



Phthalocyanines prepared from 4-chloro-/4-hexylthio-5-(4-phenyloxyacetic acid)phthalonitriles and functionalization of the related phthalocyanines with hydroxymethylferrocene

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ABSTRACT

The phthalonitrile derivative chosen for the synthesis of substituted phthalocyanines [M: 2H, Zn(II), Co(II)] with four chloro and four phenyloxyacetic acid substituents on the periphery is 4-chloro-5-(4-phenyloxyacetic acid)phthalonitrile. The sodium salt of carboxyl substituted zinc phthalocyanine is good soluble in water. Further reactions of zinc and cobalt phthalocyanines bearing phenyloxyacetic acid with thionylchloride gave the corresponding acylchlorides. This functional group reacted with hydroxymethylferrocene in dry DMF to obtain ferrocenyl substituted phthalocyanines. Also chloro substituent in new phthalonitrile was substituted with hexylsulfanyl substituent and its cyclotetramerization in the presence of $Zn(AcO)_2 \cdot 2H_2O$ and 2-(dimethylamino)ethanol resulted with zinc phthalocyanine. The compounds have been characterized by elemental analysis, MALDI-TOF mass, FT-IR, 1H NMR, UV-Vis and fluorescence data. Aggregations properties of phthalocyanines were investigated at different concentrations in tetrahydrofuran, dimethylformamide, dimethylsulfoxide, water, and water/ethanol mixture. Also fluorescence spectral properties are reported.

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1. Introduction

Phthalocyanines (Pcs) have been under systematic study more than 70 years; however, researchers are still interested in this class of compounds [1]. Pc complexes are potential functional materials for use as sensitizers, gas sensors, catalysis and electrocatalysis because of their high electron-transfer abilities [2]. Other technological applications of these macrocycles have been intensively investigated, such as electrophotography, photovoltaic and solar cells, semiconductor devices, molecular electronics, Langmuir-Blodgett films (LB), electrochromic display devices, low-dimensional conductors and synthetic metals, liquid crystals, non-linear optics, and optical disk [1,3]. Remarkable progress has been made in recent years in the use of pc derivatives as sensitizers for photodynamic therapy (PDT) of cancer [4,5]. A decisive disadvantage of pcs is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing bulky or long chain groups, e.g. alkyl, alkoxy/alkylthio into the peripheral positions of the pc framework [6–8]. For aqueous solutions it is necessary to introduce hydrophilic chemical functional groups into benzene rings of the basic pc skeleton [9]. The hydrophilic moieties which have been incorporated on the peripheral positions of pc ring in-

clude sulfonates [9–11], carboxylates [2,5,10,12], phosphonates [13], and quaternarized amino groups [14–16].

Although the symmetrically octasubstituted (where all the eight substituents are the same) and tetrasubstituted pcs have been frequently encountered, octasubstituted pcs obtained from disubstituted phthalonitrile derivatives with two different substituents in the 4,5-positions are relatively less studied and only a few well characterized species well known [17–19]. This new class of substituted pcs usually exhibit high solubility [20]. In a sense, these types of derivatives might be considered as alternatives to asymmetrically substituted pcs which are getting more and more important for their non-linear optical properties, Langmuir-Blodgett film (LB) formation and mesogenic tendencies [21,22].

Phthalocyanine-based multicomponent systems have been explored, including porphyrins, ferrocenes, crown ethers, tetra-thiafulvalenes, oligopridyl-metal complexes, dendrimers, and C_{60} [23]. Pcs have long been known to undergo electron-transfer reactions, both to and from their excited states, and strong electron donors such as ferrocene are able to quench the Pc fluorescence by intermolecular electron-transfer [24,25]. The fascinating structural properties of ferrocene and its derivatives have been the subject of increasing interest in all fields of organometallic chemistry, since the discovery of ferrocene in 1950 [26–28]. Therefore, synthesis and investigation of novel phthalocyanine-ferrocene conjugates are worthwhile.

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Recently, we have reported on the synthesis and characterization of water-soluble symmetrical pcs bearing four 4-phenyloxyacetic acid functionalities [29]. We report here the synthesis of two different singly substituted phthalonitriles with a phenyloxyacetic acid group. In these displacement reactions; one of two chloro groups was replaced only. Metal-free and divalent metal pcs [Zn(II) and Co(II)] with four peripheral chloro and four phenyloxyacetic acid substituents have been synthesized from this phthalonitrile derivative. The phenyloxyacetic acid carries carboxyl group that enables solubility in water (as a sodium salts) and, is also suitable for a conjugation to the biomolecules. Zinc metallo phthalocyanine's sodium salt was prepared using sodium hydroxide solution. Aggregation properties of this salt were investigated in water and water/ethanol mixture. Pcs containing ferrocenylmethyl 4-phenyloxyacetate moieties on the periphery have been prepared with the reaction of hydroxymethylferrocene and octa-substituted zinc and cobalt metallo pcs carrying four chloro and phenyloxyacetic acid substituents. Also a new phthalonitrile with a phenyloxyacetic acid and hexylsulfanyl substituents was synthesized and the corresponding zinc metallo pc was prepared. The bulky hexylsulfanyl substituent was chosen to prevent the aggregation [5].

2. Experimental

2.1. Materials and equipment

Infrared spectra (IR) were recorded on a Shimadzu FTIR-8300 Fourier Transform Infrared Spectrophotometer using KBr pellets, electronic spectra on a Shimadzu UV-2450 UV-Vis Spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^1H NMR spectra were recorded on a Varian Mercury-VX 400 MHz spectrometer using TMS as an internal standard. Mass spectra were performed on a Bruker Autoflex III MALDI-TOF spectrometer. A 2,5-dihydroxybenzoic acid (DHB, 20 mg/mL in THF) matrix was used. MALDI samples were prepared by mixing the complex (2 mg/mL in THF) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf micro tube. Finally, 1 μL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. Fluorescence excitation and emission spectra were recorded on a HITACHI F-7000 Fluorescence Spectrophotometer using 1 cm path length cuvettes at room temperatures. 4,5-Dichlorophthalonitrile was prepared according to the reported procedure [30] 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 was tested in each step using TLC (SiO_2).

