Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 77 (2008) 165–170
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

The synthesis and characterization of novel soluble phthalocyanines substituted with 7-octyloxy-3-(4-oxyphenyl)coumarin moieties

Meryem Çamur, Mustafa Bulut*

Marmara University, Department of Chemistry, Faculty of Science and Letters, 34722 Goztepe, Istanbul, Turkey

Received 1 December 2006; received in revised form 18 April 2007; accepted 19 April 2007
Available online 13 May 2007

Abstract

Novel, soluble, metal-free phthalocyanine and metallo phthalocyanines (M = Zn, Co, Ni and Cu) bearing four 7-octyloxy-3-(4-oxyphenyl)-coumarin substituents at peripheral positions were prepared by cyclotetramerization of 7-octyloxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin. The lactone rings of the zinc metallo phthalocyanine were opened and the released hydroxyl groups hexylated. The new compounds were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, mass and UV–vis spectral data.

Keywords: Phthalocyanine; Coumarin; Perkin coumarin synthesis; Lactone ring opening; Metallo phthalocyanines

1. Introduction

Coumarin (2*H*-1-benzopyran-2-one) and its derivatives occur widely in nature. Many natural and synthetic derivatives of coumarin have been used in various applications in chemistry, biology, medicine and physics [1], including additives in food and cosmetics, optical brightening agents as well as dispersed fluorescent and laser dyes [2–4]; the diverse biological activities of natural and synthetic coumarin derivatives as anticoagulants and antithrombotics are well known [5–7]. For these reasons, considerable attention has been paid to the preparation of coumarin derivatives substituted at different positions [1]. Phthalocyanines coupled with the coumarin moiety may exhibit biological activity.

Phthalocyanines (Pcs) form an important class of macrocyclic compounds that do not occur in nature [8]. Following the first synthesis in 1907, they have been firmly established as blue and green dyes [9] and enjoy widespread usage in diverse areas such as gas and chemical sensors [10–12], electrochromic devices [13], non-linear optics [14], ladder polymers [15], liquid crystals, Langmuir–Blodgett films, photodynamic reagents for cancer therapy and in other medical applications [16–18]. Although many Pcs are insoluble in common organic solvents, their solubility can be improved by the incorporation of substituents, such as alkyl or alkoxy groups of different chain lengths, or branched systems [14,19] at peripheral positions. Recently, we have reported on the synthesis and characterization of the soluble symmetrical cinnamyl hexanoate phthalocyanines [20].

In this paper, the synthesis and characterization of novel, soluble, metal-free and metallo phthalocyanines (M = Zn, Co, Ni, Cu) carrying 7-octyloxy-3-(4-oxyphenyl)coumarin substituents on the periphery are reported. In addition, the lactone rings of the 2,9,16,23-tetrakis[7-octyloxy-3-(4-oxyphenyl)coumarin]phthalocyaninatozinc were opened with Li/hexanol and the released hydroxyl groups hexylated. The novel phthalocyanines display good solubility in common organic solvents such as chloroform, dichloromethane and tetrahydrofuran.

2. Experimental

IR spectra were recorded on a Shimadzu FTIR-8300 Fourier Transform Infrared Spectrophotometer using KBr pellets,

* Corresponding author. Tel.: +90 216 3479641/1370; fax: +90 216 3478783.
E-mail addresses: mbulut@marmara.edu.tr, mustafabulut50@gmail.com (M. Bulut).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.04.008

UV–vis spectra on a Shimadzu UV-1601 UV–vis spectrophotometer, and ^{1}H and ^{13}C NMR spectra on a Varian UNITY INOVA 500 MHz Spectrometer. Elemental analysis was carried out using a LECO CHN 932. Mass spectra were obtained using a Varian 711 mass spectrometer. 4-Nitrophthalonitrile [21] and *p*-(3,4-dicyanophenoxy)phenylacetic acid [22] were synthesized according to reported procedures. All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified; solvents were stored over molecular sieves (4 Å). The homogeneity of the products was checked at each stage of their synthesis by TLC (SiO_2).

