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Synthesis and characterization of metal-free and metallo-phthalocyanines with four pendant coumarinthio/oxy-substituents

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Abstract

The synthesis of novel metal-free and metallo-phthalocyanines with four, peripheral 7-thio- and 7-oxo-4-methyl-2*H*-1-benzopyran-2-one (coumarin) groups were prepared by cyclotetramerization of 7-(3,4-dicyanophenylthio)-4-methylcoumarin and 7-(3,4-dicyanophenoxy)-4-methylcoumarin. The novel chromogenic compounds were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, Mass, IR and UV–vis spectral data. The electronic spectra exhibit a band of coumarin identity with characteristic Q and B bands of the phthalocyanine core. The IR spectra showed two characteristic intense bands at 1718 cm^{-1} for lactone carbonyl and at 1595 cm^{-1} for the α, β unsaturated doubled bond.

Keywords: Coumarin (2*H*-1-benzopyran-2-one); Phthalocyanines; Cobalt; Zinc; Nickel; Copper

1. Introduction

Coumarin (2*H*-1-benzopyran-2-one) is a constituent of many higher plants and essential oils, including tonka beans, sweet clover and lavender [1,2]. Some derivatives are used as anticoagulants, additives in food and cosmetics, in the preparation of insecticides, optical brighteners and dispersed fluorescent, laser dyes [1–6]. The diverse biological activities of coumarins are well known as anticoagulant, antithrombotic, antimicrobial, antibacterial, anticancer and anti-HIV activities [7]. The crown ether derivatives of some coumarins displayed the binding effect of alkaline cations on the fluorescence emission spectra [8–13].

Phthalocyanines (Pcs) are important blue and green dyes used in inks (ballpoint pens), textiles, colouring for plastic and metal surfaces and are produced at over 50 000 tons per year [14,15]. Recently they have been used as photoconducting agents in photocopying machines, as sensing elements in chemical sensors [16,17], electrochromic display devices, photodynamic reagents for cancer therapy and for other medical applications. Other applications include uses for optical read–write discs, increasing the octane rate of petrol [15], Langmuir–Blodgett films, nonlinear optics and as carrier generation materials in near-IR [18].

A major disadvantage of phthalocyanines and metallo-phthalocyanines are their low solubility in organic solvents or water. The solubility can be increased, however, by introducing crown ethers or long chain groups, such as alkyl or alkoxy into the peripheral positions of the phthalocyanine framework [18–21]. Phthalocyanines coupled with the coumarin moiety may exhibit biological activities and, after the cleavage of the lactone ring of the peripheral 2*H*-1-benzopyran-2-one (coumarin) phthalocyanine, the solubility can also be increased.

In this study, phthalocyanines with four peripheral 7-thio and 7-oxo-4-methylcoumarin substituents were prepared and their complexes with Zn (II), Cu (II), Ni (II), Co (II) metal salts were investigated. In addition, the lactone ring of the tetrakis(7-coumarinthio-4-methyl)-phthalocyaninatozinc was opened and the released hydroxyl group hexylated.

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2. Experimental

Routine IR spectra were recorded on a Shimadzu Fourier Transform FTIR-8300 Infrared Spectrophotometer using KBr pellets, electronic spectra on a Shimadzu UV-1601 UV–vis Spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz NMR Spectrophotometer using TMS as internal reference at Istanbul University Laboratory. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Ankara Test and Analysis Laboratory. Mass spectra were performed on a Varian 711 mass spectrometer.

1,2-Dicyano-4-nitrobenzene [22] and 7-hydroxy-4-methylcoumarin [23] were synthesized according to reported procedures. 7-Mercapto-4-methylcoumarin was purchased from the Merck Chemical Company.

*2.1. Synthesis of 7-(3,4-dicyanophenylthio)-4-methylcoumarin (**2a**) and 7-(3,4-dicyanophenoxy)-4-methylcoumarin (**2b**)*

7-Mercapto-4-methylcoumarin (**1a**) (2 g, 10.41 mmol) or 7-hydroxy-4-methylcoumarin (**1b**) (3 g, 17 mmol) and then 4-nitrophthalonitrile (1,2-dicyano-4-nitrobenzene) (1.80 g, 10.41 mmol for **2a** or 2.94 g, 17 mmol for **2b**) were added with stirring to dry DMF (50 ml). After stirring for 15 min, finely ground anhydrous K_2CO_3 (2.15 g, 15.6 mmol for **2a** or 3.67 g, 26.6 mmol for **2b**) was added portionwise over 2 h and the ensuing mixture was stirred vigorously at room temperature for a further 28 h. The reaction mixture was then poured into water (150 ml) and the precipitate was filtered off and washed with water to yield the yellow product (**2a**). The slightly brown product (**2b**) was purified by silica gel column chromatography using THF as eluent. Both **2a** and **2b** were soluble in acetone, ethylacetate, tetrahydrofurane, chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide.