2.2. Synthesis

2.2.1. 4-Chloro-5-(4-phenyloxyacetic acid)phthalonitrile (1)

4,5-Dichlorophthalonitrile (1.00 g, 5.08 mmol) and 4-hydroxyphenylacetic acid (1.54 g, 10.16 mmol) were dissolved in anhydrous dimethylformamide (20 cm^3) under N_2 atmosphere. After stirring for 10 min; finely ground anhydrous K_2CO_3 (2.80 g, 20.29 mmol) was added with stirring. The reaction mixture was stirred at room temperature for 6 days under vacuum. Then the mixture was treated with diluted HCl under ice cooling and the obtained precipitate was filtered off, washed with water until the washings were neutral. After drying in vacuo at 50 °C, the crude product was purified by column chromatography with chloroform. The compound is soluble in chloroform CHCl_3 , tetrahydrofuran

(THF), methanol, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Yield: 1.31 g (83%). M.p. 202–205 °C. FT-IR (KBr), $\nu_{\text{max}}/(\text{cm}^{-1})$: 3449 (carboxylic acid OH), 3098–3028 (Ar-CH), 2970–2916 (aliphatic CH), 2226 ($\text{C}\equiv\text{N}$), 1709 ($\text{C}=\text{O}$), 1582–1481 (Ar $\text{C}=\text{C}$), 1281 (Ar-O-Ar). ^1H NMR (d-DMSO 400 MHz): 12.40 (s, 1H, COOH), 8.57 (s, 1H, Ar-H), 7.65 (s, 1H, Ar-H), 7.38 (dd, 2H, $J = 8$ Hz, Ar-H), 7.13 (dd, 2H, $J = 8$ Hz, Ar-H), 3.68 (s, 2H, CH_2COOH). UV-Vis λ_{max} (nm) (log ϵ) in DMF: 281 (3.97).

2.2.2. 2,9,16,23-Tetra(chloro)-3,10,17,24-tetra(4-phenyloxyacetic acid)-phthalocyanine (2)

A mixture of **1** (0.250 g, 0.80 mmol) and lithium metal (0.080 g, 11.43 mmol) was heated and stirred at 170 °C for 5 h under N_2 atmosphere in the mixture of 1,2-dichlorobenzene (1.5 cm^3) and hexanole (1.5 cm^3). After cooling to room temperature the green mixture was treated with acetone to precipitate the product completely. The green precipitate was collected by centrifuging and then washed with acetone. It was dissolved in a small amount of methanol and precipitated by diluted HCl. In this mixture, the Li_2pc formed was converted into H_2pc . The green precipitate was centrifuged and washed several times with water, hot ethanol, hot methanol, ethyl acetate, acetone and diethyl ether, and dried in vacuo. It is soluble in THF, DMF, DMSO, pyridine and water (at pH > 7). Yield: 0.135 g (54%). M.p. >300 °C. FT-IR (KBr), $\nu_{\text{max}}/(\text{cm}^{-1})$: 3425 (carboxylic acid OH), 3283 (NH), 3036 (Ar-CH), 2932–2843 (aliphatic CH), 1732 ($\text{C}=\text{O}$), 1601–1435 (Ar $\text{C}=\text{C}$), 1250 (Ar-O-Ar). UV-Vis λ_{max} (nm) (log ϵ) in THF: 286 (4.41), 339 (4.56), 604 (4.26), 631 (4.41), 663 (4.64), 697 (4.63). MS (MALDI-TOF, DHB as matrix): m/z 1252.09 $[\text{M}]^+$, 1253.08 $[\text{M}+1]^+$, 1254.28 $[\text{M}+2]^+$, 1324.05 $[\text{M}+4\text{H}_2\text{O}]^+$. Anal. Calc. for $\text{C}_{64}\text{H}_{38}\text{N}_8\text{Cl}_4\text{O}_{12}$: C, 61.34; H, 3.04; N, 8.95. Found: C, 61.48; H, 3.01; N, 8.91%.

2.2.3. 2,9,16,23-Tetra(chloro)-3,10,17,24-tetra(4-phenyloxyacetic acid)-phthalocyaninatozinc(II) (3)

The compound **1** (0.100 g, 0.32 mmol) was dissolved in dry DMF (1.5 cm^3) and $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.013 g, 0.06 mmol) was added and the mixture was heated under stirring for 24 h at 160 °C under N_2 atmosphere in a sealed glass tube. After cooling to room temperature, the reaction mixture was treated with diluted HCl to precipitate the product. The green solid was centrifuged and washed several times successively with water, hot methanol, hot ethanol, ethyl acetate, acetone and diethyl ether, and dried in vacuo. It is soluble in DMF, DMSO, pyridine and water (at pH > 7). Yield: 0.021 g (20%). M.p. >300 °C. FT-IR (KBr), $\nu_{\text{max}}/(\text{cm}^{-1})$: 3379 (carboxylic acid OH), 3067–3036 (Ar-CH), 2947–2916 (aliphatic CH), 1728 ($\text{C}=\text{O}$), 1601–1458 (Ar $\text{C}=\text{C}$), 1242 (Ar-O-Ar). ^1H NMR (d-DMSO 400 MHz): 12.34 (br, s, 4H, COOH), 8.11–7.08 (br, 2H, Ar-H), 3.70 (s, 8H, CH_2COOH). UV-Vis λ_{max} (nm) (log ϵ) in DMF: 348 (4.33), 618 (4.03), 677 (4.54). MS (MALDI-TOF, DHB as matrix): m/z 1315.21 $[\text{M}]^+$, 1316.14 $[\text{M}+1]^+$, 1317.31 $[\text{M}+2]^+$, 1318.03 $[\text{M}+3]^+$, 1319.35 $[\text{M}+4]^+$, 1387.24 $[\text{M}+4\text{H}_2\text{O}]^+$, 1459.51 $[\text{M}+8\text{H}_2\text{O}]^+$. Anal. Calc. for $\text{C}_{64}\text{H}_{36}\text{N}_8\text{Cl}_4\text{O}_{12}\text{Zn}$: C, 58.40; H, 2.74; N, 8.52. Found: C, 58.36; H, 2.71; N, 8.55%.

2.2.4. 2,9,16,23-Tetra(chloro)-3,10,17,24-tetra(4-phenyloxyacetic acid)-phthalocyaninatocobalt(II) (4)

The compound **1** (0.100 g, 0.32 mmol) was dissolved in dry DMF (1.5 cm^3) and $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.015 g, 0.06 mmol) was added and the mixture was heated under stirring for 24 h at 160 °C under N_2 atmosphere in a sealed glass tube. After cooling to room temperature, the reaction mixture was treated with diluted HCl to precipitate the product. The green solid was centrifuged and washed several times successively with water, hot methanol, hot ethanol, ethyl acetate, acetone and diethyl ether, and dried in vacuo. It is soluble in DMF, DMSO and pyridine. Yield: 0.051 g (48%). M.p. >300 °C. FT-IR (KBr), $\nu_{\text{max}}/(\text{cm}^{-1})$: 3410 (carboxylic acid OH),

3065–3030 (Ar–CH), 2924–2876 (aliphatic CH), 1709 (C=O), 1605–1439 (Ar C=C), 1250 (Ar–O–Ar). UV–Vis λ_{\max} (nm) (log ϵ) in DMF: 299 (5.01), 321 (5.01), 454 (4.29), 597 (4.58), 659 (4.87). MS (MALDI-TOF, DHB as matrix): m/z 1309.15 [M]⁺, 1310.24 [M+1]⁺, 1311.36 [M+2]⁺, 1312.41 [M+3]⁺, 1381.04 [M+4H₂O]⁺. Anal. Calc. for C₆₄H₃₆N₈Cl₄O₁₂Co: C, 58.67; H, 2.75; N, 8.56. Found: C, 58.93; H, 2.68; N, 8.51%.