2.1. 7-Hydroxy-3-[p-(3′,4′-dicyanophenoxy)phenyl]-coumarin (1)

A mixture of *p*-(3,4-dicyanophenoxy)phenylacetic acid (2.0 g, 7.19 mmol), 2,4-dihydroxybenzaldehyde (0.99 g, 7.19 mmol), sodium acetate (2.95 g, 36 mmol) and anhydrous acetic anhydride (15 ml) was heated, with stirring, at 160–170 °C in a sealed glass tube for 8 h under nitrogen. After cooling to room temperature, water was added and the mixture stirred overnight. The resulting solid (7-acetoxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin) was filtered, washed with water and dried. The crude product 7-acetoxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin was suspended in methanol. A 10% aq HCl solution was added to adjust the pH to 3 and the ensuing mixture was heated and stirred at 60 °C for 4 h under nitrogen. The resulting solid (7-hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin) was filtered, washed with water and dried. The compound was soluble in methanol, tetrahydrofuran, dimethylsulphoxide and dimethylformamide. Yield: 1.72 g (63%); m.p. >300 °C. IR ν (cm^{-1}): 3246 (OH), 3119–3038 (Ar-H), 2926–2843 (alkyl-CH), 2224 (–C≡N), 1674 (C=O lactone), 1626 (C=C), 1583–1487 (Ar C=C), 1294 (Ar–O–Ar); ^{1}H NMR (*d*-DMSO 500 MHz) δ_H: 10.60 (s, 1H, OH), 8.18 (s, 1H, lactone 4-H), 8.09 (d, $J = 9$ Hz, 1H, Ar-H), 7.85 (d, $J = 2$ Hz, 1H, Ar-H), 7.81 (dd, $J = 9$ Hz and 2 Hz, 2H, Ar-H), 7.59 (d, $J = 9$ Hz, 1H, Ar-H), 7.42 (dd, $J = 9$ Hz and 2 Hz, 1H, Ar-H), 7.25 (dd, $J = 9$ Hz and 2 Hz, 2H, Ar-H), 6.82 (dd, $J = 9$ Hz and 2 Hz, 1H, Ar-H) and 6.74 (d, $J = 2$ Hz, 1H, Ar-H). ^{13}C NMR (*d*-DMSO 500 MHz) δ_C: 162.07 (Ar-C), 161.51 (C=O lactone), 160.72 (Ar-C), 155.64 (Ar-C), 154.32 (Ar-C), 141.89 (Ar-C), 137.03 (Ar-C), 133.21 (Ar-C), 131.16 (Ar-C), 130.74 (Ar-C), 123.63 (Ar-C), 122.95 (Ar-C), 121.78 (Ar-C), 120.62 (Ar-C), 117.44 (Ar-C), 116.56 (C≡N), 116.05 (C≡N), 114.17 (Ar-C), 112.65 (Ar-C), 109.10 (Ar-C) and 102.44 (Ar-C); UV–vis (DMSO): λ_{max} (nm) ($\log \varepsilon$): 347 (3.63). Anal. Calcd for $C_{23}H_{12}N_2O_4$: C, 72.63; H, 3.16; N, 7.37%; found: C, 72.87; H, 3.39; N, 7.26%.

2.2. 7-Octyloxy-3-[p-(3′,4′-dicyanophenoxy)phenyl]-coumarin (2)

7-Hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin **1** (1.65 g, 4.34 mmol) and 1-bromooctane (0.76 ml, *d* 1.11 g/ml, 4.34 mmol) were dissolved in dry acetonitrile (150 ml), and potassium carbonate (0.6 g, 4.34 mmol) and tetrabutylammonium bromide (0.02 g, excess) as catalyst were added. After refluxing for 4 days under nitrogen, the resulting solid was filtered, the solvent was removed and the solid then dissolved in dichloromethane and dried over $CaCl_2$. Dichloromethane was evaporated and the pure product was dried. The compound was soluble in chloroform, dichloromethane, acetone, tetrahydrofuran, hot methanol, hot ethanol, hot acetonitrile, dimethylformamide and dimethylsulphoxide. Yield: 2.125 g (99.5%); m.p. 139–142 °C. IR ν (cm^{-1}): 3105–3038 (Ar-H), 2934–2866 (alkyl-CH), 2232 (–C≡N), 1711 (C=O lactone), 1607 (C=C), 1566–1481 (Ar C=C), 1281 (Ar–O–Ar), 1217–1124 (Ar–O–C); ^{1}H NMR (*d*-DMSO 500 MHz) δ_H: 8.26 (s, 1H, lactone 4-H), 8.13 (d, $J = 9$ Hz, 1H, Ar-H), 7.86 (d, $J = 2$ Hz, 1H, Ar-H), 7.85 (dd, $J = 9$ Hz and 2 Hz, 2H, Ar-H), 7.69 (d, $J = 9$ Hz, 1H, Ar-H), 7.46 (dd, $J = 9$ Hz and 2 Hz, 1H, Ar-H), 7.23 (dd, $J = 9$ Hz and 2 Hz, 2H, Ar-H), 7.04 (d, $J = 2$ Hz, 1H, Ar-H), 6.99 (dd, $J = 9$ Hz and 2 Hz, 1H, Ar-H), 4.10 (t, $J = 6$ Hz, 2H, OCH_2), 1.80–1.74 (m, 2H, $OCCH_2$), 1.46–1.40 (m, 2H, $OCCCH_2$), 1.34–1.24 (m, 8H, $OCCC(CH_2)_4$) and 0.87 (t, $J = 6$ Hz, 3H, CH_3). ^{13}C NMR (*d*-DMSO 500 MHz) δ_C: 162.65 (Ar-C), 161.50 (C=O lactone), 160.65 (Ar-C), 155.57 (Ar-C), 154.48 (Ar-C), 141.65 (Ar-C), 137.06 (Ar-C), 133.05 (Ar-C), 131.23 (Ar-C), 130.48 (Ar-C), 123.69 (Ar-C), 123.01 (Ar-C), 122.71 (Ar-C), 120.65 (Ar-C), 117.47 (Ar-C), 116.58 (C≡N), 116.07 (C≡N), 113.78 (Ar-C), 113.62 (Ar-C), 109.15 (Ar-C), 101.40 (Ar-C), 69.10 (OCH_2), 31.93–22.78 (6C, CCH_2C) and 14.65 (CH_3); UV–vis ($CHCl_3$): λ_{max} (nm) ($\log \varepsilon$): 347 (3.92). Anal. Calcd for $C_{31}H_{28}N_2O_4$: C, 75.61; H, 5.69; N, 5.69%; found: C, 75.47; H, 5.79; N, 5.85%.