Compound **2a**: Yield: 3.09 g (93.28%); m.p.: 226–229 °C; IR (KBr) γ_{max} (cm^{-1}): 3066–3097 (aryl CH), 2950 (alkyl CH), 2231 (C≡N), 1762 (C═O lactone), 1598 (C═C), 1245 (Ar–S–Ar); ^{1}H NMR (DMSO) δ_H: 8.02–8.07 (m, 2H, Ar–H), 7.88 (s, 1H, Ar–H), 7.68–7.70 (m, 1H, Ar–H), 7.56–7.60 (m, 1H, Ar–H), 7.46–7.50 (q, 1H, Ar–H), 6.48 (s, 1H, C═C*H*), 2.46 (s, 3H, CH_3); ^{13}C NMR (DMSO) δ_C: 160.0 (C═O), 112.8 (C═*C*H), 154.1 (C–*C*═CH), 116.4 (CN), 116.5 (CN) and 153.4, 144.6, 135.2, 135.1, 133.6, 129.0, 127.6, 121.1, 121.0, 116.1, 115.9, 18.7 (CH_3) ppm; UV–vis ($CHCl_3$) λ_{max} (log ε) (nm): 330 (4.62), 302 (4.47).

Compound **2b**: Yield: 3.5 g (68%); m.p.: 228–230 °C; IR (KBr) γ_{max} (cm^{-1}): 3074 (aryl CH), 2842–2918 (alkyl CH), 2223 (C≡N), 1729 (C═O lactone), 1621 (C═C), 1257 (Ar–O–Ar); ^{1}H NMR (DMSO) δ_H: 8.16 (d, 1H, Ar–H), 7.83–7.93 (m, 2H, Ar–H), 7.53–7.61 (q, 1H, Ar–H), 6.19–7.30 (q, 2H, Ar–H), 6.20 (s, 1H, C═C*H*), 3.15 (s, 3H, CH_3); ^{13}C NMR (DMSO) δ_C: 160.2 (C═O), 114.10 (C═*C*H), 155.1 (C–*C*═CH), 117.6 (C≡N), 117.8 (C≡N), 160.2, 157.5, 153.6, 137.1, 128.2, 124.3, 124.1, 116.7, 116.5, 116.0, 110.0, 108.5, 18.8 (CH_3) ppm; UV–vis ($CHCl_3$) λ_{max} (log ε) (nm): 312 (4.50).

*2.2. Synthesis of 2,9,16,23-tetrakis(7-coumarinthio-4-methyl)-phthalocyanine (**3a**) and 2,9,16,23-tetrakis-(7-coumarinoxy-4-methyl)-phthalocyanine (**3b**)*

7-(3,4-Dicyanophenylthio)-4-methylcoumarin (**2a**) (0.5 g, 1.57 mmol) or 7-(3,4-dicyanophenoxy)-4-methylcoumarin (**2b**) (0.2 g, 0.66 mmol) was heated with 2 ml dry 2-*N*,*N*-dimethylaminoethanol in a sealed tube. The mixture was held at 145 °C for 48 h and, after cooling to room temperature, the reaction mixture was treated with dilute HCl and the mixture was filtered and washed with water until the filtrate became neutral in pH. The ensuing green product was purified by extraction with tetrahydrofurane, chloroform, dichloromethane, acetonitrile, acetone, ethylacetate, ether and dried. Compounds **3a** and **3b** were soluble in dimethylformamide and dimethylsulfoxide.

Compound **3a**: Yield: 0.31 g (62%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3269 (N–H), 3058 (aryl CH), 2850–2925 (alkyl CH), 1718 (C═O lactone), 1595 (C═C), 1242 (Ar–S–Ar); ^{1}H NMR (DMSO) δ_H: 7.0–8.04 (m, 24H, Ar–H), 6.54 (s, 4H, C═C*H*), 2.44 (s, 12H, CH_3), −3.48 (br, s, 2H, NH); UV–vis (DMF) λ_{max} (log ε) (nm): 685 (4.46), 642 (4.37), 338 (4.82); Calcd. for $C_{72}H_{42}N_8O_8S_4$: C, 67.8; H, 3.29; N, 8.79; S, 10.04%. Found: C, 67.1; H, 3.22; N, 8.1; S, 9.85%; MS [FAB] *m*/*z*: 1274 [M$^+$], 1098 [M$^+$ − 4.44].

Compound **3b**: Yield: 0.135 g (67.4%), m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3290 (N–H), 3066 (aryl CH), 2850–2918 (alkyl CH), 1722 (C═O lactone), 1602 (C═C), 1272 (Ar–O–Ar); ^{1}H NMR (DMSO) δ_H: 7.20–8.20 (m, 24H, Ar–H), 6.58 (s, 4H, C═C*H*), 2.46 (s, 12H, CH_3), −3.42 (br, s, 2H, NH); UV–vis (DMF) λ_{max} (log ε) (nm): 679 (4.17), 631 (4.22), 328 (4.70). Calcd. for $C_{72}H_{42}N_8O_{12}$: C, 71.40; H, 3.47; N, 9.25%. Found: C, 69.8; H, 3.10; N, 9.1%.