2.2.5. Sodium salt of zinc metallo phthalocyanine (5)

Zinc metallo phthalocyanine (3) (0.02 g, 0.015 mmol) was dissolved in aqueous sodium hydroxide solution (5 cm³, 2 M), heated until boiling, and cooled to the room temperature. Finally the solution was poured into ethanol to precipitate the product. The resulting mixture was centrifuged and the precipitate collected. After washing with ethanol and acetone, the sodium salt of carboxylated zinc metallo phthalocyanine was dried in vacuo. It is soluble in water. Yield: 0.017 g (80%). M.p. >300 °C. FT-IR (KBr), ν_{\max} (cm⁻¹): 3441, 3001, 1647, 1566, 1501, 1450, 1412, 1246, 1204. UV–Vis λ_{\max} (nm) (log ϵ) in water: 280 (4.62), 332 (4.62), 609 (4.45). UV–Vis λ_{\max} (nm) (log ϵ) in water/EtOH (1/1): 280 (4.20), 341 (4.36), 628 (4.30), 658 (4.22).

2.2.6. 2,9,16,23-Tetra(chloro)-3,10,17,24-tetra(ferrocenylmethyl 4-phenyloxyacetate)-phthalocyaninatozinc(II) (6)

Zinc metallo phthalocyanine (3) (0.075 g, 0.057 mmol) was dissolved in thionylchloride (2 cm³) and refluxed for 4 h. At the end of the reaction, thionylchloride was removed under reduced pressure. The resulting solid was dissolved in 2 cm³ of freshly distilled DMF. Hydroxymethylferrocene (0.062 g, 0.287 mmol) was dissolved in dry DMF (1 cm³) and dropped into acid chloride at 0 °C. Triethylamine (0.5 cm³) was added under continuous stirring and the mixture was allowed to react for 24 h at room temperature. The resulting solution was treated with methanol to precipitate the product. The green solid was centrifuged and washed several times successively with water, hot methanol, hot ethanol, ethyl acetate, acetone and diethyl ether, and dried in vacuo. It is soluble in DMF, DMSO and pyridine. Yield: 0.082 g (68%). M.p. >300 °C. FT-IR (KBr), ν_{\max} (cm⁻¹): 3064–3030 (Ar–CH), 2930–2910 (aliphatic CH), 1723 (C=O), 1647–1431 (Ar C=C), 1243 (Ar–O–Ar). ¹H NMR (d-DMSO 400 MHz): 7.68–7.08 (br, 24H, Ar–H), 5.20 (s, 8H, ferrocene-CH₂), 3.75 (s, 8H, CH₂COOH), 4.31 (m, 16H, ferrocene), 4.14 (m, 20H, ferrocene). UV–Vis λ_{\max} (nm) (log ϵ) in DMF: 317 (4.67), 609 (4.04), 681 (4.62). MS (MALDI-TOF, DHB as matrix): m/z 2107.06 [M]⁺, 2108.36 [M+1]⁺. Anal. Calc. for C₁₀₈H₇₆N₈Cl₄O₁₂ZnFe₄: C, 61.51; H, 3.61; N, 5.32. Found: C, 61.64; H, 3.18; N, 5.35%.

2.2.7. 2,9,16,23-Tetra(chloro)-3,10,17,24-tetra(ferrocenylmethyl 4-phenyloxyacetate)-phthalocyaninatocobalt(II) (7)

Cobalt metallo phthalocyanine (4) (0.075 g, 0.057 mmol) was dissolved in thionylchloride (2 cm³) and refluxed for 4 h. At the end of the reaction, thionylchloride was removed under reduced pressure. The resulting solid was dissolved in 2 cm³ of freshly distilled DMF. Hydroxymethylferrocene (0.062 g, 0.287 mmol) was dissolved in dry DMF (1 cm³) and dropped into acid chloride at 0 °C. Triethylamine (0.5 cm³) was added under continuous stirring and the mixture was allowed to react for 24 h at room temperature. The resulting solution was treated with methanol to precipitate the product. The green solid was centrifuged and washed several times successively with water, hot methanol, hot ethanol, ethyl acetate, acetone and diethyl ether, and dried in vacuo. It is soluble in DMF, DMSO and pyridine. Yield: 0.044 g (36.6%). M.p. >300 °C. FT-IR (KBr), ν_{\max} (cm⁻¹): 3070–3055 (Ar–CH), 2936–2915 (aliphatic CH), 1719 (C=O), 1641–1435 (Ar C=C), 1249 (Ar–O–Ar). UV–Vis λ_{\max} (nm) (log ϵ) in DMF: 327 (5.11), 465 (4.47), 599 (4.33), 662 (4.78). MS (MALDI-TOF, DHB as matrix): m/z

2101.54 [M]⁺, 2102.23 [M+1]⁺. Anal. Calc. for C₁₀₈H₇₆N₈Cl₄O₁₂-CoFe₄: C, 61.68; H, 3.62; N, 5.33. Found: C, 61.75; H, 3.68; N, 5.78%.

2.2.8. 4-Hexylthio-5-(4-phenyloxyacetic acid)phthalonitrile (8)

4-Chloro-5-(4-phenyloxyacetic acid)phthalonitrile (1) (1.00 g, 3.20 mmol) and *n*-hexanethiol (0.46 cm³, 3.20 mmol) were dissolved in dry DMF (20 cm³). After stirring for 10 min, anhydrous K₂CO₃ (0.4416 g, 3.20 mmol) was added portion wise during 15 min with efficient stirring. The reaction mixture was stirred under N₂ atmosphere at room temperature for 7 days. Then the mixture was poured into 100 cm³ ice–water. The resulting creamy solid was collected by filtration and washed with water until the washings were neutral. After drying in vacuo at 50 °C, the crude product was purified by column chromatography with chloroform. The compound is soluble in CHCl₃, CH₂Cl₂, THF, methanol and acetone. Yield: 0.160 g (12.7%). M.p. 106–108 °C. FT-IR (KBr), ν_{\max} (cm⁻¹): 3092–3038 (Ar–CH), 2965–2864 (aliphatic CH), 2237 (C≡N), 1709 (C=O), 1578–1483 (Ar C=C), 1252 (Ar–O–Ar). ¹H NMR (d-DMSO 400 MHz): 12.28 (s, 1H, COOH), 8.04 (s, 1H, Ar–H), 7.36 (s, 1H, Ar–H), 7.33 (dd, 2H, J = 8 Hz, Ar–H), 7.03 (dd, 2H, J = 8 Hz, Ar–H), 3.58 (s, 2H, –CH₂COOH), 3.11 (t, 2H, J = 6 Hz, –SCH₂R), 1.62 (m, 2H, –SCCH₂R), 1.40 (m, 2H, –SCCCH₂R), 1.25 (m, 4H, –SCCCH₂CH₂CH₃), 0.86 (t, 3H, J = 6 Hz, –SCCCH₂CH₃). UV–Vis λ_{\max} (nm) (log ϵ) in DMF: 313 (4.19). MS (MALDI-TOF, DHB as matrix): m/z 416.993 [M+Na]⁺, 432.968 [M+K]⁺, 466.108 [M+4H₂O]⁺.

