), 4.19 (t, 8H, COOCH₂R), 1.72–1.05 (m, 48H, COOCH₂(CH₂)₆CH₃), 0.84 (t, 12H, CH₃). UV–Vis λ_{max} (nm) (log ε) in DMSO: 287 (4.75), 339 (4.39), 617 (4.49), 664 (4.25).

2.1.5.5. 2,9,16,23-Tetrakis(octyl 4-phenyloxyacetate)phthalocyaninatocopper (II) (4d). This is soluble in THF, CHCl₃, CH₂Cl₂, DMF, DMSO and pyridine. Yield: 0.020 g (74%). M.p. >300 °C. Anal. Calc. for C₉₆H₁₀₄N₈O₁₂Cu: C, 70.96; H, 6.41; N, 6.90. Found: C, 70.62; H, 6.52; N, 7.04%. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3067 (Ar–CH), 2926–2858 (aliphatic CH), 1732 (C=O), 1591–1462 (Ar C=C), 1246 (Ar–O–Ar), 1165–1101 (ester C–O), 1020, 980, 908, 841, 741, 619 and 519. UV–Vis λ_{max} (nm) (log ε) in DMSO: 346 (4.20), 630 (4.17), 641 (4.12), 679 (4.21).

2.2. Electrochemistry

The cyclic voltammetry, differential pulse voltammetry and controlled potential chronocoulometry measurements were carried out with a Princeton Applied Research Model Versostat II potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt plate with a surface area of 0.10 cm^2 . The surface of the working electrode was polished with a H₂O suspension of Al₂O₃ before each run. The last polishing was done with a particle size of 50 nm. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and 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 dimethylsulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 mol dm⁻³. High purity N₂ was used for deoxygenating the solution for at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. For CPC studies, a Pt gauze working electrode (10.5 cm² surface area), Pt wire counter electrode separated by a glass bridge and a SCE as a reference electrode were used.

3. Results and discussion

3.1. Synthesis and characterization

p-(3,4-Dicyanophenoxy)phenylacetic acid (1) was obtained by the base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with 4-hydroxyphenylacetic acid (Scheme 1) [15,16]. The reaction was carried out in a single-step synthesis using K_2CO_3 as the nitrodisplacing base at 50–60 °C in dry DMF under a N_2 atmosphere. Conversion of 1 into the metal-free phthalocyanine (2) is accomplished in a mixture of 1,2-dichlorobenzene and pentanol in the presence of lithium [17]. Dilithium Pcs can be labile towards water and acid, and can easily be converted to the metal-free phthalocyanine (2). The metallophthalocyanines (2a–d) [M = Co(II),



Scheme 1. p-(3,4-Dicyanophenoxy)phenylacetic acid (1) and phthalocyanines derived from it.

Zn(II), Ni(II) and Cu(II)] were prepared from compound 2 and the corresponding metal salts $[CoCl_2 \cdot 6H_2O, Zn-(AcO)_2 \cdot 2H_2O, NiCl_2 \cdot 6H_2O and CuCl_2]$ in dimethylformamide [17]. Further reactions of these phthalocyanines (2, 2a–d) with thionylchloride and benzylamine in tetrahydrofuran, and octanol in pyridine gave amide (3, 3a–d) and ester (4, 4a–d) derivatives, respectively (Scheme 2) [18]. Formation of the amides and esters from the phenyloxyacetic acid groups of the phthalocyanine derivatives (2, **2a-d**) was carried out in order to show the reactivity of these side groups.

The four polar peripheral substituents conferred upon these macromolecules (2, 2a-d, 3, 3a-d) good solubility in polar solvents such as pyridine, DMF and DMSO. The products (2, 2a-d, 3, 3a-d) were obtained in sufficient purity after successive washing with different solvents. The ester derivatives (4, 4a-d) show good solubility in organic solvents such as CHCl₃, THF and CH₂Cl₂. The products



Scheme 2. Phthalocyanines bearing N-benzyl-4-phenyloxyacetamide and octyl 4-phenyloxyacetate moieties.

(4, 4a–d) were purified by silica gel column chromatography with chloroform as the eluent.

Characterization of the products involved a combination of methods including elemental analysis, FT-IR, UV–Vis, mass and ¹H NMR spectroscopy. The spectroscopic data of the new compounds were in accordance with the structures.