2.3. 2,9,16,23-Tetrakis[7-octyloxy-3-(4-oxyphenyl)-coumarin]phthalocyanine (3)

Compound **2** (0.5 g, 1.02 mmol) and anhydrous 2-(dimethylamino)ethanol (3 ml) were refluxed, with stirring, for 48 h in a sealed glass tube under N_2. After cooling to room temperature, methanol (2 ml) was added to precipitate the green product which was filtered and washed with water, methanol, acetonitrile and diethyl ether, followed by purification on a silica gel column using chloroform as eluent. The compound was soluble in chloroform and dichloromethane. Yield: 0.2 g (40%); m.p. >300 °C. IR ν (cm^{-1}): 3298 (N–H), 3066–3038 (Ar-H), 2926–2851 (alkyl-CH), 1726 (C=O lactone), 1610 (C=C), 1502–1425 (Ar C=C), 1269–1234 (Ar–O–Ar), 1169–1094 (Ar–O–C); ^{1}H NMR (*d*-DMSO 500 MHz) δ_H: 8.20 (s, 4H, lactone 4-H), 6.78–7.77 (m, 44H, Ar-H), 3.95 (t, 8H, OCH_2), 1.73–1.81 (m, 8H, $OCCH_2$), 1.47–1.53 (m, 8H, $OCCCH_2$), 1.21–1.42 (m, 32H, $OCCC(CH_2)_4$), 0.87 (t, 12H, CH_3) and –3.45 (br s, 2H, NH); UV–vis ($CHCl_3$): λ_{max} (nm) ($\log \varepsilon$): 347 (5.31), 612 (sh, 4.55), 642 (sh, 4.72), 667 (4.99), 702 (5.03). Anal. Calcd for $C_{124}H_{114}N_8O_6$: C, 75.53; H, 5.79; N, 5.68%; found: C, 75.57; H, 5.67; N, 5.82%. MS (LC–MS, Scan ES^+) *m/z*: 1970 $[M]^+$, 1794 $[M - 4.44]^+$.

2.4. General procedures for the synthesis of metallo phthalocyanines (**3a–d**)

A mixture of compound **2** (0.05 g, 0.1 mmol), metal salt [$Zn(AcO)_2 \cdot 2H_2O$ (0.0055 g, 0.025 mmol), $CoCl_2 \cdot 6H_2O$ (0.0060 g, 0.025 mmol), $NiCl_2 \cdot 6H_2O$ (0.0060 g, 0.025 mmol) and $CuCl_2$ (0.0034 g, 0.025 mmol)] and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (0.07 ml, 0.04 mmol) in hexanol (1.5 ml) was heated and stirred at 160 °C for 24 h under N_2. For the Zn derivative **3a** no DBU was required and 2-(dimethylamino)ethanol was used instead of hexanol. The resulting green mixtures were cooled to room temperature and then methanol (2 ml) was added in order to precipitate the product which was filtered and washed with water, hot methanol, hot acetonitrile and diethyl ether and then dried. The Cu derivative **3d** was also washed with NH_4OH (24%, 3 × 5 ml) to remove inorganic residues and then water until the filtrate became neutral. The metallo phthalocyanines **3a–d** were purified on a silica gel column using chloroform as eluent.