2.2.9. 2,9,16,23-Tetra(hexylthio)-3,10,17,24-tetra(4-phenyloxyacetic acid)-phthalocyaninatozinc (II) (9)

A mixture of compound 8 (0.100 g, 0.253 mmol), Zn(AcO)₂·2H₂O (0.0139 g, 0.063 mmol) and dry 2-(dimethylamino)ethanol (1.5 cm³) was heated and stirred at 160 °C in a sealed glass tube for 24 h under N₂ atmosphere. After cooling to room temperature, diluted HCl was added in order to precipitate the product. The green solid was centrifuged and washed with water until the washings were neutral. It was dissolved in THF and precipitated with chloroform. The product was washed several times with chloroform. It is soluble in methanol, ethylacetate, THF, acetone, DMF and DMSO. Yield: 0.026 g (27%). M.p. >300 °C. FT-IR (KBr), ν_{\max} (cm⁻¹): 3404 (carboxylic acid OH), 3067–3028 (Ar–CH), 2924–2857 (aliphatic CH), 1734 (C=O), 1599–1383 (Ar C=C), 1238 (Ar–O–Ar). ¹H NMR (d-DMSO 400 MHz): 12.03 (br, s, 4H, COOH), 8.20–7.03 (br, 24H, Ar–H), 3.61 (s, 8H, –CH₂COOH), 2.94 (m, 8H, –SCH₂R), 1.60–1.19 (m, 32H, –SC(CH₂)₄CH₃), 0.81 (m, 12H, –SCCCH₂CH₃). UV–Vis λ_{\max} (nm) (log ϵ) in DMF: 356 (4.34), 616 (3.92), 686 (4.61). MS (MALDI-TOF, DHB as matrix): m/z 1641.24 [M]⁺, 1642.35 [M+1]⁺, 1643.20 [M+2]⁺, 1666.26 [M+Na]⁺. Anal. Calc. for C₈₈H₈₈N₈O₁₂S₄Zn: C, 64.35; H, 5.36; N, 6.83. Found: C, 64.31; H, 5.41; N, 6.87%.

3. Results and discussion

The precursor material chosen for the synthesis of substituted pcs with four chloro and four phenyloxyacetic acid substituents on the periphery is 4-chloro-5-(4-phenyloxyacetic acid)phthalonitrile (1). It was synthesized from 4,5-dichlorophthalonitrile by displacement of the one chloro group by the phenolic –OH function of the 4-hydroxyphenylacetic acid in DMF at room temperature. In a study, when K₂CO₃ was used as a base, the chloro groups were only partially substituted. However, in the case of Na₂CO₃, both of the chloro groups were substituted [18,31]. In this study, accordingly the corresponding compound was obtained when either of these carbonates was used and the composition and structure of the singly substituted phthalonitrile derivative is consistent with all analytical results. The usual synthetic routes were applied to obtain the metal-free pc (2) and the metallo pcs (3 and 4). Conver-

sion of **1** into the metal-free pc **2** is accomplished in a mixture of 1, 2-dichlorobenzene and hexanole in the presence of lithium. Dilithium pcs are labile towards water and acids, and can easily be converted to the metal-free pc (**2**). The metallo pcs [M: Zn (**3**) and M: Co (**4**)] were synthesized directly by cyclotetramerization of the corresponding dicyano compound **1** in the presence of metal salts [Zn(AcO)₂·2H₂O and Co(AcO)₂·4H₂O] in DMF. Sodium salt of zinc pc (**5**) was obtained by heating **3** in diluted NaOH. Pcs (**2–4**) are soluble in DMF, DMSO, pyridine and water (at pH>7). The series of reactions are outlined in Scheme 1. Further reactions of 4-phenyloxyacetic acid substituted phthalocyanines (**3** and **4**) first with thionylchloride and then hydroxymethylferrocene in DMF gave ferrocenyl substituted phthalocyanines (**6** and **7**) (Scheme 2). Ferrocenyl substituted pcs (**6** and **7**) are slightly soluble in DMF and DMSO.

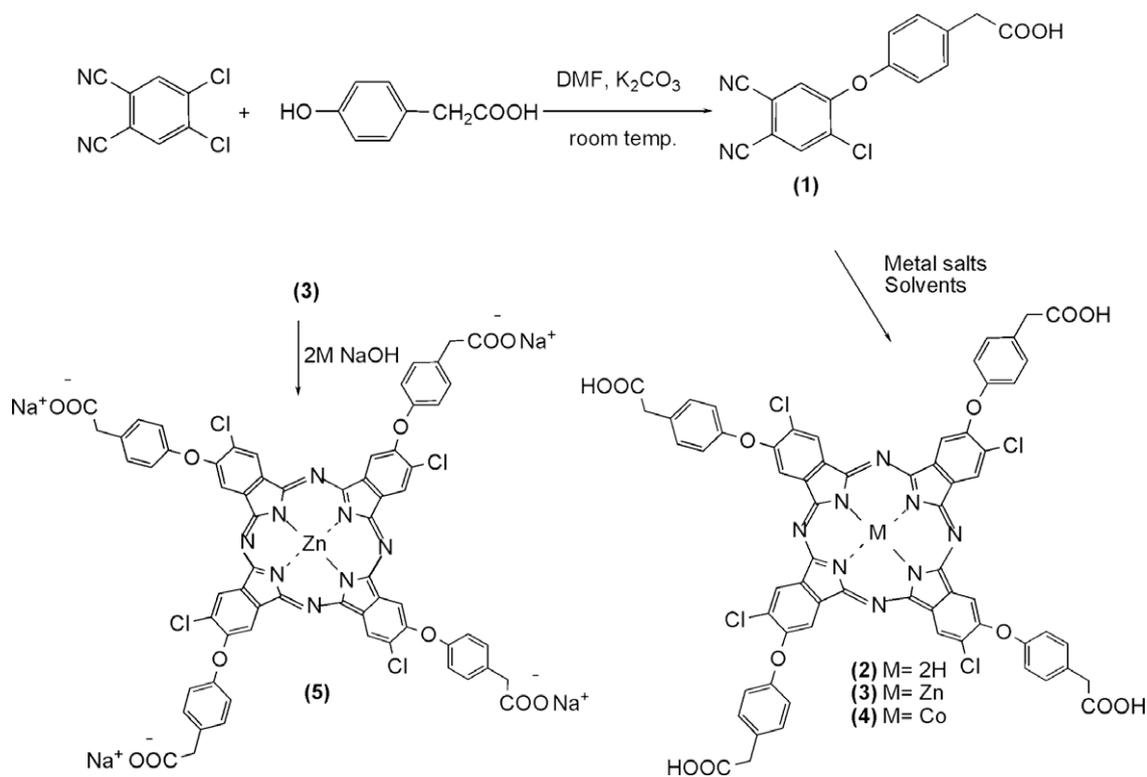
Compound **1** was reacted with *n*-hexanethiol in presence of a base (K₂CO₃) in anhydrous DMF at room temperature for seven days to give 4-hexylthio-5-(4-phenyloxyacetic acid)phthalonitrile (**8**). In this reaction, the long reaction times were necessary for good yield. Cyclotetramerization of this new asymmetrically disubstituted phthalonitrile derivative **8** into zinc metallo pc (**9**) was accomplished by reaction with Zn(AcO)₂·2H₂O in anhydrous 2-(dimethylamino)ethanol (Scheme 3). The most obvious feature of the zinc metallo pc (**9**), when compared with that of the 1-chloro-3,4-dicyano-6-(4-phenyloxyacetic acid)benzene substituted analog (**2–4**) is its extensive solubility in common organic solvents (e.g. methanol, ethylacetate, acetone, THF, DMF, DMSO). The structure of each compound was elucidated using elemental analysis, FT-IR, ¹H NMR, UV-Vis and MALDI-TOF methods. All the analytical and spectral data were consistent with predicted structures.