*2.3. Synthesis of metallo-phthalocyanines (**4a–7a**, **4b–7b**)*

*2.3.1. Synthesis of 2,9,16,23-tetrakis(7-coumarinthio-4-methyl)-phthalocyaninatozinc (**4a**) and 2,9,16,23-tetrakis(7-coumarinoxy-4-methyl)-phthalocyaninatozinc (**4b**)*

A mixture of compound **2a** (0.5 g, 1.5 mmol) or **2b** (0.1 g, 0.33 mmol) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.086 g, 0.39 mmol for **2a**; 0.018 g, 0.082 mmol for **2b**) was heated at 195 °C with dry quinoline (2 ml) in a sealed tube with stirring for 24 h. After cooling to room temperature, the reaction mixture was treated with ethanol and then filtered off and washed with water to remove unreacted $Zn(CH_3COO)_2 \cdot 2H_2O$. The green product was purified by extraction with tetrahydrofurane, chloroform, dichloromethane, acetonitrile, acetone, ethylacetate, ether and dried. Both **4a** and **4b** were soluble in dimethylformamide and dimethylsulfoxide.

Compound **4a**: Yield: 0.5 g (95.13%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3053 (aryl CH), 2850–2925 (alkyl CH), 1722 (C═O lactone), 1595 (C═C), 1242 (Ar–S–Ar); ^{1}H NMR

δ_H (DMSO): 7.06–7.94 (m, 24H, Ar–H), 6.61 (s, 4H, C=CH), 2.40 (s, 12H, CH_3); UV–vis (DMF) λ_{max} (log ε) (nm): 688 (5.08), 617 (4.38), 340 (4.78); Calcd. for $C_{72}H_{40}N_8O_8S_4Zn$: C, 64.62; H, 2.99; N, 8.37; S, 9.57%. Found: C, 64.21; H, 3.02; N, 8.1; S, 9.75%; MS [FAB] *m*/*z*: 1337 [M^+], 1161 [$M^+ - 4.44$].

Compound **4b**: Yield: 0.068 g (64.4%); m.p: >300 °C; IR γ_{max} (cm^{-1}): 3058 (aryl CH), 2738–2918 (alkyl CH), 1714 (C=O, lactone), 1602 (C=C), 1269 (Ar–O–Ar); ^1H NMR δ_H (DMSO): 7.0–8.1 (m, 24H, Ar–H), 6.80 (s, 4H, C=C*H*), 2.45 ppm (s, 12H, CH_3); UV–vis (DMF) λ_{max} (log ε) (nm): 689 (4.58), 616 (4.38), 339 (4.68); Calcd. for $C_{72}H_{40}N_8O_{12}Zn$: C, 67.87; H, 3.14; N, 8.79%. Found: C, 68.17; H, 3.42; N, 9.19%.

*2.3.2. Synthesis of 2,9,16,23-tetrakis(7-coumarinthio-4-methyl)-phthalocyaninatocopper (**5a**) and 2,9,16,23-tetrakis(7-coumarinoxy-4-methyl)-phthalocyaninatocopper (**5b**)*

Compound **2a** (0.1 g, 0.31 mmol) or **2b** (0.1 g, 0.33 mmol) and anhydrous CuCl (0.0078 g, 0.078 mmol for **2a**; 0.082 g, 0.082 mmol for **2b**) were heated at 155 °C with dry hexanole (2 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 ml) for **5a**, at 195 °C with dry quinoline (2 ml) for **5b** in a sealed tube with stirring for 24 h. After cooling to room temperature, the reaction mixture was treated with dilute HCl and filtered off and then washed with water until the filtrate became neutral in pH. The green product was washed with NH_4OH (24%, 3 × 50 ml) to remove unreacted CuCl and then washed with water until the filtrate became neutral in pH. The product was purified by extraction with tetrahydrofurane, chloromethane, dichloromethane, acetonitrile, acetone, ethylacetate, ether and dried. The compounds **5a** and **5b** were partially soluble in dimethylformamide and dimethylsulfoxide.

Compound **5a**: Yield: 0.1 g (95.2%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3045 (aryl CH), 2827–2910 (alkyl CH), 1722 (C=O, lactone), 1595 (C=C), 1249 (Ar–S–Ar). UV–vis (DMF) λ_{max} (log ε) (nm): 685 (4.90), 615 (4.36), 317 (4.99); MS [FAB] *m*/*z*:1336 [M^+], 1160 [$M^+ - 4.44$].

Compound **5b**: Yield: 0.1 g (95%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3074 (aryl CH), 2746–2933 (alkyl CH), 1722 (C=O, lactone), 1598 (C=C), 1269 (Ar–O–Ar); UV–vis (DMF λ_{max} (log ε) (nm)): 688 (4.74), 612 (4.24), 325 (5.0).

