

Synthesis and characterization of new metal-free and metallophthalocyanines fused α -methylferrocenylmethoxy units

Ahmet Bilgin · Çiğdem Yağcı · Ayşegül Mendi ·
Ufuk Yıldız

Received: 12 October 2009 / Accepted: 3 December 2009 / Published online: 18 December 2009
© Springer Science+Business Media B.V. 2009

Abstract Synthesis of metal-free and metallophthalocyanines bearing α -methylferrocenylmethoxy units was described. Precursor **3** required for the preparation of phthalocyanines **4–9**, was synthesized by the nucleophilic aromatic substitution reaction between α -methylferrocenylmethanol and 4-nitrophthalonitrile in dry DMF. The metal-free phthalocyanine **4** was prepared from 4-(α -methylferrocenylmethoxy)phthalonitrile **3** in 1-pentanol with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Metallophthalocyanines (M = Zn, Cu, Co, Ni and Pb) were prepared by cyclotetramerization reaction of phthalonitrile with appropriate materials. The phthalonitrile, metal-free and metallophthalocyanines were characterized by ^1H and ^{13}C NMR, FT-IR UV–Vis and mass spectral data, as well as elemental analyses, which were consistent with the proposed structures.

Keywords Phthalonitrile · Ferrocene · Metallophthalocyanine · Metal-free phthalocyanine

Introduction

Phthalocyanines (Pcs) and their metal complexes (MPcs) have attracted considerable interest and have been found to be highly promising candidates for a variety of uses such as liquid crystals [1, 2], photosensitizers [3–5], semiconductors,

electron transfer and in various chemical sensing applications [6–9]. Pcs are compounds of special interest for their unique redox [10] and photophysical properties.

Studies of electronic interactions in systems containing multiple redox-active centers are of fundamental importance in the development of molecular-based electronic devices [11, 12]. Owing to the high stability, ease of functionalization, and well-defined electrochemistry, ferrocene has been widely used as the redox-active centers which are linked together with a wide variety of structural units such as saturated and unsaturated carbon bridges, delocalized fused rings [13], and polymeric and dendritic backbones [14–17]. Although different extents of metal–metal interactions have been revealed for some of these systems, examples showing electronic coupling between the ferrocenyl units through a two-dimensional π system are extremely rare [18, 19]. Several phthalocyanine derivatives incorporated with ferrocenyl groups have been reported [20–26].

We lately outlined a concept for the synthesis of a new type of monomeric and polymeric phthalocyanine with various functional groups. These phthalocyanines have N-, O- and S-containing functionalities such as diazadioxo, cylindrical and spherical macrotricycles, crown ether fused diloop, diazadithia macrocyclic with *tert*-butyl [27–31].

In the present paper we have synthesized and characterized novel metal-free and metallophthalocyanines from a phthalonitrile derivative containing α -methylferrocenylmethoxy unit.

Experimental

Materials and instrumentation

Phosphorus pentoxide (P_2O_5), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), ethanol, 1-pentanol, dimethylformamide (DMF),

A. Bilgin (✉) · Ç. Yağcı
Department of Science Education, Kocaeli University,
41380 Kocaeli, Turkey
e-mail: abilgin@kocaeli.edu.tr

A. Mendi · U. Yıldız
Department of Chemistry, Kocaeli University, 41380 Kocaeli,
Turkey

tetrahydrofuran (THF), toluene, chloroform, dichloromethane, quinoline, hydrochloric acid, acetone, silica gel, neutral alumina, ammonia, MgSO_4 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, yellow PbO were received from Merck and used as supplied. Potassium carbonate (K_2CO_3) was received from Merck and used after drying in oven at 250 °C for 36 h. All organic solvents were dried and purified by usual methods. α -Methylferrocenemethanol [32] and 4-nitrophthalonitrile [33] were prepared by published procedures.

Melting points of the compounds were determined with an electrothermal melting point apparatus and were uncorrected. ^1H -NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer with CDCl_3 and $\text{DMSO}-d_6$ as solvents and tetramethylsilane as an internal standard. ^{13}C -NMR spectra were recorded on a Varian Mercury 50 MHz spectrometer with CDCl_3 as the solvent and tetramethylsilane as an internal standard. Transmission IR spectra of samples were recorded on a FT-IR spectrophotometer (Shimadzu FT-IR-8201 PC); solid substances were ground with KBr and pressed to pellets. UV-Vis spectra were recorded on a Shimadzu 1601 UV-Vis spectrometer using a 1 cm quartz cell at room temperature. Mass spectra were measured on Micromass Quatro LC/ULTIMA LC-MS spectrometer. The elemental analysis of the compounds was determined on a CHNS-932 LECO instrument. The metal contents of the metallophthalocyanine were determined with a Unicam 929 AA spectrophotometer.

Preparation of 4-(α -methylferrocenylmethoxy)phthalonitrile (**3**)

A mixture of α -methylferrocenemethanol **1** (1.19 g, 5.0 mmol) and 4-nitrophthalonitrile **2** (0.437 g, 2.5 mmol) in dry DMF (6 mL) was dissolved in a 100 mL three-necked flask and stirred at room temperature under inert nitrogen atmosphere and degassed three times. Then temperature was increased up to 70 °C. Finely powdered dry K_2CO_3 (1.73 g, 12.5 mmol) was added to the solution in eight equal portions at 45 min intervals with efficient stirring and the reaction mixture was stirred at 70 °C for 3 days. The reaction was monitored by a thin layer chromatography [CHCl_3 -MeOH (9:1)]. At the end of this period, the mixture was cooled and poured into 5% ice-HCl (100 mL) solution and mixed for 2 h. Precipitate was filtered and solution part was taken and extracted with chloroform (6 \times 50 mL). After drying over MgSO_4 , solvent was evaporated under reduced pressure to yield a viscous brown residue. The viscous brown residue and the solid part were combined and chromatographed using (silica gel, 9:1 chloroform:methanol) to give compound **3**. The compound **3** was isolated as brown crystals after recrystallized from ethanol and dried under vacuum over

P_2O_5 . R_f : 0.33 (silica gel, 9:1 chloroform:methanol) Yield: 0.7 g (78%), m.p.: 169–173 °C (dec.).