2.4.1. 2,9,16,23-Tetrakis[7-octyloxy-3-(4-oxyphenyl)-coumarin]phthalocyaninatozinc(II) (**3a**)

The compound was soluble in chloroform, dichloromethane, tetrahydrofuran, DMF and DMSO. Yield: 0.033 g (64%); m.p. >300 °C. IR ν (cm^{-1}): 3066–3038 (Ar-H), 2926–2843 (alkyl-CH), 1718 (C=O lactone), 1610 (C=C), 1499–1469 (Ar C=C), 1272–1235 (Ar–O–Ar), 1169–1091 (Ar–O–C); ^1H NMR (*d*-DMSO 500 MHz) δ_H: 8.20 (s, 4H, lactone 4-H), 6.10–7.42 (m, 44H, Ar-H), 3.82 (t, 8H, OCH_2), 1.64–1.73 (m, 8H, $OCCH_2$), 1.50–1.59 (m, 8H, $OCCCH_2$), 1.21–1.28 (m, 32H, $OCCC(CH_2)_4$) and 0.83 (t, 12H, CH_3); UV–vis ($CHCl_3$): λ_{max} (nm) (log ε): 353 (5.01), 619 (sh, 4.29), 683 (5.05). Anal. Calcd for $C_{124}H_{112}N_8O_6Zn$: C, 73.19; H, 5.51; N, 5.51%; found: C, 73.37; H, 5.32; N, 5.69%. MS (LC–MS, Scan ES^+) *m/z*: 2033.8 $[M]^+$, 2034.1 $[M+1]^+$, 2035.3 $[M+2]^+$.

2.4.2. 2,9,16,23-Tetrakis[7-octyloxy-3-(4-oxyphenyl)-coumarin]phthalocyaninatocobalt(II) (**3b**)

The compound was soluble in chloroform, dichloromethane, tetrahydrofuran, DMF and DMSO. Yield: 0.046 g (89%); m.p. >300 °C. IR ν (cm^{-1}): 3044–3038 (Ar-H), 2918–2851 (alkyl-CH), 1718 (C=O lactone), 1610 (C=C), 1506–1462 (Ar C=C), 1261–1232 (Ar–O–Ar), 1173–1091 (Ar–O–C); UV–vis ($CHCl_3$): λ_{max} (nm) (log ε): 339 (5.01), 614 (sh, 4.33), 673 (4.69). Anal. Calcd for $C_{124}H_{112}N_8O_6Co$: C, 73.41; H, 5.53; N, 5.53%; found: C, 73.68; H, 5.84; N, 5.65%. MS (LC–MS, Scan ES^+) *m/z*: 2027 $[M]^+$, 1851 $[M-4.44]^+$.

2.4.3. 2,9,16,23-Tetrakis[7-octyloxy-3-(4-oxyphenyl)-coumarin]phthalocyaninatonickel(II) (**3c**)

The compound was soluble in chloroform, dichloromethane, tetrahydrofuran, DMF and DMSO. Yield: 0.042 g (82%); m.p. >300 °C. IR ν (cm^{-1}): 3052–3038 (Ar-H), 2926–2851 (alkyl-CH), 1725 (C=O lactone), 1603 (C=C), 1502–1466 (Ar C=C), 1272–1232 (Ar–O–Ar), 1173–1091 (Ar–O–C); UV–vis ($CHCl_3$): λ_{max} (nm) (log ε): 347 (5.05), 614 (sh, 4.39), 673 (4.60). Anal. Calcd for $C_{124}H_{112}N_8O_6Ni$: C, 73.41; H, 5.53; N, 5.53%; found: C, 73.85; H, 5.15; N, 5.74%.

2.4.4. 2,9,16,23-Tetrakis[7-octyloxy-3-(4-oxyphenyl)-coumarin]phthalocyaninatocopper(II) (**3d**)