*2.3.3. Synthesis of 2,9,16,23-tetrakis(7-coumarinthio-4-methyl)-phthalocyaninatonickel (**6a**) and 2,9,16,23-tetrakis(7-coumarinoxy-4-methyl)-phthalocyaninatonickel (**6b**)*

Compound **2a** (0.1 g, 0.31 mmol) or **2b** (0.1 g, 0.33 mmol) and $NiCl_2 \cdot 6H_2O$ (0.018 g, 0.078 mmol for **2a**; 0.019 g, 0.039 mmol for **2b**) were heated at 155 °C with dry hexanole (2 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 ml) for **6a**, at 195 °C with dry quinoline (2 ml) for **6b** in a sealed tube with stirring for 24 h. After cooling to room temperature, the reaction mixture was treated with dilute HCl, filtered and washed with water until the filtrate became neutral in pH. The ensuing green product was purified by extraction with tetrahydrofurane, chloroform, dichloromethane, acetonitrile, acetone, ethylacetate, ether and dried. The compounds (**6a**, **6b**) were partly soluble in dimethylformamide and dimethylsulfoxide.

Compound **6a**: Yield: 0.1 g (96%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3066 (aryl CH), 2850–2925 (alkyl CH), 1714 (C=O lactone), 1595 (C=C), 1234 (Ar–S–Ar); UV–vis (DMF) λ_{max} (log ε) (nm): 686 (4.78), 620 (4.40), 340 (4.76); MS [FAB] *m*/*z*:1331 [M^+], 1155 [$M^+ - 4.44$].

Compound **6b**: Yield: 0.052 g (50%); m.p: >300 °C; IR γ_{max} (cm^{-1}): 3037 (aryl CH), 2731–2902 (alkyl CH), 1714 (C=O, lactone), 1602 (C=C), 1269 (Ar–O–Ar); UV–vis (DMF) λ_{max} (log ε) (nm): 688 (4.23), 614 (4.03), 318 (4.38); MS [FAB] *m*/*z*: 1267 [M^+], 1091 [$M^+ - 4.44$].

*2.3.4. Synthesis of 2,9,16,23-tetrakis(7-coumarinthio-4-methyl)-phthalocyaninatocobalt (**7a**) and 2,9,16,23-tetrakis(7-coumarinoxy-4-methyl)-phthalocyaninatocobalt (**7b**)*

Compound **2a** (0.1 g, 0.31 mmol) or **2b** (0.05 g, 0.16 mmol) and $CoCl_2 \cdot 6H_2O$ (0.018 g, 0.0078 mmol for **2a**; 0.0098 g, 0.041 mmol for **2b**) were heated at 155 °C with dry hexanole (2 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 ml) in a sealed tube with stirring for 24 h. After cooling to room temperature, the reaction mixture was treated with dilute HCl, filtered and washed with water until the filtrate became neutral in pH. The green product was purified by extraction with tetrahydrofurane, chloroform, dichloromethane, acetonitrile, acetone, ethylacetate, ether and dried. Both **7a** and **7b** were soluble in dimethylformamide and dimethylsulfoxide.

Compound **7a**: Yield: 0.1 g (96%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3053 (aryl CH), 2866–2925 (alkyl CH), 1714 (C=O, lactone), 1587 (C=C), 1242 (Ar–S–Ar); UV–vis (DMF) λ_{max} (log ε) (nm): 686 (4.46), 620 (4.10), 338 (4.57).

Compound **7b**: Yield: 0.049 g (94%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3067 (aryl CH), 2940 (alkyl CH), 1710 (C=O, lactone), 1598 (C=C), 1269 (Ar–O–Ar); UV–vis (DMF) λ_{max} (log ε) (nm): 675 (4.95), 612 (4.28), 325 (4.77).