Anal. calc. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{OFe}$ (356.21): C, 67.44; H, 4.53; Fe, 15.68; N, 7.86%. Found C, 67.23; H, 4.72; Fe, 15.45; N, 7.64. FT-IR (KBr): 3103, 3078, 3042, 2980–2872 ($-\text{CH}_2-$), 2234 ($\text{C}\equiv\text{N}$), 1589, 1568, 1530, 1485, 1307, 1282, 1252 ($\text{CHO}-\text{Ar}$), 966, 851, 526, 495 cm^{-1} . ^1H NMR (CDCl_3): δ = 7.78 (d, 1H, Ar-H), 7.65 (d, 1H, Ar-H), 7.43 (dd, 1H, Ar-H), 4.82 (q, 1H, CHOAr), 4.26 (t, 2H, Cp), 4.16 (s, 5H, Cp), 4.07 (t, 2H, Cp), 1.47 (d, 3H, CH_3). ^{13}C NMR (CDCl_3): δ = 161.4, 135.1, 124.6, 117.3, 116.4, 115.7, 113.4, 106.9, 84.2, 71.1, 69.2, 69.0, 68.3, 27.9 (CH_3). MS (ES^+) m/z : 356.3 [M] $^+$.

Preparation of the metal-free phthalocyanine (**4**)

A mixture of **3** (0.178 g, 0.5 mmol), 1-pentanol (1.0 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) was placed in a standard Schlenk tube under nitrogen atmosphere and degassed three times. Then temperature was increased up to 160 °C. The reaction system was stirred at 160 °C for 12 h. After the reaction mixture was cooled to room temperature, 10 mL ethyl alcohol was added and mixed for half an hour. Precipitate was filtered and washed with cold acetone. The crude residue was purified by column chromatography (eluant: CHCl_3/THF , 100:1) and gave **4** as a dark green solid and dried under vacuum over P_2O_5 . Yield: 0.12 g (67.3%), m.p.: >300 °C.

Anal. calc. for $\text{C}_{80}\text{H}_{66}\text{N}_8\text{O}_4\text{Fe}_4$ (1426.84): C, 67.34; H, 4.66; N, 7.85; Fe, 15.66%. Found C, 67.59; H, 4.82; N, 7.56; Fe, 15.82. FT-IR (KBr): 3245 (N-H), 3104, 3060, 3040, 2926–2855 ($-\text{CH}_2-$), 1628 ($\text{C}=\text{N}$), 1568, 1549, 1510, 1460, 1321, 1263, 1225 ($\text{CHO}-\text{Ar}$), 1099, 1055 (N-H), 976, 887, 826, 574, 489 cm^{-1} . ^1H NMR (CDCl_3): δ = 8.01–6.97 (m, br, 12H, Ar-H), 5.01–4.90 (m, 4H, CHOAr), 4.30–4.06 (m, 36H, Cp), 1.42 (d, 12H, CH_3), –3.90 (s, br, 2H, pyrrole). ^{13}C NMR (CDCl_3): δ = 154.1, 135.8, 125.2, 118.9, 117.2, 108.1, 85.1, 70.9, 69.4, 68.9, 68.5, 28.7 (CH_3). UV-Vis (CHCl_3): λ_{max} (log ϵ) = 691 (4.46), 659 (4.39), 630 (3.93), 605 (3.66), 418 (4.00), 355 (4.38), 318 (4.61) nm. MS (ES^+) m/z : 1426.9 [M] $^+$.

Preparation of Zn and Cu-containing phthalocyanines (**5**, **6**)

A mixture of **3** (100 mg, 0.28 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (22 mg, 0.10 mmol) or $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (22 mg, 0.10 mmol) in 1-pentanol (3 mL) was heated to 90 °C under inert nitrogen atmosphere and degassed three times, then DBU (0.01 mL, 0.07 mmol) was added. The mixture was stirred at 160 °C overnight and then poured into a mixture of methanol:water (1:1, 50 mL). The obtained precipitate was filtered off and washed with methanol, water and acetone,

respectively. The crude product was chromatographed on a neutral alumina column using CHCl_3 :THF (5:1) for **5** or CHCl_3 :MeOH (100:1) for **6** as eluent to give **5** or **6** as green powders. The final products (**5** and **6**) were dried under vacuum over P_2O_5 .

Compound (5):

Yield = 0.078 g (74.6%), m.p.: >300 °C.

Anal. calc. for $\text{C}_{80}\text{H}_{64}\text{N}_8\text{O}_4\text{Fe}_4\text{Zn}$ (1490.21): C, 64.48; H, 4.33; N, 7.52; Fe, 14.99; Zn, 4.39%. Found C, 64.27; H, 4.12; N, 7.34; Fe, 15.23; Zn, 4.57. FT-IR (KBr): 3100, 3063, 3045, 2928–2857 ($-\text{CH}_2-$), 1632 (C=N), 1584, 1558, 1510, 1489, 1373, 1261, 1229 (CHO–Ar), 1130, 957, 853, 781, 740, 636, 447 cm^{-1} . ^1H NMR (CDCl_3): δ = 8.24–7.12 (m, br, 12H, Ar–H), 4.98–4.76 (m, 4H, CHOAr), 4.32–4.01 (m, 36H, Cp), 1.54 (d, 12H, CH_3). UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 677 (4.49), 634 (3.86), 607 (3.55), 420 (3.93), 364 (4.47), 311 (4.65) nm. MS (ES^+), m/z : 1491.3 [$\text{M} + 1$] $^+$.