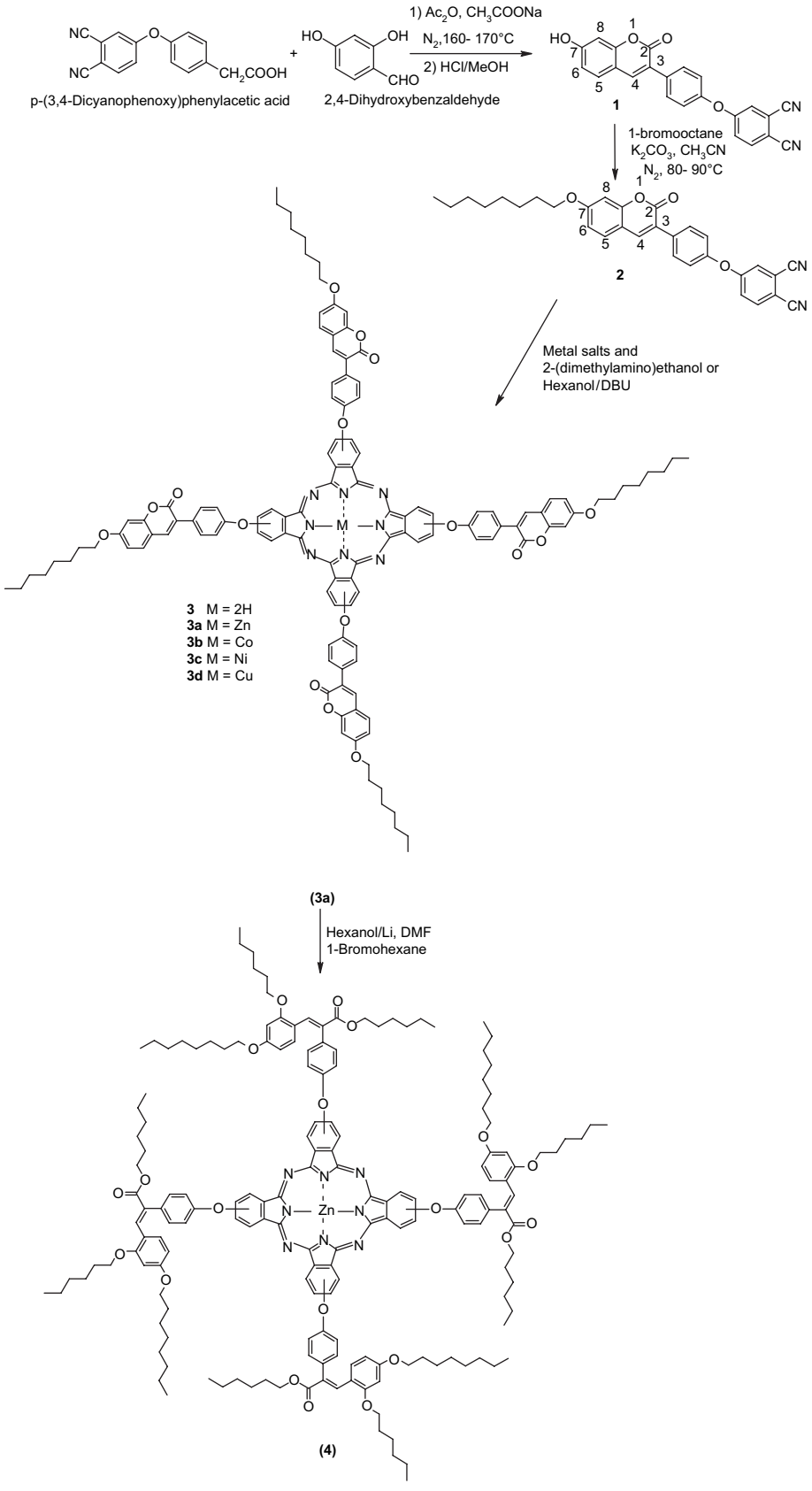
The compound was soluble in chloroform, dichloromethane, tetrahydrofuran, DMF and DMSO. Yield: 0.035 g (68%); m.p. >300 °C. IR ν (cm^{-1}): 3052–3038 (Ar-H), 2933–2843 (alkyl-CH), 1721 (C=O lactone), 1607 (C=C), 1510–1402 (Ar C=C), 1272–1228 (Ar–O–Ar), 1176–1123 (Ar–O–C); UV–vis ($CHCl_3$): λ_{max} (nm) (log ε): 346 (5.02), 620 (sh, 4.37), 680 (4.64). Anal. Calcd for $C_{124}H_{112}N_8O_6Cu$: C, 73.25; H, 5.51; N, 5.51%; found: C, 73.56; H, 5.76; N, 5.14%.

2.5. 2,9,16,23-Tetrakis[(*E*)-hexyl-3-(2-hexyloxy)-4-(octyloxy)phenyl-2-(4-oxyphenyl)acrylate]-phthalocyaninatozinc(II) (**4**)