The IR spectrum of **1**, peaks around 1709 cm⁻¹ indicate the presence of C=O group and the band at 3449 cm⁻¹ corresponds to -OH of the COOH group. In addition, the characteristic vibrations of the C≡N appear at 2226 cm⁻¹. After conversion of the

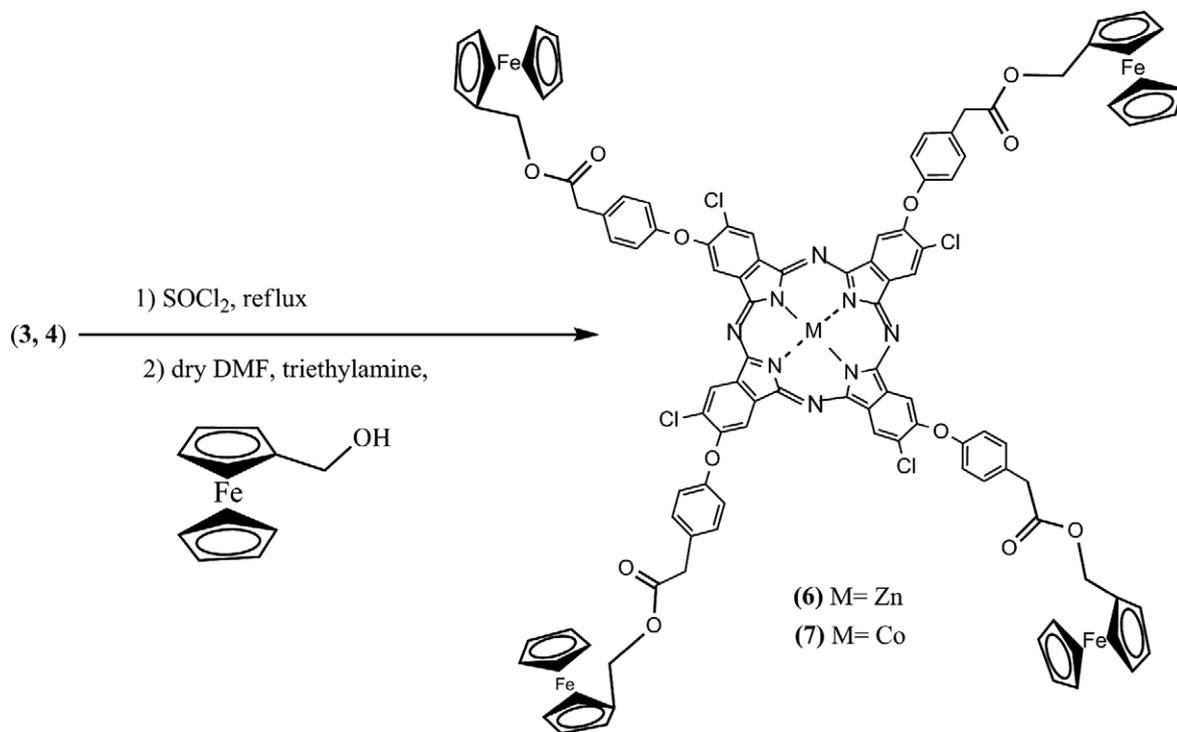
dinitrile derivative (**1**) into pcs (**2–4**), the sharp peak for the C≡N vibrations disappeared. The NH group of the metal-free pc (**2**) in the inner core gave a weak absorption peak at 3283 cm⁻¹. In the IR spectra, C-H stretching vibrations of aliphatic and ferrocene methylene groups and C=O vibration of ester appear at ca. 2930–2910, 1723 cm⁻¹ for **6** and 2936–2915, 1719 cm⁻¹ for **7**, respectively. In the ¹H NMR analysis of **1** in d-DMSO, the carboxylic acid proton appear as a singlet at δ 12.40 ppm, the aromatic protons of phenyloxy group as doublet of doublet at δ 7.38 and 7.13 ppm. The aromatic proton ortho to chloro group appears as a singlet at δ 7.65 ppm and the other aromatic proton ortho to phenyloxy group as a singlet at δ 8.57 ppm. The ¹H NMR spectra of the pcs are rather broad, owing probably to the aggregation of the pcs which is frequently encountered at the concentrations used for NMR spectroscopy. The ¹H NMR spectrum of **3** indicates carboxylic acid protons at δ 12.34 ppm as a broad singlet, aromatic protons at δ 8.11–7.08 ppm as broad and aliphatic protons (CH₂) δ 3.70 ppm as a singlet. When going from **3** to **6**, chemical shifts for the ferrocene groups emerge at δ 4.31 and 4.14 ppm as multiplets.

The MALDI-TOF mass spectra of **2**, **3**, **4**, **6** and **7** confirmed the proposed structures; molecular ions were easily identified at *m/z*: 1252 [M]⁺ for **2**, at *m/z*: 1315 [M]⁺ for **3** (Fig. 1), at *m/z*: 1309 [M]⁺ for **4**, at *m/z*: 2107 [M]⁺ for **6** and at *m/z*: 2101 [M]⁺ for **7**.