Compound (6):

Yield: 0.087 g (83%), m.p.: >300 °C.

Anal. calc. for $\text{C}_{80}\text{H}_{64}\text{N}_8\text{O}_4\text{Fe}_4\text{Cu}$ (1488.37): C, 64.56; H, 4.33; N, 7.53; Fe, 15.01; Cu, 4.27%. Found C, 64.75; H, 4.09; N, 7.30; Fe, 14.87; Cu, 4.49. FT-IR (KBr): 3122, 3063, 3036, 2930–2861 ($-\text{CH}_2-$), 1638 (C=N), 1597, 1572, 1446, 1363, 1269, 1227 (CHO–Ar), 1113, 981, 837, 725, 690, 619, 505 cm^{-1} . UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 673 (4.50), 627 (3.75), 610 (3.42), 414 (4.10), 375 (4.51), 332 (4.64) nm. MS (ES^+), m/z : 1488.6 [M] $^+$.

Preparation of Co and Ni containing phthalocyanines (7, 8)

A mixture of phthalonitrile compound **3** (0.10 g, 0.28 mmol), dry quinoline (1 mL) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.034 g, 0.14 mmol) or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.034 g, 0.14 mmol) was kept in a flask and degassed three times with nitrogen. The reaction mixture was refluxed at 210–220 °C for 18 h under nitrogen inert atmosphere. After refluxing, the reaction mixture was cooled and then 10 mL of ethanol was added to the system and stirred at room temperature for 0.5 h. The crude product was filtered and washed with distilled water and methanol:diethyl ether solution (1:1, 25 mL). The final products (**7** and **8**) as dark green solids were purified by passing through neutral alumina column with CH_2Cl_2 :MeOH (85:15) elution and dried under vacuum over P_2O_5 .

Compound (7):

Yield: 0.060 g (57.6%), m.p.: >300 °C.

Anal. calc. for $\text{C}_{80}\text{H}_{64}\text{N}_8\text{O}_4\text{Fe}_4\text{Co}$ (1483.76): C, 64.76; H, 4.35; N, 7.55; Fe, 15.06; Co, 3.97%. Found C, 64.51; H, 4.54; N, 7.30; Fe, 15.39; Co, 4.26. FT-IR (KBr): 3107, 3056, 3035, 2925–2864 ($-\text{CH}_2-$), 1628 (C=N), 1585, 1550, 1508, 1464, 1377, 1311, 1273, 1225 (CHO–Ar), 1130,

1065, 991, 958, 851, 781, 741, 636, 488 cm^{-1} . UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 685 (4.66), 641 (3.70), 613 (3.40), 413 (3.96), 368 (4.40), 338 (4.65) nm. MS (ES^+), m/z : 1483.9 [M] $^+$.

Compound (8):

Yield: 0.072 g (69.2%), m.p.: >300.

Anal. calc. for $\text{C}_{80}\text{H}_{64}\text{N}_8\text{O}_4\text{Fe}_4\text{Ni}$ (1483.52): C, 64.77; H, 4.35; N, 7.55; Fe, 15.06; Ni, 3.96%. Found C, 64.94; H, 4.14; N, 7.72; Fe, 14.76; Ni, 3.68. FT-IR (KBr): 3110, 3059, 3042, 2935–2867 ($-\text{CH}_2-$), 1636 (C=N), 1599, 1580, 1501, 1464, 1375, 1315, 1271, 1231 (CHO–Ar), 1120, 1094, 1063, 975, 808, 752, 692, 617, 473 cm^{-1} . ^1H NMR (CDCl_3): δ = 8.27–7.03 (m, br, 12H, Ar–H), 5.00–4.87 (m, 4H, CHOAr), 4.23–4.05 (m, 36H, Cp), 1.41 (d, 12H, CH_3). UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 681 (4.51), 636 (3.81), 606 (3.54), 410 (3.91), 366 (4.44), 327 (4.66) nm. MS (ES^+), m/z : 1484.6 [$\text{M} + 1$] $^+$.

Preparation of Pb containing phthalocyanine (9)