To a solution of 2,9,16,23-tetrakis[7-octyloxy-3-(4-oxyphenyl)coumarin]phthalocyaninatozinc (**3a**) (0.030 g, 0.0148 mmol) in dry DMF (5 ml), hexanol (5 ml) and lithium metal (0.0012 g, 0.178 mmol) were added. The mixture was refluxed for 24 h and then cooled to room temperature. 1-Bromohexane (0.3 ml) was added and the reaction mixture was heated at 50 °C for 3 days under N_2. After cooling to room temperature, the mixture was treated with 2 M aq HCl solution with ice-cooling. The precipitate was collected by filtration, washed with water and dried. Purification of the product was accomplished by column chromatography on silica gel using $CHCl_3$ as eluent. The compound was soluble in chloroform, dichloromethane, tetrahydrofuran, DMF and DMSO. Yield: 0.015 g (37%); m.p. >300 °C. IR ν (cm^{-1}): 3059 (Ar-H), 2926–2858 (alkyl-CH), 1726 (C=O ester), 1610 (C=C), 1510–1474 (Ar C=C), 1269–1234 (Ar–O–Ar), 1173–1094 (Ar–O–C); ^1H NMR (*d*-DMSO 500 MHz) δ_H: 6.55–8.17 (m, 40H, Ar-H), 7.84 (s, 4H, C=CH), 4.06 (t, 16H, OCH_2), 3.97 (t, 8H, $COOCH_2$), 1.31–1.76 (m, 112H, $OCCH_2C$) and 0.88 (t, 36H, CH_3); UV–vis ($CHCl_3$): λ_{max} (nm) (log ε): 355 (5.11), 623 (sh, 4.21), 660 (sh, 4.53), 681 (4.91). Anal. Calcd for $C_{172}H_{216}N_8O_{20}Zn$: C, 74.32; H, 7.78; N, 4.03%; found: C, 74.65; H, 7.52; N, 4.43%. MS (LC–MS, Scan ES^+) *m/z*: 2772.8 $[M-4]^+$, 2770 $[M-7]^+$.

3. Results and discussion

Starting from *p*-(3,4-dicyanophenoxy)phenylacetic acid, the general route for the synthesis of the new phthalocyanines is shown in Scheme 1. 7-Hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin **1** was synthesized by reaction of *p*-(3,4-dicyanophenoxy)phenylacetic acid with 2,4-dihydroxybenzaldehyde via Perkin synthesis which was unaffected by the presence of the phthalonitrile subunit [23,24]. 7-Octyloxy-3-[*p*-(3′,4′-dicyanophenoxy)phenyl]coumarin **2** was synthesized by alkylation of **1** with 1-bromooctane in acetonitrile for 4 days under N_2 [25]. Conversion of **2** into the 2,9,16,23-tetrakis[7-octyloxy-3-(4-oxyphenyl)coumarin]phthalocyanine



Scheme 1. Summary of the synthesis of coumarins (**1**, **2**) and phthalocyanines (**3**, **3a**–**d**, **4**).