When the IR spectrum of 4-nitrophthalonitrile is compared with that of 1, a distinct difference is the disappearance of the aromatic $-NO_2$ band at 1548 cm⁻¹ and the appearance of a new absorption at 1246 cm^{-1} , attributable to aromatic (C–O–C). In the IR spectrum of 1 the presence of C=N and C=O groups is indicated by intense stretching bands at 2231 cm⁻¹ and 1703 cm⁻¹, respectively. The ¹H NMR spectrum of 1 in deuterated DMSO gave a singlet at δ 12.36 ppm (COOH), a singlet at δ 3.63 ppm (CH₂) and the doublets at δ 8.09–7.15 ppm correspond to aromatic protons. The ¹³C NMR spectrum of 1 indicated nitrile carbons at δ 116.61 and 116.09 ppm as expected. Protonated aromatic and unsaturated carbon atoms appeared in the range δ 161.83–108.80 ppm. Also the carbon atom of carboxylic acid was observed at the lowest field value at δ 173.20 ppm.

Cyclotetramerization of the dinitrile (1) into the phthalocyanine (2) was confirmed by the disappearance of the sharp C \equiv N vibration at 2231 cm⁻¹. The IR band characteristic of the metal-free phthalocyanine ring is an N-H stretching at 3290 cm^{-1} . The IR spectra of the metal-free (2) and metallo (2a-d) phthalocyanines are very similar, except the v(NH) vibrations of the inner phthalocyanine core in the metal-free molecule. These protons are also very well characterized by the ¹H NMR spectra which show a peak at δ -7.22 ppm, -8.0 ppm and -7.80 ppm for 2, 3 and 4, respectively, and the signals disappeared after the addition of D_2O . The ¹H NMR spectrum of 2 indicates carboxylic acid protons (COOH) at δ 12.40 ppm as a singlet, aromatic protons at δ 7.24– 6.02 ppm as a broad peak and aliphatic protons (CH₂) δ 3.97 ppm as a singlet. ¹H NMR measurements were precluded owing to the paramagnetic nature of the cobalt (II) phthalocyanines (2a, 3a and 4a) and copper (II) phthalocyanines (2d, 3d and 4d). The only difference between the ¹H NMR spectra of the metal-free phthalocyanines (2, 3 and 4) and the metallo derivatives (2b, 2c, 3b, 3c, 4b and 4c) is the lack of broad chemical shifts of the inner core NH protons. The ¹H NMR spectra of the phthalocyanines are rather broad, owing probably to the aggregation of the phthalocyanines which is frequently encountered at the concentrations used for NMR spectroscopy [2].

Comparison of the IR spectral data indicated the formation of compounds **3**, **3a–d** by the disappearance of the COOH band of compounds **2**, **2a–d** at 3400–3500 cm⁻¹, and the appearance of amide NH bands at 3290 and 1655 cm⁻¹. In the ¹H NMR analysis of **3** in deuterated DMSO, the aromatic protons appear as a broad peak at δ 7.63–7.11, the amide NH protons as a singlet at δ 8.65 and the NH<u>CH₂Ar</u> protons as a doublet at δ 4.31 ppm. The phthalocyanines containing octyl 4-phenyloxyacetate moieties (4, 4a–d) were confirmed by the disappearance of the COOH band of 2, 2a–d at 3400–3500 cm⁻¹, and the appearance of ester C–O bands at 1157–1101 cm⁻¹ and more intense aliphatic CH₂ bands at 2926– 2858 cm⁻¹. The ¹H NMR spectrum of 4 showed the aromatic protons as a broad peak at δ 8.21–6.75 and the COO*CH*₂R protons as a triplet at δ 4.11 ppm. The – CCH₂C– protons in the long aliphatic chain appear at δ 1.72–1.08 and the CH₃ at the end of the chain as a triplet at δ 0.89 ppm.