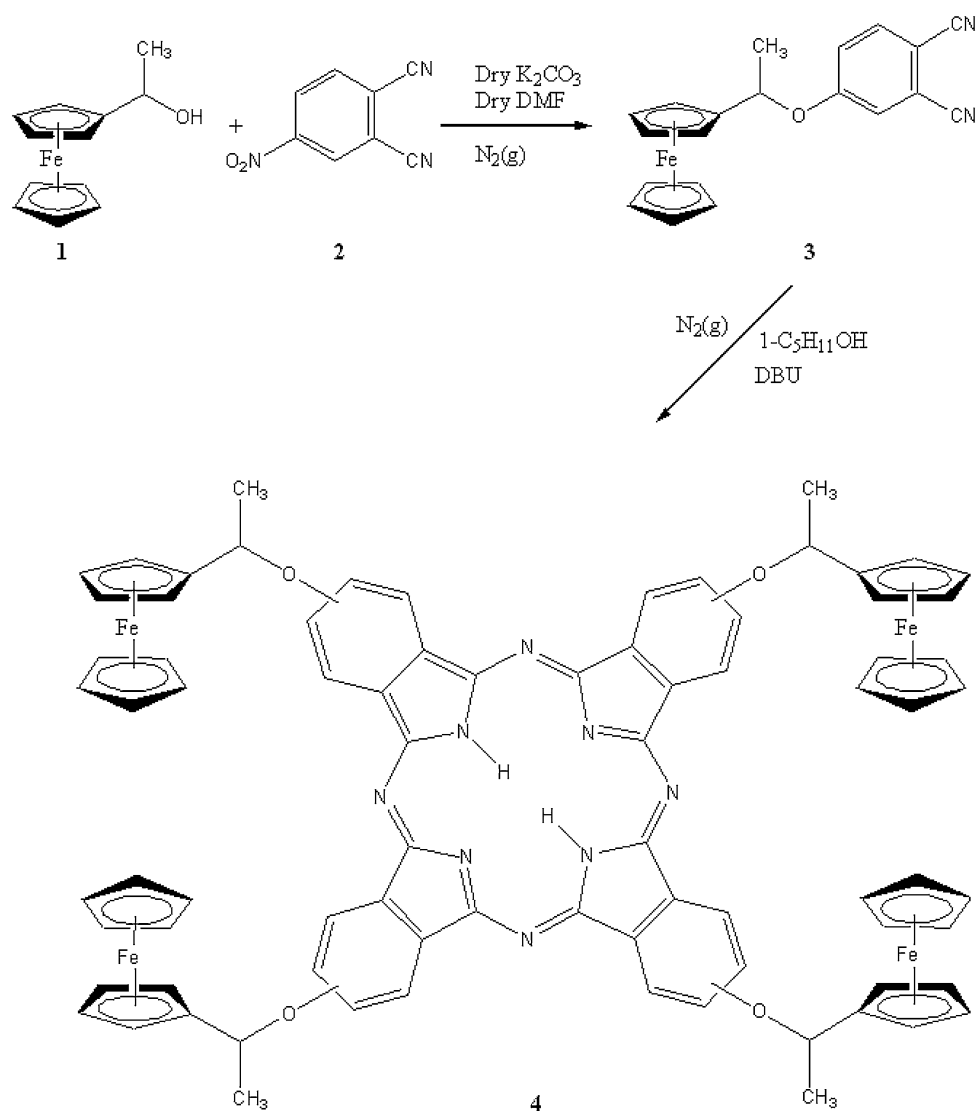
A mixture of compound **3** (0.10 g, 0.28 mmol), ethylene glycol (3 mL) and yellow PbO (0.048 g, 0.21 mmol) was charged in a standard Schlenk tube and degassed three times with nitrogen. The reaction mixture was treated at 220 °C under reflux and nitrogen inert atmosphere. After 18 h of stirring, the reaction mixture was cooled and then 10 mL of ethyl alcohol added and then filtered off. The crude product was dissolved in 10 mL of CH_2Cl_2 , filtered and purified by passing through a silica column with toluene elution. The final product was dried under vacuum over P_2O_5 to yield a green solid. Yield: 0.062 g, 54.2% m.p.: >300.

Anal. calc. for $\text{C}_{80}\text{H}_{64}\text{N}_8\text{O}_4\text{Fe}_4\text{Pb}$ (1632.03): C, 58.88; H, 3.95; N, 6.87; Fe, 13.69; Pb, 12.70%. Found C, 58.63; H, 4.21; N, 6.89; Fe, 13.97; Pb, 12.53. FT-IR (KBr): 3102, 3064, 3045, 2922–2835 ($-\text{CH}_2-$), 1630 (C=N), 1600, 1585, 1512, 1460, 1388, 1316, 1262, 1229 (CHO–Ar), 1122, 1070, 980, 829, 752, 690, 626, 424 cm^{-1} . ^1H NMR (CDCl_3): δ = 8.16–6.97 (m, br, 12H, Ar–H), 4.96–4.83 (m, 4H, CHOAr), 4.20–4.02 (m, 36H, Cp), 1.48 (d, 12H, CH_3). UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 683 (4.60), 640 (3.91), 618 (3.65), 410 (3.99), 375 (4.57), 336 (4.69) nm. MS (ES^+), m/z : 1632.2 [M] $^+$.

Results and discussion

The synthetic procedures, as outlined in Schemes 1 and 2, started with the synthesis of a precursor compound **3** with the reaction of α -methylferrocenylmethanol and 4-nitrophthalonitrile in dry DMF under alkaline condition. The self-condensation of the dicyano compound **3** in a

Scheme 1 Synthesis of phthalonitrile **3** and metal-free phthalocyanine **4**



high-boiling solvent in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under a dry nitrogen atmosphere afforded the metal-free phthalocyanine **4** in 67% yield as a green solid after purification by column chromatography on silica gel using $\text{CHCl}_3:\text{THF}$ (100:1) as eluent. Conversion of **3** into metallophthalocyanine derivatives (**5–9**) was accomplished through the usual cyclotetramerization reactions in the presence of metal salts [$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, PbO] and a suitable solvent, 1-pentanol, quinoline or ethylene glycol. The metallophthalocyanines were purified by column chromatography on silica gel or neutral alumina using appropriate eluents as the mobile phase in 54–83% yields as green or dark green solids.