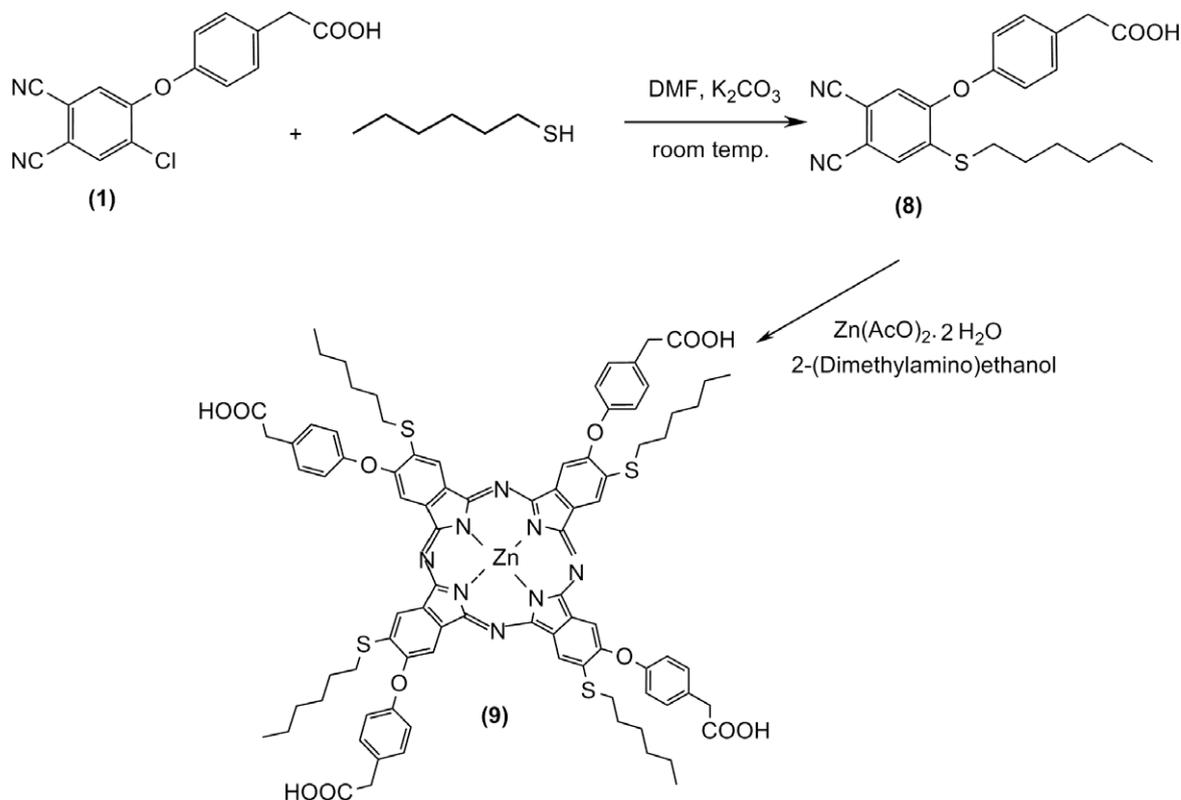
Comparison of the IR spectra of **1** and **8** gave some hints the nature of the products. The IR spectrum of **8** clearly indicates the presence of the alkylsulfanyl substituent by the intense stretching bands at 2965–2864 cm⁻¹ (aliphatic C-H). In addition, the characteristic vibrations of the C≡N appear at 2237 cm⁻¹. In the ¹H NMR analysis of **8** in d-DMSO, the carboxylic acid proton appear as a singlet at δ 12.28 ppm, the aromatic protons of phenyloxy group as a doublet of doublet at δ 7.33 and 7.03 ppm. The aromatic protons ortho to the cyano group appear as two singlets at δ 8.04 and 7.36 ppm. The aliphatic CH₃ protons appear as triplet at δ 0.86 ppm, the -SCH₂ protons as triplet at δ 3.11 ppm, and the -CCH₂C- in the long chain as multiplets at the range of δ 1.25–



Scheme 1. Synthetic pathway of 4-chloro-5-(4-phenyloxyacetic acid)phthalonitrile (**1**) and phthalocyanines (**2–5**).



Scheme 2. Synthesis of ferrocenyl substituted phthalocyanines (6 and 7).



Scheme 3. Chemical structure and synthesis of 4-hexylthio-5-(4-phenyloxyacetic acid)phthalonitrile (8), zinc metallo phthalocyanine (9).

1.62 ppm. The ^1H NMR spectrum of **9** indicates the carboxylic acid protons at δ 12.03 ppm as a broad singlet, the aromatic protons at δ 8.20–7.03 ppm as broad, the $-\text{SCH}_2$ protons at δ 2.94 ppm as multiplet, the $-\text{SC}(\text{CH}_2)_4\text{C}-$ protons in the long chain at δ 1.60–1.19 ppm as multiplet and the $-\text{CH}_3$ protons at the end of the chain

at δ 0.85 ppm as multiplet. The MALDI-TOF mass spectra of zinc pc (**9**) confirmed the proposed structure; molecular ion was easily identified at m/z : 1641 $[\text{M}]^+$.

The ground state electronic spectra of the complexes showed characteristic absorption in the Q band region at 697 and 663 nm