The phthalocyanines 2, 2a-d, 3, 3a-d, 4 and 4a-d show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300-350 nm (B band) and the other in the visible part of the spectrum around 600-700 nm (Q band) [19]. The Q band of all the compounds was attributed to the $\pi \to \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine (-2) ring [20,21]. The B band of all the phthalocyanines arise from the deeper π levels \rightarrow LUMO transitions [20–22]. The electronic absorption spectrum of the metal-free phthalocyanine 2 exhibits a partly split Q band absorption at 699 and 667 nm, that of 3 at 704 and 682 nm and 4 at 681 and 644 nm. There is a shoulder at the slightly higher energy side for each phthalocyanine (2, 3 and 4) at 638 nm, 646 nm and 619 nm, respectively. The B band of these pcs appeared in the UV region at 340 nm, 330 nm and 320 nm, respectively. The metallo derivatives (2a-d, 3a-d and 4a-d) show only an intense single O band absorption for the $\pi \to \pi^*$ transitions at around 660-680 nm with weaker absorptions at around 609-620 nm. Weaker absorptions on the higher energy side of the Q bands are generally observed in the case of metallophthalocyanines, indicating the presence of aggregated species together with the monomeric ones which are essentially responsible for the intense absorption occurring in the main Q bands [2]. When the electronic spectra of the metal-free phthalocyanine (2), nickel and copper phthalocyanines (2c-d, 3c-d and 4c-d) were carefully examined, a clear difference from the usual phthalocyanines could be easily observed. The Q band of 2 was split into three peaks. The Q band of the nickel and copper phthalocyanines was split into two peaks (Fig. 1). At higher concentrations, the intensity of the higher energy peak corresponding to aggregated species increased while that of the monomeric ones at lower energy decreased. At lower concentrations, the intensity of the peak corresponding to monomeric species increased. ZnPc (unsubstituted) dye is characterized by a band with a maximum at 673 nm as observed in the literature for ZnPc [23]. The zinc metallophthalocyanines (2b, 3b, and 4b) showed a bathochromic shift of 6 nm, 10 nm, 7 nm, respectively. The B band absorptions of these pcs were observed at 356 nm, 360 nm and 353 nm, respectively (Fig. 2).



Fig. 1. Changes in the electronic spectra of 2, 2a-d with different concentrations.

3.2. Electrochemistry

The solution redox properties of ligand 2 and its metal complexes (2a-d) were studied using cyclic voltammetry, differential pulse voltammetry and controlled potential chronocoulometry in DMSO on a platinum electrode. Voltammetric data and the assignment of the redox couples recorded for the ligand and its complexes are listed in Table 1.

Fig. 3 shows the cyclic voltammogram of the metal-free phthalocyanine 2 in DMSO containing TBAP. It gives three one-electron reduction processes labelled as R_1 at -0.65 V, R_2 at -0.96 V and R_3 at -1.78 V, and a

one-electron oxidation process labelled as O_1 at 0.83 V vs. SCE at 0.100 V s⁻¹ scan rate. Reduction and oxidation redox processes, usually associated with the transfer of one electron and thus the formation of anionic and cationic radicals, occur only at the ligand in metal-free phthalocyanines and in some metallophthalocyanines involving a redox-inactive metal center, while they occur both at the metal center and at the phthalocyanine ring in those with redox-active metal centers [6,24–30]. Thus, all the couples of **2** are assigned undoubtedly to the phthalocyanine ring. The ratio of the anodic to cathodic peak currents for these couples are usually close to unity, suggesting reversible redox processes. Anodic to cathodic peak separations



Fig. 2. Electronic spectra of 2b, 3b and 4b in DMF.

 $(\Delta E_{\rm p})$ changed from 0.050 to 0.160 V within the scan rates from 0.010 to 0.500 V s⁻¹ ($\Delta E_{\rm p}$ changed from 0.060 to 0.140 V for ferrocene), providing additional support for a reversible electron transfer. The peak currents increased linearly with the square root of the scan rates for scan rates ranging from 0.010 to 0.500 V s⁻¹, indicating purely diffusion-controlled behavior [31].

Voltammetric studies revealed that the redox behaviour of metallophthalocyanines **2b**, **2c** and **2d** is very similar to that of the metal-free phthalocyanine **2** (Table 1). The inset in Fig. 3 exemplifies a typical cyclic voltammogram of **2c**. This similarity suggests that all the one-electron redox processes of **2b**, **2c** and **2d** are phthalocyanine ring based. However, the redox potentials of these metallophthalocya-

2d

Table 1					
The electrochemical	data	of 2,	2a,	2b,	2c and

Complex	Redox processes	$E_{1/2}$ (V vs. SCE) ^a	${\Delta E_{ m p}\over { m (mV)}^{ m b}}$	$I_{ m pa}/I_{ m pc}$	$(V)^d$
2	R1	-0.65	0.070	0.96	1.48
	R2	-0.96	0.080	0.98	
	R3	-1.78	0.160	e	
	01	0.83	0.060	e	
2a	R1	-0.37	0.100	1.00	0.82
	R2	-1.28	0.080	0.95	
	01	0.45	0.100	0.94	
2b	R1	-0.73	0.080	0.96	1.44
	R2	-1.06	0.080	0.98	
	R3	-1.84	0.100	e	
	01	0.71	0.120	1.00	
2c	R1	-0.72	0.080	0.94	1.45
	R2	-1.05	0.090	1.00	
	R3	-1.84	0.120	e	
	01	0.73	0.140	0.98	
2d	R1	-0.71	0.090	0.94	1.45
	R2	-1.06	0.080	1.00	
	R3	-1.82	0.100	e	
	O1	0.74	0.150	0.98	

^a $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.100 V s⁻¹.