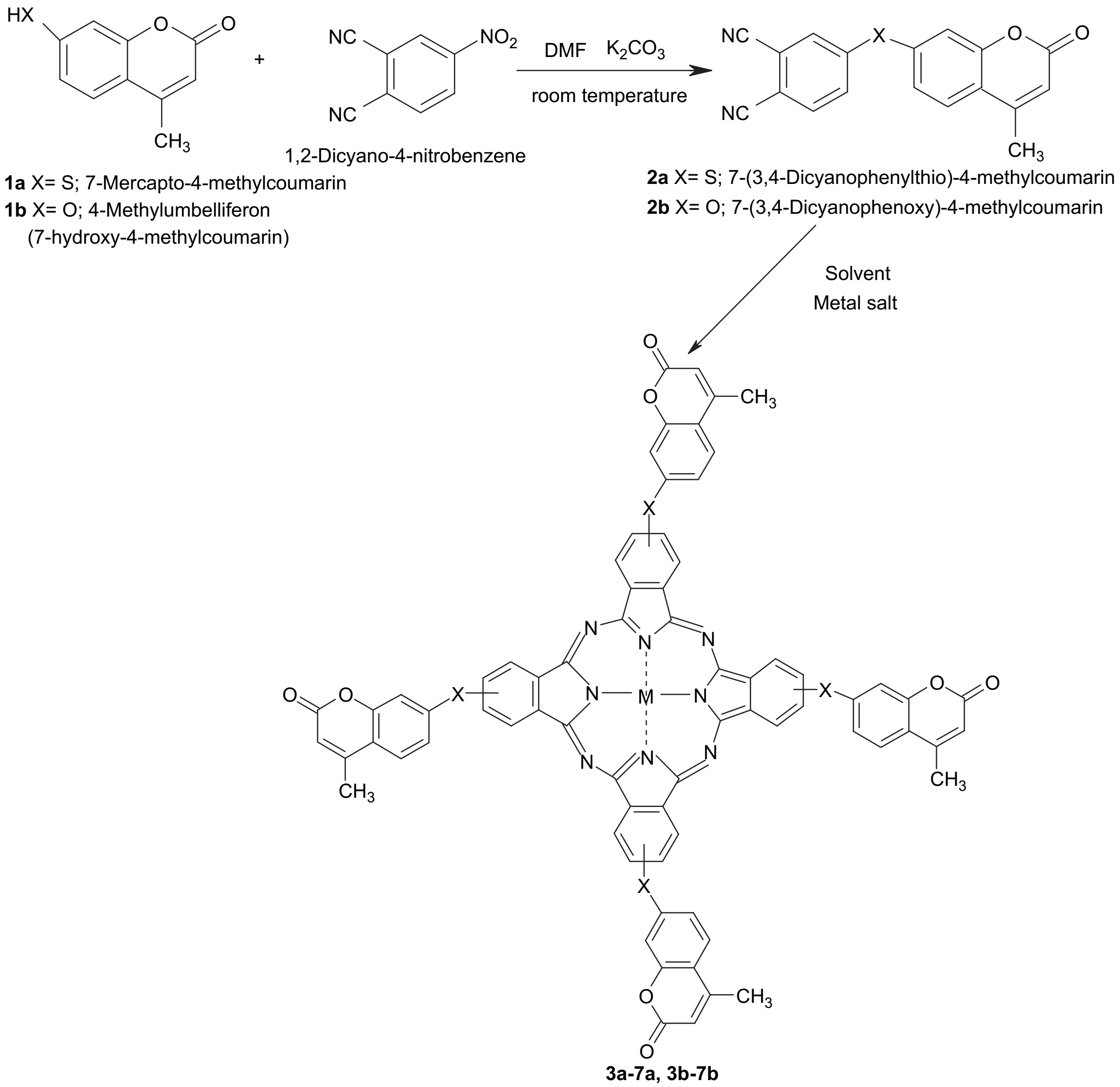
*2.4. 2,9,16,23-Tetrakis[(Z)-hexyl-3-(2-(hexyloxy)-4-mercaptophenyl)but-2-enoate]-phthalocyaninatozinc (**4c**)*

To a solution of 2,9,16,23-tetrakis(7-coumarinthio-4-methyl)phthalocyaninatozinc (0.1 g, 0.0748 mmol) (**4a**) in dry DMF (15 ml) was added hexanole (15 ml) and metallic lithium (0.0052 g, 0.748 mmol). The mixture was refluxed for 4 h, after which, it was cooled to room temperature and 1-bromohexane (0.5 ml) was added. The mixture was held at 50 °C in a sealed tube for 48 h and the product concentrated and ice–water was added. After being acidified with 2 M HCl, the precipitate was collected by filtration, washed with water and dried. The green product was purified by extraction with ethylacetate, ethanol and methanol. The compound was soluble in DMF, DMSO, $CHCl_3$, CH_2Cl_2, and THF. Yield: 0.045 g (29%); m.p.: >300 °C; IR γ_{max} (cm^{-1}): 3059 (aryl CH), 2918–2948 (alkyl CH), 2842 (alkyl CH), 1706 (C=O ester), 1595 (C=C), 1245 (Ar–O–C); ^1H NMR δ_H (DMSO): 7.22–8.09 (m, 24H, Ar–H), 6.24 (s, 4H,

$C{=}CH$), 4.30–4.40 (t, 8H, OCH_2Ar), 3.65–3.70 (t, 8H, OCH_2), 2.40 (s, 12H, CH_3), 1.74–2.10 (t, 8H, CH_2CH_2OAr), 1.59 (m, 8H, CH_2CH_2OCO), 0.85–1.43 (m, 72H, alkyl CH); UV–vis (DMF) λ_{max} (log ε) (nm): 690 (5.08), 625 (4.40), 344 (4.79); Calcd. for $C_{120}H_{144}N_8O_{12}S_4Zn$: C, 69.19; H, 6.91; N, 5.38; S, 6.15%. Found: C, 68.17; H, 6.42; N, 5.27; S, 6.22%; MS [FAB] *m*/*z*: 2081 $[M]^+$, 2079 $[M-2]^+$.