3 was accomplished directly by refluxing this reagent in 2-(dimethylamino)ethanol for 48 h to realise the cyclotetramerization. 2,9,16,23-Tetrakis[7-octyloxy-3-(4-oxyphenyl)-coumarin]phthalocyaninatozinc(II) **3a** was synthesized by reaction of **2** with zinc(II) acetate in 2-(dimethylamino)ethanol for 24 h under N_2 atmosphere. Cobalt, nickel and copper metallo phthalocyanines (**3b–d**) were synthesized by reaction of **2** with metal salts ($CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2$) in hexanol in the presence of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) for 24 h under N_2 atmosphere. The opening of the lactone rings of **3** with hexanol/Li in DMF, followed by alkylation of the released hydroxyl groups with 1-bromohexane gave **4** [20]. The new phthalocyanines **3**, **3a–d**, **4** were reasonably soluble in chloroform, dichloromethane and tetrahydrofuran due to the long alkyl substituents. Elemental analyses, IR, ^{1}H NMR, mass and UV–vis spectra confirmed the proposed structures of all of the new compounds **1–4**. Comparison of the IR spectral data clearly indicated the formation of **1** by the disappearance of the COOH band of *p*-(3,4-dicyanophenoxy)phenylacetic acid at 3500 cm^{-1}, and the shifted absorptions at 3246 cm^{-1} (OH), 2224 cm^{-1} (C≡N) and 1674 cm^{-1} (C=O lactone). The broad absorption band at 3246 cm^{-1} in the IR spectrum of **1** corresponding to OH bands, disappeared after its conversion to **2**. The ^{1}H NMR spectrum of **1** indicated the –OH proton at δ 10.60 ppm as a singlet, the aromatic protons at δ 6.74–8.09 ppm as doublets and the proton of coumarin at position 4 at δ 8.18 ppm as a singlet. The ^{13}C NMR spectrum of **1** in deuterated DMSO gave signals at 161.51 (C=O lactone), 102.44–162.07 (Ar-C), 116.56 (C≡N) and 116.05 (C≡N) ppm. The IR spectrum of **2** exhibited characteristic frequencies at 2866–2934 (alkyl-CH), 2232 (C≡N) and 1711 (C=O lactone) cm^{-1}. In the ^{1}H NMR analysis of **2** in deuterated DMSO, the proton of coumarin at position 4 appeared as a singlet at δ 8.26 ppm, the aromatic protons as multiplets at δ 6.99–8.13 ppm, the $-CCH_2C-$ in the long chain at δ 1.24–1.80 ppm as multiplets and the $-CH_3$ protons at the end of the chain as a triplet at δ 0.87 ppm. The peak at δ 4.10 ppm indicated the presence of an $-OCH_2-$ group adjacent to an aromatic ring. The ^{13}C NMR spectrum of **2** in deuterated DMSO gave signals at 161.50 (C=O lactone), 101.40–162.65 (Ar-C), 116.58 (C≡N), 116.07 (C≡N), 69.10 ($-OCH_2-$), 22.78–31.93 (6C, $-CCH_2C-$) and 14.65 ($-CH_3$) ppm. The IR spectrum of **3** was very similar to that of **2**. A diagnostic feature of the phthalocyanine formation from the dicyano compound **2** was the disappearance of the sharp and intense C≡N vibration at 2232 cm^{-1}. In the IR spectrum of the metal-free phthalocyanine **3**, the cavity NH stretching vibrations were observed at 3298 cm^{-1}. The ^{1}H NMR spectrum of **3** indicated lactone 4-H at δ 8.20 ppm as a singlet, aromatic protons at δ 6.78–7.77 ppm as broad, the $-OCH_2-$ protons at δ 3.95 ppm as triplets, the $-CCH_2C-$ protons in the long chain at δ 1.21–1.81 ppm as multiplets and the $-CH_3$ protons at the end of the chain at δ 0.87 ppm as a triplet. The NH protons of the metal-free phthalocyanine **3** were also identified. The ^{1}H NMR spectrum indicated a broad peak at δ –3.45 ppm for **3** and the signal disappeared after the addition of D_2O. The IR and ^{1}H NMR spectra of **3** and the metallo phthalocyanines **3a–d** were very similar, except for the NH peak of the inner phthalocyanine core in the metal-free molecule. In the IR spectra of **4** the intense bands of the long alkyl groups at 2858–2926 cm^{-1}, the ester C=O band at 1726 cm^{-1} and C=C band at 1610 cm^{-1} were apparent. In the ^{1}H NMR analysis of **4** in $CDCl_3$, the proton of C=CH apperared as a singlet at δ 7.84 ppm, the aromatic protons as broad at δ 6.55–8.17 ppm, the $-OCH_2-$ protons as a triplet at δ 4.06 ppm, the $-COOCH_2-$ protons as a triplet at δ 3.97 ppm. The $-CCH_2C-$ protons in the long aliphatic chain appear at δ 1.31–1.76 ppm as multiplets, and the $-CH_3$ at the end of the chain as a triplet at δ 0.88 ppm.

A close investigation of the mass spectra of **3**, **3a**, **3b**, **4** confirmed the proposed structures. In the mass spectrum of **3** and **3b**, in addition to the $[M]^+$ peak, a fragment ion corresponding to the loss of $4 \times COO$ $[M - 4.44]^+$ was easily identified. In the mass spectrum of **3a** and **4** the presence of the characteristic molecular ion peaks at $m/z = 2033.8$ $[M]^+$, 2034.1 $[M + 1]^+$ and 2035.3 $[M + 2]^+$ (**3a**), and 2772.8 $[M - 4]^+$, 2770 $[M - 7]^+$ (**4**) confirmed the proposed structures.

A typical UV spectrum of the metal-free phthalocyanine **3** in chloroform showed a doublet in the Q band region at 667 and 702 nm while each metallo phthalocyanine gave intense single bands at 683, 673, 673 and 680 nm for the corresponding compounds **3a**, **3b**, **3c** and **3d**, respectively. Pcs (**3**, **3a–d**) also showed B bands around 347 nm. There was also a shoulder at slightly higher energy side of the Q band for each Pc. The shoulders at around 642 and 612 nm for **3**, 619 nm for **3a**, 614 nm for **3b**, 614 nm for **3c** and 620 nm for **3d** indicated the aggregation of Pc molecules. The UV–vis spectra of 2,9,16,23-tetrakis[(*E*)-hexyl-3-(2-hexyloxy)-4-(octyloxy)phenyl-2-(4-oxyphenyl)acrylate]phthalocyaninatozinc(II) (**4**) in chloroform showed Q band absorption at 681 nm with two shoulders at 660, 623 nm, and B band absorption at 355 nm. On comparing **3a** with **4**, the UV–vis spectra showed a shift of about 2 nm because of the opening of all the four lactone rings in **3a** (Fig. 1).