^b $\Delta E_{\rm p} = \dot{E_{\rm pa}} - \dot{E_{\rm pc}}$ at 0.100 V s⁻¹.

^c $I_{\rm pa}/I_{\rm pc}$ for reduction, $I_{\rm pc}/I_{\rm pa}$ for oxidation processes at 0.100 V s⁻¹.

^d $\Delta E_{1/2} = E_{1/2}$ (first oxidation) – $E_{1/2}$ (first reduction). This value reflects

the HOMO–LUMO gap for the ligand and its complexes, except 2a. ^e $\Delta E_{\rm p}$ could not be determined due to an ill-defined redox wave.



Fig. 3. Cyclic voltammogram of **2** and **2c** (inset) at 0.100 V s⁻¹ in TBAP/DMSO.

nines occur usually at potentials slightly more negative as compared to 2. The shift in the potentials can be attributed to the polarizing effect of the M(II) ions. When we compare the redox potentials of the phthalocyanines bearing four 4-phenyloxyacetic acid moieties with those of the relevant unsubstituted phthalocyanines in the literature [24] it is clear that the redox potentials of 2, 2a, 2b, 2c and 2d shift to relatively more positive potentials, probably due to the electron withdrawing effect of the phenyloxyacetic acid substituents (Table 1). Reduction of the phthalocyanine ligand is associated with the position of the LUMO, whereas oxidation of the ligand is associated with the position of the HOMO. Thus, the difference between the potentials of the first oxidation and the first reduction processes $(\Delta E_{1/2})$ reflects the HOMO–LUMO gap for the metal free Pcs and it is closely related with the HOMO-LUMO gap in MPc species involving the redox inactive metal center. The $\Delta E_{1/2}$ values recorded for 2, 2b, 2c and 2d in this study are in agreement with the values reported previously for the relevant phthalocyanines [24].

The redox potential of **2a** is considerably different as compared with that of 2, 2b, 2c and 2d. Fig. 4 shows the cyclic and differential pulse voltammograms of 2a in DMSO containing TBAP. Within the electrochemical window of TBAP/DMSO, compound 2a undergoes a quasireversible one-electron oxidation and two quasi-reversible one-electron reductions at 0.45, -0.37 and -1.28 versus SCE at 0.100 V s^{-1} scan rate, respectively. The difference in the voltammetric behaviour of 2a is due to the fact that metallophthalocyanines such as MnPc, CoPc and FePc, having a metal that possesses energy levels lying between the HOMO and the LUMO of the phthalocyanine ligand, in general exhibit redox processes centered on the metal [24-26,28,29]. For CoPc complexes, the first oxidation and first reduction processes occur on the metal center in polar solvents such as DMF and DMSO, however the first oxidation process occurs on the Pc ring in non-polar solvents such as DCM and THF. Therefore, the first reduction and the first oxidation processes of 2a could be



Fig. 4. Cyclic and differential pulse voltammograms of 2a in TBAP/DMSO.

assigned easily to the $[Co(II)Pc(-2)]/[Co(I)Pc(-2)]^{1-}$ and $[Co(II)Pc(-2)]/[Co(III)Pc(-2)]^{+}$ redox couples and the second reduction process to the phthalocyanine ring as $[Co(I)Pc(-2)]^{-}/[Co(I)Pc(-3)]^{2-}$. The separation between the first oxidation and the first reduction potentials of the metal center (~0.82 V) is comparable with the relevant values in the literature [24–26,28,29], and does not reflect the HOMO–LUMO gap.

In conclusion, we have described the synthesis and spectral characterization of some new phthalocyanines with 4phenyloxyacetic acid, *N*-benzyl-4-phenyloxyacetamide and octyl 4-phenyloxyacetate substituents on the periphery. Cyclic voltammetry of these compounds is also presented. Esterification of carboxy groups brings forward more soluble products in less polar solvents such as chloroform, THF and dichloromethane.