3. Results and discussion

Novel 7-(3,4-dicyanophenylthio)-4-methylcoumarin **2a** and 7-(3,4-dicyanophenoxy)-4-methylcoumarin **2b** were prepared by a base catalyzed nucleophilic aromatic nitro displacement of 1,2-dicyano-4-nitrobenzene with 7-mercapto-4-methylcoumarin **1a** and 7-hydroxy-4-methylcoumarin **1b**, respectively.



Complex (X=S)	M	Solvent	Complex (X=O)	M	Solvent
3a	H	2-N,N-dimethylaminoethanol	3b	H	2-N,N-dimethylaminoethanol
4a	Zn	quinoline	4b	Zn	quinoline
5a	Cu	hexanole	5b	Cu	quinoline
6a	Ni	hexanole	6b	Ni	quinoline
7a	Co	hexanole	7b	Co	hexanole

Scheme 1. Synthesis of the starting compounds, metal-free and metallo-phthalocyanines.

The reaction was carried out in a single step synthesis by using K_2CO_3 as the nitro-displacing base at room temperature in dimethylformamide under N_2 atmosphere and the yields were obtained 93.28% for **2a** and 68% for **2b**. Cyclotetramerization of the phthalonitrile derivative **2a** or **2b** to the metal-free phthalocyanine **3a** or **3b** was accomplished in 2-*N*,*N*-dimethylaminoethanol (DMAE) at 145 °C in sealed tube. The metallophthalocyanines **4a–7a** and **4b–7b** were obtained from the dicyano derivative and the corresponding metal salts [$Zn(CH_3COO)_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, CuCl and $CoCl_2 \cdot 6H_2O$] in suitable anhydrous solvents (e.g. hexanole or quinoline). The yields were satisfactory and depended upon the transition metal ion. The tetrasubstituted phthalocyanine products were soluble in DMF and DMSO and purified by extraction with THF, $CHCl_3$, CH_2Cl_2, acetone, acetonitrile, ethylacetate and ether. Characterization of the products involved a combination of methods including elemental analysis, ^1H and ^{13}C NMR, UV–vis and mass spectroscopy.

Starting from 7-mercapto-4-methylcoumarin **1a** or 7-hydroxy-4-methylcoumarin **1b** and 1,2-dicyano-4-nitrobenzene, the derived novel coumarin-substituted phthalocyanines **3a–7a**, **3b–7b** were prepared according to the route shown in Scheme 1.

Spectral data of the newly synthesized compounds are consistent with the proposed structures. Comparison of the IR spectral data clearly indicated the formation of compounds **2a** and **2b**, the appearance of new absorption bands at 2231 cm^{-1} (C≡N) and 1245 cm^{-1} (Ar–S–Ar) for **2a**, at 2223 cm^{-1} (C≡N) and 1257 cm^{-1} (Ar–O–Ar) for **2b** (the band OH of 7-hydroxy-4-methylcoumarin at 3141 cm^{-1} disappeared in this spectrum). After conversion of the dinitrile derivatives (**2a** or **2b**) into the phthalocyanines (**3a–7a** or **3b–7b**), the sharp peak for the C≡N vibration around 2231 cm^{-1} for **3a–7a** and 2223 cm^{-1} for **3b–7b** disappeared. The IR spectra of the metal-free phthalocyanine **3a/3b** and the metal complexes **4a–7a/4b–7b** were very similar, with the exception of **3a/3b** showing NH stretching band due to the inner core. These bands were absent from the spectra of the complexes. The NH group of the metal-free phthalocyanine (**3a/3b**) in the inner core gave a weak absorption peak at 3269 cm^{-1} for **3a** and at 3290 cm^{-1} for **3b**.

The ^1H NMR spectra of **2a** and **2b** were almost identical except for small shift; ^1H NMR spectrum exhibited lactone protons (C=CH) at 6.48/6.20 ppm (**2a/2b**) and methyl protons at 2.46/3.15 ppm (**2a/2b**). The aromatic protons of both compounds appeared at 8.07–6.48/8.16–6.20 ppm (**2a/2b**). The ^{13}C NMR data are in accord with expected structure. The ^{13}C NMR spectrum of both compounds **2a** and **2b** indicates the nitrile carbons at 116.4, 116.5 for **2a**, 117.6, 117.8 for **2b** as expected. The carbonyl carbon of lactone ring appeared at 160.0 ppm for **2a**, 160.2 ppm for **2b**.

The ^1H NMR spectra of phthalocyanines **4a–7a** and **4b–7b** were almost identical. A common feature of these spectra is the broad absorptions probably caused by the aggregation of phthalocyanine.

The NH protons of metal-free phthalocyanine **3a**, **3b** were also identified. In the ^1H NMR spectra with a broad peak at $\delta = -3.48$ ppm for **3a**, $\delta = -3.42$ ppm for **3b** and the signals disappeared after the addition of D_2O.