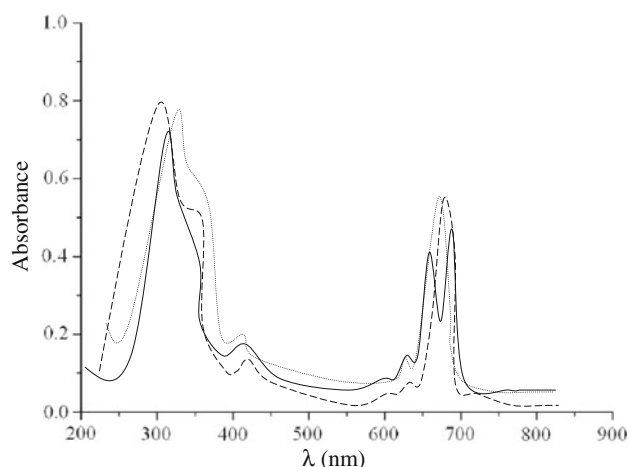
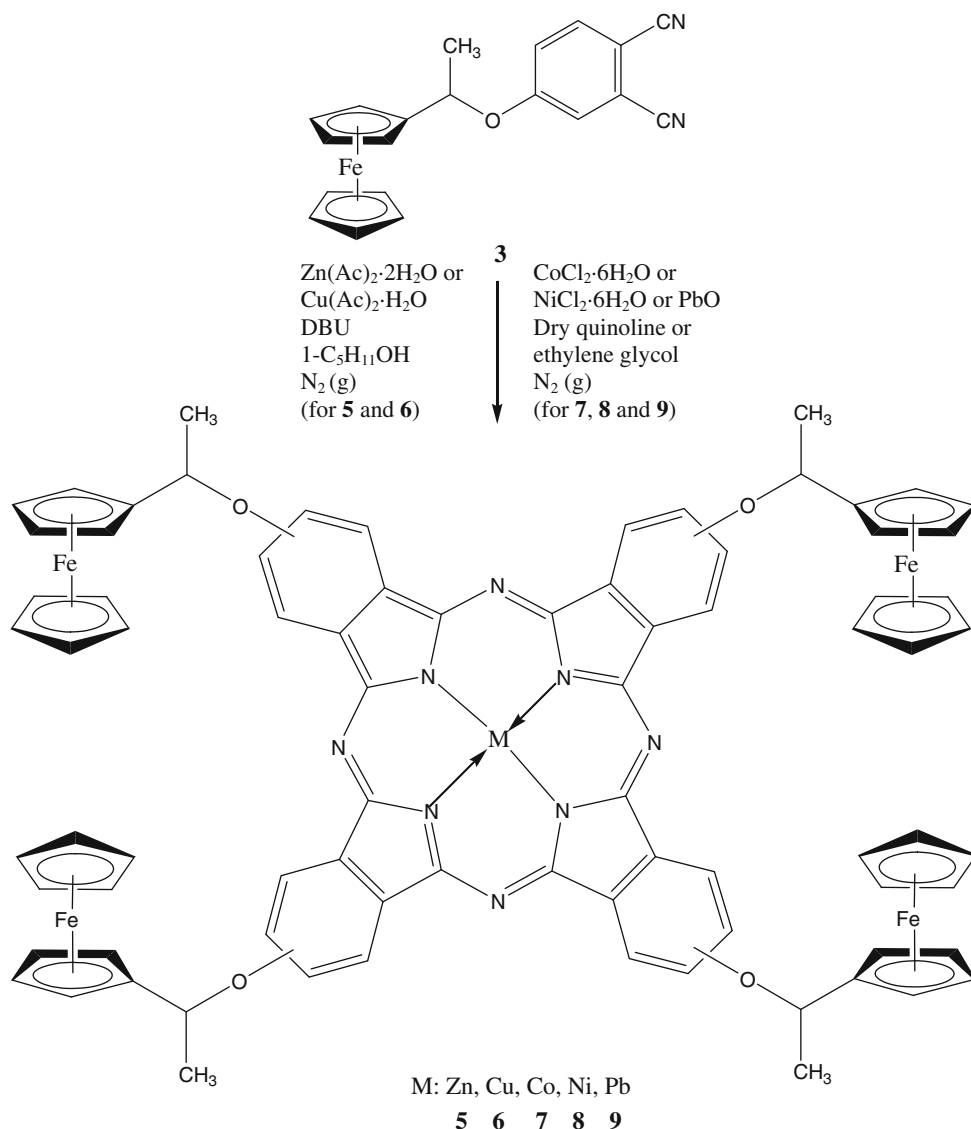
The phthalonitrile, metal-free and metallophthalocyanines were characterized by ^1H and ^{13}C NMR, FT-IR

UV–Vis, mass spectral data and elemental analyses which were consistent with the proposed structures.

The IR spectrum of the starting compound **3** clearly indicates the presence $\text{C}\equiv\text{N}$ and $\text{Ar}-\text{O}-\text{C}$ stretching vibrations at $2,234$ and $1,282\text{ cm}^{-1}$ and the disappearance of $\text{O}-\text{H}$ stretching band of α -methylferrocenylmethanol **1** at $3,209\text{ cm}^{-1}$.

Cyclotetramerization of the phthalonitrile derivative was confirmed by the disappearance of the sharp $\text{C}\equiv\text{N}$ vibration at $2,234\text{ cm}^{-1}$. The IR spectra of phthalocyanines **4–9** are very similar, with the exception of the metal-free **4** showing $\text{N}-\text{H}$ stretching and pyrrole ring vibration bands at $3,245$ and $1,055\text{ cm}^{-1}$ due to the inner core [34].

In ^1H NMR (CDCl_3) spectrum of **3**, OH group of **1** disappeared as expected. ^1H NMR spectrum of **3** showed new signals at $\delta = 7.78$ (d, 1H, Ar-H), 7.65 (d, 1H, Ar-H), 7.43 (dd, 1H, Ar-H) and also the proton-decoupled

Scheme 2 Synthesis of metallophthalocyanine (**5–9**)**Fig. 1** UV-Vis spectra of **4** (solid line), **5** (dashed line) and **6** (dotted line) in chloroform ($C = 1.8 \times 10^{-5}$ M)

^{13}C NMR spectrum of **3** indicates the presence of corresponding carbon atoms at $\delta = 115.7$ and 113.4 (CN). In the ^1H NMR spectra of **4**, the typical shielding of inner core protons were seen as broad signals at $\delta = -3.90$ ppm, which could be attributed to the NH resonances as confirmed by deuterium exchange [35–37]. In the ^{13}C NMR spectrum of this compound, all signals are identical for the precursor dicyano derivative **3** except for the CN carbons. The appearance of CN signals at 154.1 ppm for **4** concerning the inner core instead of CN absorptions in **3** is supported by the formation of phthalocyanine.