Acknowledgements

The support of State Planning of Organization (DPT), Project No: 2003K 120810 is gratefully acknowledged. We are also thankful to the Research Fund of Marmara University, Commission of Scientific Research Project under grant FEN-055/070403, 2005.

References

 J. Sleven, C. Görller-Walrand, K. Binnemas, Mater. Sci. Eng. C 18 (2001) 229.

- [2] C.C. Leznoff, A.B.P. Lever, Phthalocyanines Properties and Applications, VCH, Weinheim, 1989.
- [3] N. Kobayashi, Curr. Opin. Solid State Mater. Sci. 4 (1999) 345.
- [4] Ş. Abdurrahmanoğlu, A. Altındal, A.R. Özkaya, M. Bulut, Ö. Bekaroğlu, Chem. Commun. (2004) 2029.
- [5] Ş. Abdurrahmanoğlu, A.R. Özkaya, M. Bulut, Ö. Bekaroğlu, J. Chem. Soc., Dalton Trans. (2004) 4022.
- [6] M. Özer, A. Altındal, A.R. Özkaya, M. Bulut, Ö. Bekaroğlu, Synth. Met. 155 (2005) 222.
- [7] M. Kandaz, H.S. Çetin, A. Koca, A.R: Özkaya, Dyes Pigm, doi:10.1016/j.dyepig.2006.02.008, in press (2006).
- [8] Ü. Salan, A. Altındal, M. Bulut, Ö. Bekaroğlu, Tetrahedron Lett. 46 (2005) 6057.
- [9] R. Zhou, F. Josse, W. Göpel, Z.Z. Öztürk, Ö. Bekaroğlu, Appl. Organomet. Chem. 10 (1996) 557.
- [10] M. Liu, A. Hu, C. Tai, M. Sain, F. Chou, J. Photochem. Photobiol. A: Chem. (2004) 1.
- [11] L. Xi-you, K.P.Ng. Dennis, Tetrahedron Lett. 42 (2001) 305.
- [12] Ö. Bekaroğlu, Appl. Organomet. Chem. 10 (1996) 605.
- [13] M. Kandaz, İ. Yılmaz, Ö. Bekaroğlu, Polyhedron 19 (2000) 115.
- [14] J.G. Young, W. Onyebuagu, J. Org. Chem. 55 (1990) 2155.
- [15] A.W. Snow, J.R. Griffith, N.P. Marullo, Macromolecules 17 (1984) 1614.
- [16] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, Synthesis (1993) 194.
- [17] P. Zimcik, M. Miletin, M. Kostka, Z. Fiedler, J. Photochem. Photobiol. A: Chem. 155 (2003) 127.
- [18] M.A. Dekeyser, R.A. Davis, J. Agric. Food Chem. 46 (1998) 2827.
- [19] E. Hamuryudan, S. Merey, Z.A. Bayır, Dyes Pigm. 59 (2003) 263.
- [20] S. Dabak, G. Gümüş, A. Gül, Ö. Bekaroğlu, J. Coord. Chem. 8 (1996) 287.
- [21] J. Simon, P. Bassoul, Design of Molecular Materials, Wiley, New York, 2000, pp. 196–296 (Chapter 6).
- [22] S. Gürsoy, A. Cihan, M.B. Koçak, Ö. Bekaroğlu, Monatsh für Chem. 32 (2001) 813.
- [23] D. Wrobel, A. Boguta, J. Photochem. Photobiol. A: Chem. 150 (2002) 67.
- [24] A.B.P. Lever, E.R. Milaeva, G. Speier, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 3, VCH Publishers, New York, 1993, pp. 1–63.
- [25] M. Özer, A. Altindal, A.R. Özkaya, M. Bulut, Ö. Bekaroglu, Polyhedron 25 (2006) 3593.
- [26] A.R. Özkaya, E. Hamuryudan, Z.A. Bayır, Ö. Bekaroglu, J. Porphyrin Phthalocy. 4 (2000) 689.
- [27] A.R. Özkaya, A.I. Okur, A. Gül, Ö. Bekaroglu, J. Coord. Chem. 33 (1994) 311.
- [28] M. Kandaz, A.R. Özkaya, Ö. Bekaroğlu, Monats Chem. 132 (2001) 1013.
- [29] A. Koca, H.A. Dinçer, H. Çerlek, A. Gül, M.B. Koçak, Electrochim. Acta 52 (2006) 1199.
- [30] A. Koca, H.A. Dincer, M.B. Kocak, A. Gül, Russ. J. Electrochem. 42 (2006) 31.
- [31] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., Wiley, New York, 2001.