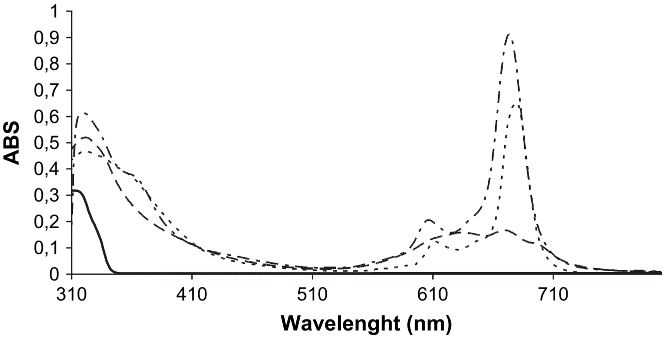


Fig. 1. UV–vis spectra of **2b** (———) in $CHCl_3$ (1×10^{-5} M), **3b** (– – –), **4b** (·······················) and **7b** (—···—···—···) in DMF (1×10^{-5} M).

A closed investigation of the mass spectra of the phthalocyanines confirmed the proposed structure. In the mass spectrum of coumarino-phthalocyanines **3a–7a**, **3b–7b** in addition to the [M^+] peak, a fragment ion corresponding to the loss of $4 \times$ COO [$M^+ - 4.44$] is easily identified. The phthalocyanines **3a–7a**, **3b–7b** are only soluble in DMF and DMSO.

The coumarins show maximum absorption with single band at 270–310 nm. UV–vis spectra of **2b** in $CHCl_3$ showed a single band at 312 nm (Fig. 1).

The phthalocyanines **3a–7a/3b–7b** 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). Increasing the concentration leads to aggregation, which is easily observed by the values of the Q bands, which shift to higher energies by a parallel decrease in the molar absorption coefficient. On the other hand metal-free derivatives with D_{2h} symmetry show two intense absorptions in the visible region, that having D_{4h} symmetry dives only a single band in this region, these two absorptions around 700 nm are due to the π–π* transition of the fully conjugated 18π electron system. Tetrasubstitution with oxygen or sulfur bridged groups causes shift (10–15 nm) of the intense Q band to longer wavelengths when compared with the unsubstituted derivatives. A typical spectrum of the metal-free phthalocyanine (**3b**) in DMF showed a doublet in the Q band region at 631 and 679 nm, B band region at 328 nm; while the metallo-phthalocyanines each gave an intense Q band at 689, 675 nm and B band at 339, 325 nm for

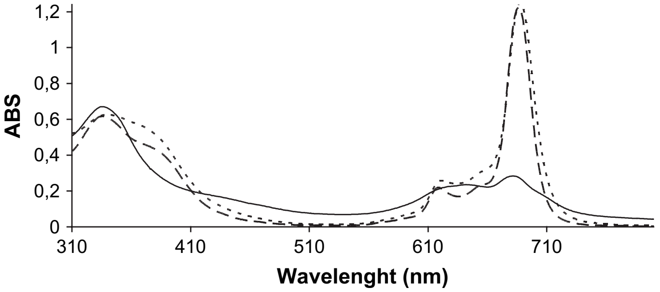
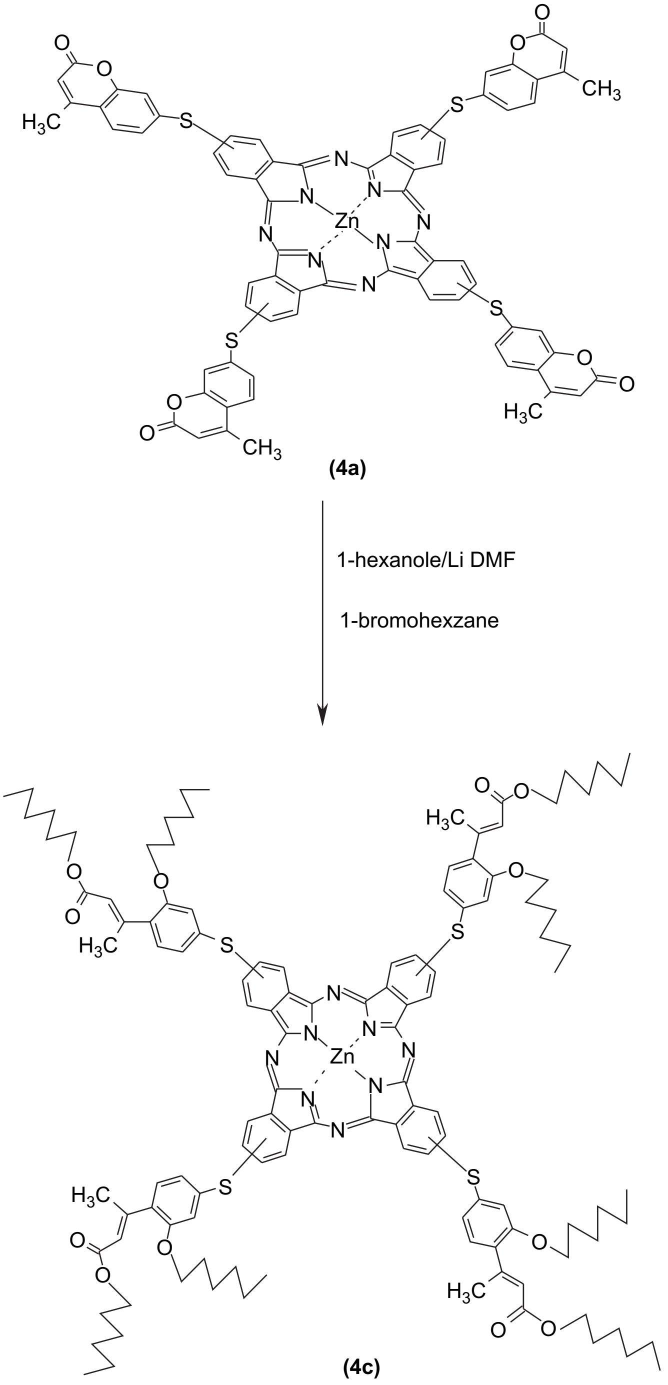