The ^1H NMR spectra of the metallophthalocyanines **5**, **8** and **9** were almost identical with those of the metal-free phthalocyanine **4**, with the absence of the N–H protons belonging to the cavity of the porphyrine core. Also, it should be mentioned that the peaks of the ^1H NMR spectra are broad as encountered in some other

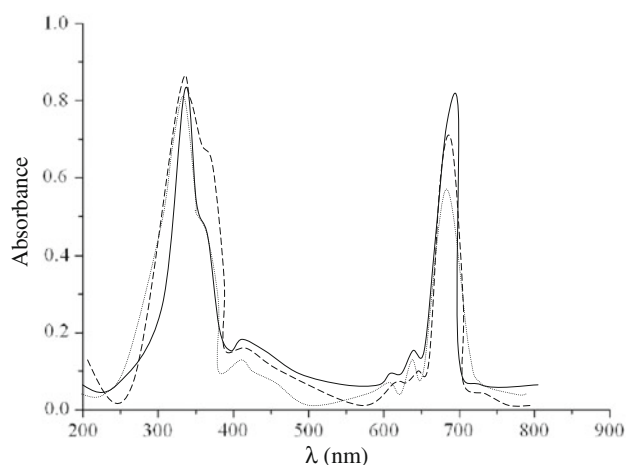


Fig. 2 UV–Vis spectra of **7** (solid line), **8** (dotted line) and **9** (dashed line) in chloroform ($C = 1.8 \times 10^{-5}$ M)

soluble phthalocyanines [27, 31]. On the other hand ^1H NMR spectra of metallophthalocyanines **6**, **7** could not be taken due to the paramagnetic cobalt(II) and copper(II) centers.

In the mass spectra of compounds **3–9**, the presence of the characteristic molecular ion peaks at $m/z = 356.3$ $[\text{M}]^+$ **3**, 1426.9 $[\text{M}]^+$ **4**, 1491.3 $[\text{M} + 1]^+$ **5**, 1488.6 $[\text{M}]^+$ **6**, 1483.9 $[\text{M}]^+$ **7**, 1484.6 $[\text{M} + 1]^+$ **8** and 1632.2 $[\text{M}]^+$ **9** confirmed the proposed structures. Elemental analysis of **3–9** were also consistent with the calculated values.

Phthalocyanines **4–9** reveal typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–420 nm (B band and ferrocene units) arising from the deeper π -levels \Rightarrow LUMO transition and the other in the visible region of the spectrum around 600–700 nm (Q band) attributed to the $\pi \Rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the pc^{-2} ring (Figs. 1, 2) [38–40]. The characteristic Q band transition of metallophthalocyanines with D_{4h} symmetry is observed as a single band of high intensity in visible region. The D_{2h} symmetry of metal-free phthalocyanine **4** is verified by two absorptions in the visible region (691 and 659 nm) with shoulders at 630 and 605 nm. Compared with metal-free phthalocyanine, the λ_{max} of metallophthalocyanines moved to shorter wavelengths.

Conclusion

We have presented the synthesis and characterization of a new phthalonitrile derivative **3**, metal-free **4** and metallophthalocyanines **5–9** with α -methylferrocenylmethoxy units. Precursor **3** was synthesized by the nucleophilic aromatic substitution reaction between α -methylferrocenylmethanol

and 4-nitrophthalonitrile in dry DMF. The metal-free phthalocyanine **4** was prepared from 4-(α -methylferrocenylmethoxy)phthalonitrile **3** in 1-pentanol with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Metallophthalocyanines ($M = \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}$ and Pb) were prepared by cyclotetramerization reaction of phthalonitrile with appropriate materials. Four α -methylferrocenylmethoxy bearing phthalocyanines show more solubility in organic solvents such as chloroform, dichloromethane, toluene, DMF, DMSO and pyridine than octa-substituted phthalocyanines. The reason for the enhancement of solubility in the tetra-substitution is probably based on it being a mixture of positional isomers rather than a single product.

Acknowledgements This study was supported by The Scientific & Technical Research Council of Turkey (TUBITAK), Project Number: TBAG-2453(104T065) (Ankara, Turkey).