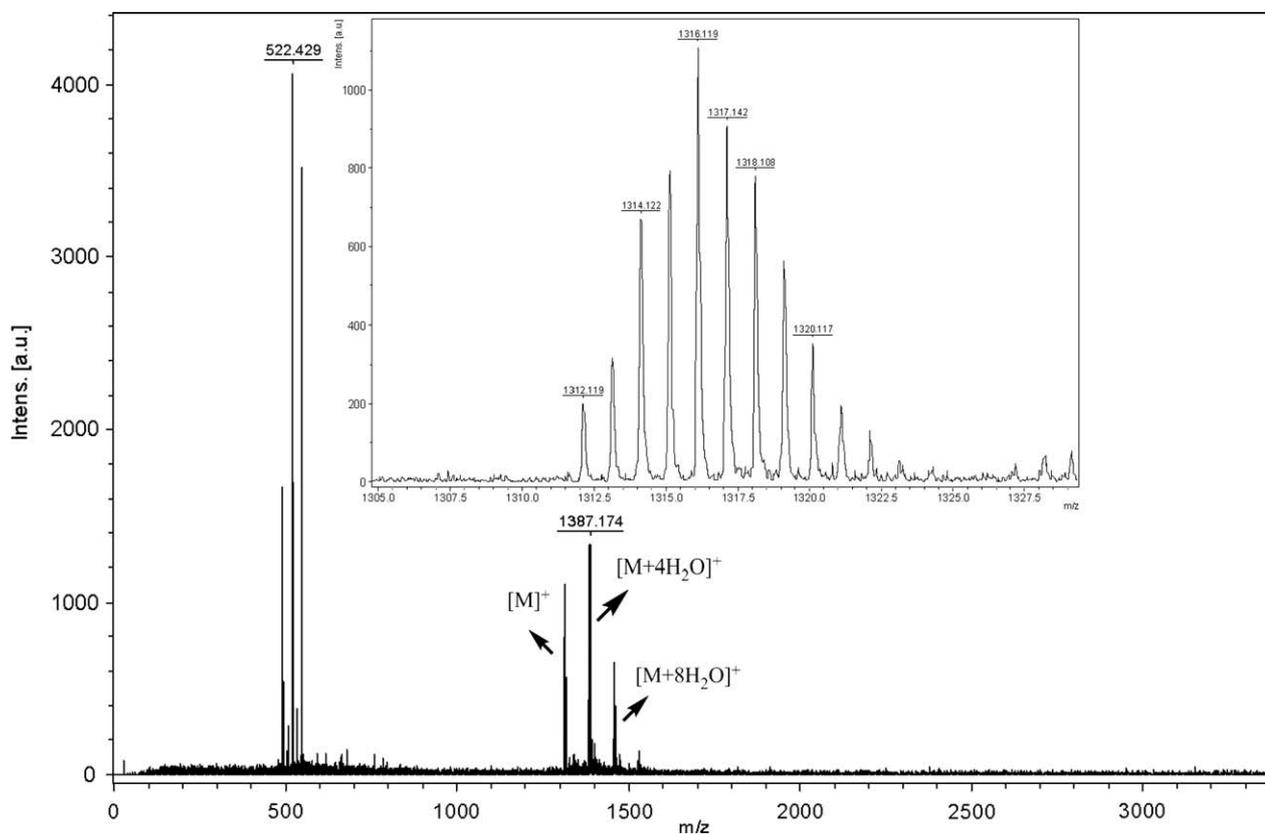


Fig. 1. Mass spectrum of **3**.

for **2**, 677 nm for **3**, 659 nm for **4**, 681 nm for **6**, 662 nm for **7** and 686 nm for **9**. The B band region was observed around 320–356 nm (Fig. 2). The spectra showed monomeric behavior evidenced by a single Q band, typical of metalated pc complexes for **3**, **4**, **6**, **7** and **9** in DMF which depict the monomeric nature of these complexes. The metal-free pc **2** gave doublet Q band as a result of the D_{2h} symmetry. It was found that the Q band of zinc metallo pc **3** is red shifted (18 nm) as compared with that of cobalt metallo pc **4** in DMF. Compared with the corresponding phthalocyanines **3**, **4**, the absorption maxima of **6**, **7** are bathochromically shifted by about 3 nm (Fig. 3). It is possible to suggest that the ferrocenyl group is electronically independent in compound **3** and **4**. When compared with phenyloxyacetic acid and chloro substituted zinc metallo pc (**3**), substitution of chloro group with alkylsulfanyl moiety leads to a shift of 9 nm to longer wavelength (Fig. 3). In this

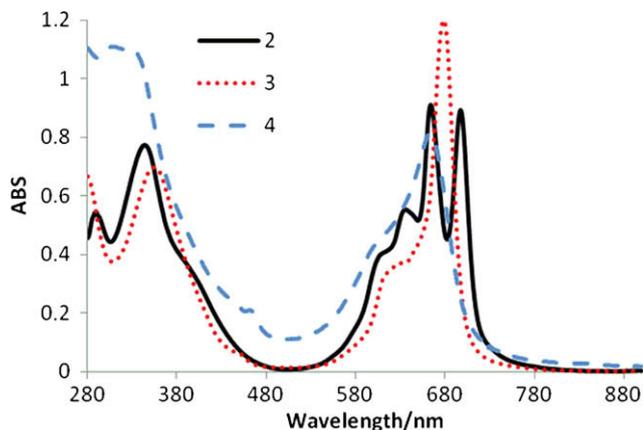


Fig. 2. Absorption spectra of the compounds **2** (in THF), **3** (in DMF) and **4** (in DMF).

study, the aggregation behavior of the metal-free pc **2** is investigated in THF, DMF and DMSO. While compound **2** did not showed an aggregation in THF, it showed aggregation in DMF and DMSO as judged by a blue shift of the Q band [32] (Fig. 4). In general, DMSO and DMF are strong coordinating solvents since they are known as the aggregation preventing solvents. However, compound **2** showed aggregation in these solvents and the same effect has been observed in the literature [33]. The aggregation behavior of the pc **2** was also investigated at different concentrations in THF. In THF, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands due to the aggregated species.

In order to improve the solubility of pcs in water, four hydrophilic carboxylic acid groups at the periphery of the ring structure was introduced. The sodium salt of carboxyl substituted pc (**5**) is

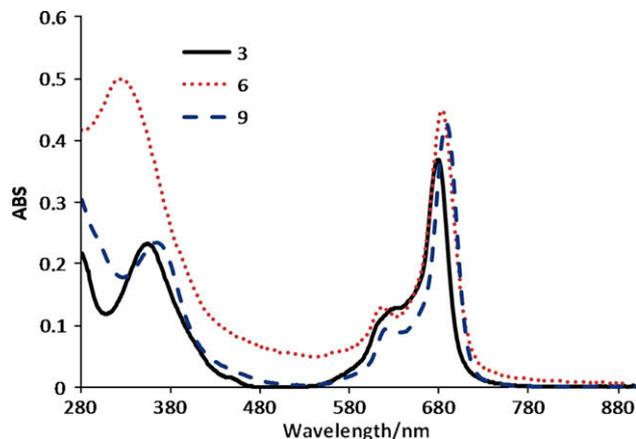


Fig. 3. Absorption spectra of the compounds **3**, **6** and **9** in DMF.

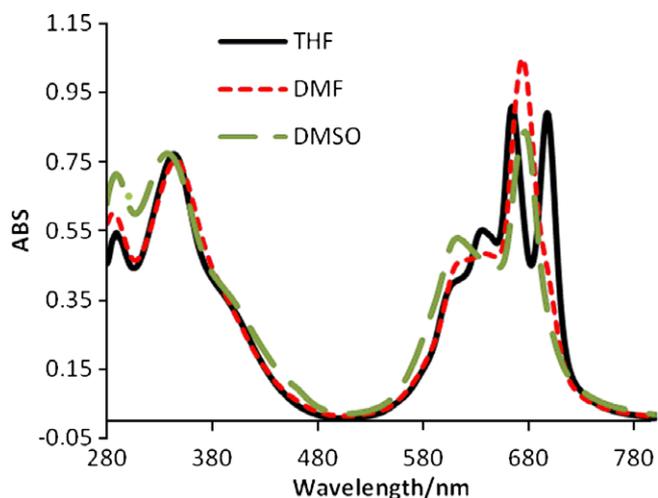


Fig. 4. Absorption spectra of the compound 2 in different solvents.