Fig. 2. UV–vis spectra of **3a** (———), **4a** (– – –), and **4c** (········) in DMF (1×10^{-5} M).



Scheme 2. The synthesis of 2,9,16,23-tetrakis[(*Z*)-hexyl-3-(2-(hexyloxy)-4-mercaptophenyl)but-2-enoate]-phthalocyaninatozinc.

the corresponding compounds **4b**, **7b** (Fig. 1). In Fig. 2 is indicated Q band region at 685 and at 642 nm for **3b**, at 688 nm for **4b**; B band region at 338 nm for **3b** and at 340 nm for **4b** in DMF.

Comparison of the UV spectral data clearly indicated the formation of the compound (**3a–7a/3b–7b**), the appearance of Q band at about 685 nm.

ZnPc (unsubstituted) dye is characterized by the band with the maximum at 673 nm as observed in the literature for ZnPc [24]. ZnPc substituted with four coumarin moieties show a bathochromic shift of 5 nm (band with the maximum at 688 nm for **4a** and at 689 nm for **4b**).

The shoulder at around 616 for **4b** and 612 nm for **7b** indicated the aggregation Pc molecules in Fig. 1 (the similar aggregation showed **4a**, **7a** and coumarin-substituted metallo Pcs). Aggregation occurs also readily at low concentrations making the spectral data more difficult to interpret.

The coumarin substituents on the periphery of the phthalocyanine bring out a vast number of possibilities for binding with different nucleophiles. To achieve a better solubility of **4a**, hexyl and hexyloxy substituents were introduced into the lactone ring of the coumarin moiety. Opening of all the four lactone rings in **4c** with hexanole/Li in DMF, then concomitant reaction of released hydroxy group with 1-bromohexane gave phthalocyanine **4c** in 29% yield. The product **4c** shows good solubility in organic solvents such as DMF, DMSO, CH_2Cl_2, $CHCl_3$, and THF (Scheme 2).

The IR spectra of **4c** clearly proved the presence of the long alkyl chain by the intense absorption peak for aliphatic group at around 2918–2948 cm^{-1}.

The appearance of new absorption bands at 3059 (aryl CH), 2918–2948 (alkyl CH), 2842 (alkyl CH), 1706 (C=O ester), 1595 (C=C) and 1245 (Ar–O–C) cm^{-1} confirmed the opening of the lactone ring and the structure of the new ester.

The ^1H NMR spectrum of **4c** in DMSO confirmed the proposed structure: 0.85–1.43 (m, 72H, alkyl CH), 1.59 (m, 8H, CH_2CH_2OCO), 1.74–2.10 (t, 8H, CH_2CH_2OAr), 2.40 (s, 12H, CH_3), 3.65–3.70 (t, 8H, OCH_2), 4.3–4.4 (t, 8H, OCH_2Ar), 6.24 (s, 4H, C=C*H*), 7.22–8.09 (m, 24H, Ar–H). The broad signals in **4c** were probably due to the aggregation of phthalocyanine molecules. The mass spectra of **4c** confirmed the proposed structure; molecular ions were easily identified at 2081 $[M^+]$, and 2079 $[M-2]^+$.

A typical UV-spectrum of the 2,9,16,23-tetrakis[(*Z*)-hexyl-3-(2-(hexyloxy)-4-mercaptophenyl)but-2-enoate]-phthalocyaninatozinc (**4c**) in DMF showed Q band at 690 nm and B band at 344 nm. The shoulder of **4c** registered at 625 nm. It is enhanced by the solvent polarity and the presence of aliphatic side chains. Opening of all the four lactone rings in **4c** causes shift (about 2 nm) of Q band to longer wavelengths when compared with **4a** in the UV–vis spectra (Fig. 2).

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