References

- Bryant, G.C., Cook, M.J., Ryan, T.G., Thorne, A.J.: Liquid crystalline polymeric phthalocyanines. *J. Chem. Soc. Chem. Commun.* 467–468 (1995). doi:10.1039/C39950000467
- Piechocki, C., Simon, J., Skoulios, A., Guillon, D., Weber, P.: Discotic mesophases obtained from substituted metallophthalocyanines—toward liquid-crystalline one-dimensional conductors. *J. Am. Chem. Soc.* **104**, 5245–5247 (1982). doi:10.1021/ja00383a050
- Tedesco, A.C., Rotta, J.C.G., Lunardi, C.N.: Synthesis, photophysical and photochemical aspects of phthalocyanines for photodynamic therapy. *Curr. Org. Chem.* **7**, 187–196 (2003). doi:10.2174/1385272033373076
- Margaron, P., Gregoire, M.J., Scasnar, V., Ali, H., Van Lier, J.E.: Structure–photodynamic activity relationships of a series of 4-substituted zinc phthalocyanines. *Photochem. Photobiol.* **63**, 217–223 (1996). doi:10.1111/j.1751-1097.1996.tb03017
- Liu, W., Jensen, T.J., Fronczek, F.R., Hammer, R.P., Smith, K.M., Vicente, M.G.H.: Synthesis and cellular studies of non-aggregated water-soluble phthalocyanines. *J. Med. Chem.* **48**, 1033–1041 (2005). doi:10.1021/jm049375b
- Göpel, W.: Phthalocyanine prototype interfaces: their importance for designing chemical sensor and molecular electronic devices. *Synth. Met.* **41**, 1087–1093 (1991). doi:10.1016/0379-6779(91)91560-W
- Zhou, R., Josse, F., Göpel, W., Öztürk, Z.Z., Bekaroğlu, Ö.: Phthalocyanines as sensitive materials for chemical sensors. *Appl. Organomet. Chem.* **10**, 557–577 (1996). doi:10.1002/(SICI)1099-0739(199610)10:8<557:AID-AOC521>3.0.CO;2-3
- de la Torre, G., Claessens, C.G., Torres, T.: Phthalocyanines: old dyes, new materials. Putting color in nanotechnology. *J. Chem. Soc. Chem. Commun.* 2000–2015 (2007). doi:10.1039/b614234f
- Leznoff, C.C., Lever, A.B.P. (eds.): *Phthalocyanines: properties and Applications*, vols. 1–4. VCH, Weinheim (1989, 1993, 1996)
- Lever, A.B.P., Milaeva, E.R., Speier, G.: In: Leznoff, C.C., Lever, A.B.P. (eds.) *Phthalocyanines: properties and applications*, vol. 3, p. 1. VCH, Weinheim (1996)
- Ashwell, G.J. (ed.): *Molecular Electronics*. Wiley, New York (1992)
- Joachim, C., Gimzewski, J.K., Aviram, A.: Electronics using hybrid-molecular and mono-molecular devices. *Nature* **408**, 541–548 (2000). doi:10.1038/35046000