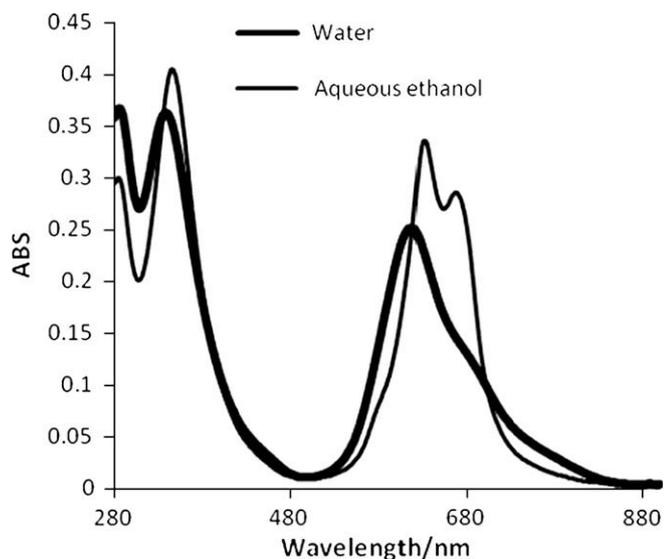


Fig. 5. Absorption spectra of 5. Thick line: in water; thin line: in aqueous ethanol solution ($v/v = 1/1$).

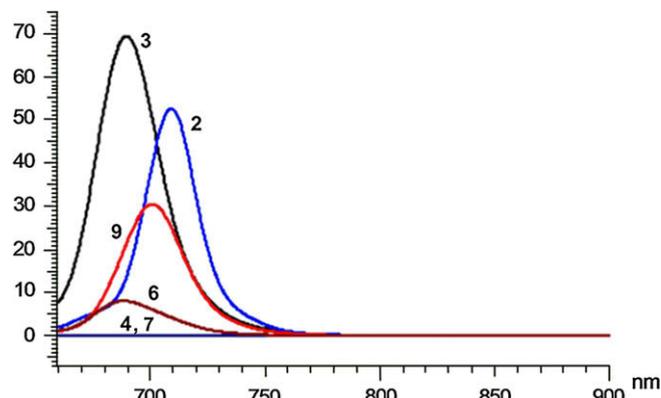


Fig. 6. Emission spectra of 2, 3, 4, 6, 7 and 9 in DMF. Excitation wavelength = 630 nm for 2; 615 nm for 3, 602 nm for 4, 609 nm for 6, 599 nm for 7 and 616 nm for 9.

Table 1
Absorption, excitation and emission spectral data for phthalocyanines 2, 3, 4 and 9.

Compound	Q band λ_{\max} (nm)	Log ϵ	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift $\Delta\lambda_{\text{Stokes}}$ (nm)
2	697, 663	4.63, 4.64	703, 670	709	12
3	677	4.54	684	690	13
4	659	4.87	–	–	–
9	686	4.61	694	701	15

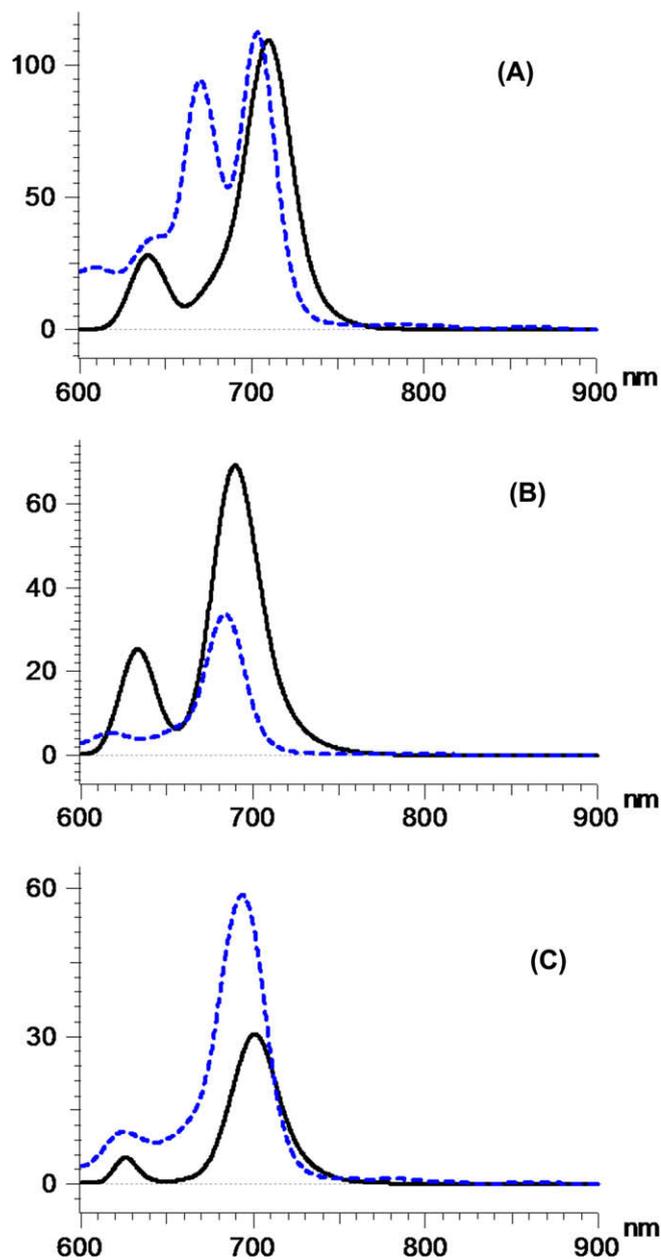


Fig. 7. Fluorescence emission and excitation spectra of 2 in THF. Excitation wavelength = 630 nm (A); fluorescence emission and excitation spectra of 3 in DMF. Excitation wavelength = 615 nm (B); fluorescence emission and excitation spectra of 9 in DMF. Excitation wavelength = 616 nm (C).

soluble in water. However, the absorption band in water and that in aqueous solution differs because aggregation takes place in water [11,34], which makes the Q band blue shifted due to the exciton coupling effectively raising the energy level of the excited state [3]. With addition of ethanol to the aqueous solution, disaggregation takes place as shown in Fig. 5.

Fig. 6 shows the fluorescence emission spectra for compounds **2**, **3**, **4**, **6**, **7** and **9**. While the pcs **2**, **3**, **6** and **9** are fluorescent, the pcs **4** and **7** do not show fluorescence at excitation wavelength. The pcs **2**, **3** and **9** showed similar fluorescence behavior in DMF. In DMF, emission peaks were observed at 709 nm (**2**), 690 nm (**3**) and 701 nm (**9**) (Table 1). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescence spectra [35] (Fig. 7). In contrast to absorption properties, fluorescence properties of the phenyloxyacetic acid substituted pc (**3**) is strongly affected by the presence of ferrocenyl substituents. Pc **3** possesses high fluorescence intensity, while the ferrocene-substituted pc **6** is poor fluorescent intensity. In fact, it has been reported that covalently linked ferrocenes substantially quenched the fluorescence emission of other chromophores, for example; porphyrins, through an intramolecular electron-transfer process [36,37]. The proximity of wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for pcs **2**, **3** and **9** suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMF. The observed Stokes shifts (Table 1) were typical of pc complexes in DMF.

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