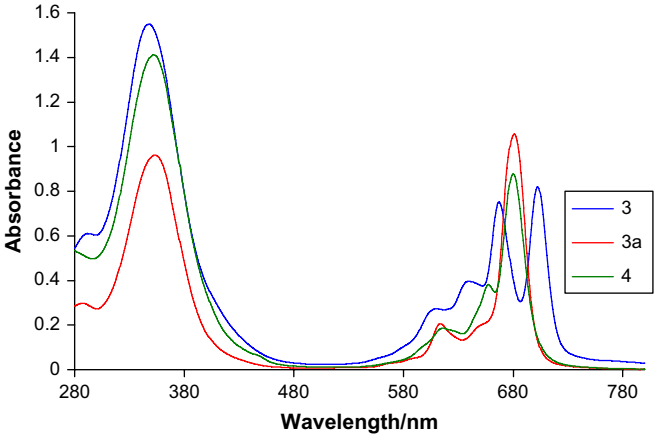


Fig. 1. UV–vis spectra of **3**, **3a** and **4** in $CHCl_3$.

4. Conclusions

p-(3,4-Dicyanophenoxy)phenylacetic acid and the metal-free and metallo phthalocyanines with coumarin substituents were synthesized, separated by column chromatography and fully characterized. The opening of the peripheral lactone rings with Li/hexanol and hexylation of the ensuing released hydroxyl groups enhanced the solubility of the phthalocyanines.

Acknowledgements

We are thankful to the Research Foundation of Marmara University, Commission of Scientific Research Project (BAPKO) [FEN-YLS-290506-0124] and the State Planning Organization (DPT) [2003K 120810].

References

[1] Kaholek M, Hrdlovic P. J Photochem Photobiol A 1997;108:283–8.
[2] Van TN, Debenetti S, De Kimpe N. Tetrahedron Lett 2003;44:4199–201.
[3] Suratwala T, Gardlund Z, Davidson K, Uhlmann DR. Chem Mater 1998;10:190–8.
[4] Bose SD, Rudradas AP, Babu MH. Tetrahedron Lett 2002;43:9195–7.
[5] Reddy NS, Mallireddigari MR, Cosenza S, Gumireddy K, Bell SC, Reddy EP, et al. Bioorg Med Chem Lett 2004;14:4093–7.
[6] O'Kennedy R, Thornes RD. Coumarins: biology, applications and mode of action. England: John Wiley & Sons Ltd.; 1997. p. 1–336.
[7] Jung J, Lee J, Oh S, Lee J, Park O. Bioorg Med Chem Lett 2004;14:5527–31.
[8] Sleven J, Görller-Walrand C, Binnemas K. Mater Sci Eng C 2001;18:229–38.
[9] Kobayashi N. Curr Opin Solid State Mater Sci 1999;4:345–53.
[10] Özer M, Altındal A, Özkaya AR, Bulut M, Bekaroğlu Ö. Synth Met 2005;155:222–31.
[11] Salan Ü, Altındal A, Bulut M, Bekaroğlu Ö. Tetrahedron Lett 2005;46:6057–61.
[12] Zhou R, Josse F, Göpel W, Öztürk ZZ, Bekaroğlu Ö. Appl Organomet Chem 1996;10:557–77.
[13] Abdurrahmanoğlu Ş, Altındal A, Özkaya AR, Bulut M, Bekaroğlu Ö. Chem Commun 2004;2096–7.
[14] Dini D, Barthel M, Hanack M. Eur J Org Chem 2001;3759–69.
[15] Mc Keown B. J Mater Chem 2000;10:1979–95.
[16] Leznoff CC, Lever ABP. Phthalocyanines properties and applications, vols. 1–4. Weinheim: VCH; 1989–1996.
[17] Bekaroğlu Ö. Appl Organomet Chem 1996;10:605–22.
[18] Xi-you L, Dennis KPNg. Tetrahedron Lett 2001;42:305–9.
[19] Kandaz M, Yaraşır M, Koca A, Bekaroğlu Ö. Polyhedron 2002;21:255–63.
[20] Esenpınar AA, Bulut M. Dyes Pigments 2008;76(1):249–55.
[21] Young JG, Onyebuagu W. J Org Chem 1990;55:2155–9.
[22] Çamur M, Özkaya AR, Bulut M. Polyhedron 2007; doi:10.1016/j.poly.2007.01.010.
[23] Çakır Ü, Özer M, İçen MA, Uğraş Hİ, Bulut M. Dyes Pigments 2004;60:177–85.
[24] Erk Ç, Bulut M, Göçmen A. J Inclusion Phenom Macrocyclic Chem 2000;37:441–50.
[25] Fang J, Whitaker C, Weslowski B, Chen M, Naciri J, Shashidhar R. J Mater Chem 2001;11:2992–5.