13. Barlow, S., O'Hare, D.: Metal–metal interactions in linked metallocenes. *Chem. Rev.* **97**, 637–669 (1997). doi:[10.1021/cr960083v](https://doi.org/10.1021/cr960083v)
14. Casado, C.M., Cuadrado, I., Morán, M., Alonso, B., García, B., González, B., Losada, J.: Redox-active ferrocenyl dendrimers and polymers in solution and immobilised on electrode surfaces. *Coord. Chem. Rev.* **185–186**, 53–79 (1999). doi:[10.1016/S0010-8545\(98\)00252-5](https://doi.org/10.1016/S0010-8545(98)00252-5)
15. Nlate, S., Ruiz, J., Sartor, V., Navarro, R., Blais, J.-C., Astruc, D.: Molecular batteries: ferrocenylsilylation of dendrons, dendritic cores, and dendrimers: new convergent and divergent routes to ferrocenyl dendrimers with stable redox activity. *Chem. Eur. J.* **6**, 2544–2553 (2000). doi:[10.1002/1521-3765\(20000717\)6:14<2544:AID-CHEM2544>3.0.CO;2-J](https://doi.org/10.1002/1521-3765(20000717)6:14<2544:AID-CHEM2544>3.0.CO;2-J)
16. Köllner, C., Pugin, B., Togni, A.: Dendrimers containing chiral ferrocenyl diphosphine ligands for asymmetric catalysis. *J. Am. Chem. Soc.* **120**, 10274–10275 (1998). doi:[10.1021/ja981137g](https://doi.org/10.1021/ja981137g)
17. Uno, M., Dixneuf, P.H.: Metallorganische triskelien: neuartige Tris(vinylidenruthenium(II)-, tris(alkinylruthenium(II)- und triruthenium-triferrocenyl-komplexe. *Angew. Chem.* **110**, 1822–1824 (1998). doi:[10.1002/\(SICI\)1521-3757\(19980619\)110:12<1822:AID-ANGE1822>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1521-3757(19980619)110:12<1822:AID-ANGE1822>3.0.CO;2-H)
18. Boyd, P.D.W., Burrell, A.K., Campbell, W.M., Cocks, P.A., Gordon, K.C., Jameson, G.B., Officer, D.L., Zhao, Z.: Bis(ferrocenyl)porphyrins. Compounds with strong long-range metal–metal coupling. *Chem. Commun.* 637–638 (1999). doi:[10.1039/a900691e](https://doi.org/10.1039/a900691e)
19. Beer, P.D., Drew, M.G.B., Jagessar, R.: Selective anion recognition by novel 5,10,15,20-tetrakis(o-ferrocenyl-carbonylamino-phenyl-substituted) zinc metalloporphyrin receptors. *J. Chem. Soc. Dalton Trans.* 881–886 (1997). doi:[10.1039/a606082j](https://doi.org/10.1039/a606082j)
20. Jin, Z., Nolan, K., McArthur, C.R., Lever, A.B.P., Leznoff, C.C.: Synthesis, electrochemical and spectroelectrochemical studies of metal-free 2, 9, 16, 23-tetraferrocenylphthalocyanine. *J. Organomet. Chem.* **468**, 205–212 (1994). doi:[10.1016/0022-328X\(94\)80051-0](https://doi.org/10.1016/0022-328X(94)80051-0)
21. Dabak, S., Bekaroğlu, Ö.: Synthesis of phthalocyanines crosswise-substituted with two alkylsulfanyl and two amino groups. *New J. Chem.* **21**, 267–272 (1997)
22. Silver, J., Sosa-Sanchez, J.L., Frampton, C.S.: Structure, electrochemistry, and properties of bis(ferrocenecarboxylato)(phthalocyaninato)silicon(IV) and its implications for (Si(Pc)O)_n polymer chemistry. *Inorg. Chem.* **37**, 411–417 (1998). doi:[10.1021/ic970934x](https://doi.org/10.1021/ic970934x)
23. Poon, K.-W., Yan, Y., Li, X.-Y., Ng, D.K.P.: Synthesis and electrochemistry of ferrocenylphthalocyanines. *Organometallics* **18**, 3528–3533 (1999). doi:[10.1021/om990208x](https://doi.org/10.1021/om990208x)
24. Poon, K.-W., Liu, W., Chan, P.-K., Yang, Q., Chan, T.-W.D., Mak, T.C.W., Ng, D.K.P.: Tetrapyrrole derivatives substituted with ferrocenylethynyl moieties. Synthesis and electrochemical studies. *J. Org. Chem.* **66**, 1553–1559 (2001). doi:[10.1021/jo0004308](https://doi.org/10.1021/jo0004308)
25. Gonzalez-Cabello, A., Claessens, C.G., Martin-Fuch, G., Ledoux-Rack, I., Vazquez, P., Zyss, J., Agullo-Lopez, F., Torres, T.: Phthalocyanine-ferrocene dyads and triads for nonlinear optics. *Synth. Met.* **137**, 1487–1488 (2003). doi:[10.1016/S0379-6779\(02\)01211-0](https://doi.org/10.1016/S0379-6779(02)01211-0)
26. Mısır, M.N., Gök, Y., Kantekin, H.: Synthesis and characterization of metal-free and metallophthalocyanines containing N₂S₂-type macrocyclic moieties linked ferrocenyl groups. *J. Organomet. Chem.* **692**, 1451–1456 (2007). doi:[10.1016/j.jorgchem.2006.11.054](https://doi.org/10.1016/j.jorgchem.2006.11.054)
27. Bilgin, A., Gök, Y.: Synthesis and characterization of new metal-free and metallophthalocyanines containing macrobicyclic moieties. *Supramol. Chem.* **18**, 491–499 (2006). doi:[10.1080/10610270600717672](https://doi.org/10.1080/10610270600717672)
28. Bilgin, A., Ertem, B., Gök, Y.: Synthesis and characterization of novel metal-free and metallophthalocyanines diazadioxamacrocycles. *Supramol. Chem.* **17**, 277–281 (2005). doi:[10.1080/10610270500054051](https://doi.org/10.1080/10610270500054051)
29. Bilgin, A., Ertem, B., Gök, Y.: Synthesis and characterization of novel metal-free phthalocyanines containing four cylindrical or spherical macrotricyclic moieties. *Tetrahedron Lett.* **44**, 6937 (2003). doi:[10.1016/S0040-4039\(03\)01670-8](https://doi.org/10.1016/S0040-4039(03)01670-8)
30. Bilgin, A., Ertem, B., Gök, Y.: The synthesis and properties of new metal-free and metallophthalocyanines containing four di-loop macrocyclic moieties. *Supramol. Chem.* **18**, 361–369 (2006). doi:[10.1080/10610270600650667](https://doi.org/10.1080/10610270600650667)
31. Bilgin, A., Ertem, B., Gök, Y.: Highly organosoluble metal-free phthalocyanines and metallophthalocyanines: Synthesis and characterization. *Eur. J. Inorg. Chem.* 1703–1712 (2007). doi:[10.1002/ejic.200600943](https://doi.org/10.1002/ejic.200600943)
32. Neuse, E.W., Trifan, D.S.: Polycondensation of ferrocenylcarbinols and substitution orientation effects. *J. Am. Chem. Soc.* **85**, 1952–1958 (1963). doi:[10.1021/ja00896a013](https://doi.org/10.1021/ja00896a013)
33. Young, J.G., Onyebugu, W.: Synthesis and characterization of di-disubstituted phthalocyanines. *J. Org. Chem.* **55**, 2155–2159 (1990). doi:[10.1021/jo00294a032](https://doi.org/10.1021/jo00294a032)
34. Avram, M., Mateescu, G.: *Infrared Spectroscopy*, p. 298. Wiley-Interscience, New York (1966)
35. Ertem, B., Bilgin, A., Kantekin, H., Gök, Y.: Synthesis and characterization of new soluble phthalocyanines containing macrocycle units. *Polyhedron* **27**, 2186–2192 (2008). doi:[10.1016/j.poly.2008.03.017](https://doi.org/10.1016/j.poly.2008.03.017)
36. Snow, A.W., Griffith, J.R., Marullo, N.P.: Synthesis and characterization of heteroatom bridged metal-free phthalocyanine network polymers and model compounds. *Macromolecules* **17**, 1614–1624 (1984). doi:[10.1021/ma00138a033](https://doi.org/10.1021/ma00138a033)
37. Marcuccio, S.M., Svirskaya, P.I., Greenberg, S., Lever, A.B.P., Leznoff, C.C., Tomer, K.B.: Binuclear phthalocyanines covalently linked through two- and four-atom bridges. *Can. J. Chem.* **63**, 3057–3069 (1985)
38. Kasuga, K., Idehara, T., Handa, M., Isa, K.: Preparation of unsymmetrical phthalocyanine by means of a ring expansion of subphthalocyanine. *Inorg. Chim. Acta* **196**, 127–128 (1992). doi:[10.1016/S0020-1693\(00\)86113-7](https://doi.org/10.1016/S0020-1693(00)86113-7)
39. Kobayashi, N., Lever, A.B.P.: Cation- or solvent-induced supermolecular phthalocyanine formation: crown ether substituted phthalocyanines. *J. Am. Chem. Soc.* **109**, 7433–7441 (1987). doi:[10.1021/ja00258a030](https://doi.org/10.1021/ja00258a030)
40. Özçeşmeci, İ., Okur, A.İ., Gül, A.: New phthalocyanines bearing tetra(hydroxyethylthio) functionalities. *Dyes Pigments* **75**, 761–765 (2007). doi:[10.1016/j.dyepig.2006.08.003](https://doi.org/10.1016/j.dyepig.2006.08.003)