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The synthesis and characterization of functionalized polyfluorinated phthalocyanines

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Abstract

4-(2′,3′,4′,5′,6′-Pentafluorobenzyloxy)phthalonitrile was employed with hexanethiol to prepare 4-(2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy)-phthalonitrile, by the selective displacement of the *para*-fluorine atom using K_2CO_3 in DMF. The new Zn(II), Ni(II) and Co(II) phthalocyanines with four, peripheral fluoro-hexylthiobenzyloxy groups were synthesized from 4-(2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy)phthalonitrile and the corresponding divalent metal salt ($Zn(CH_3COO)_2$, $NiCl_2$ or $CoCl_2$). The blue-green phthalocyanines were soluble in common organic solvents. The structures of the target compounds were confirmed using elemental analysis, UV–vis, FT-IR, ^1H NMR, ^{19}F NMR and mass spectroscopic methods.

Keywords: Metallophthalocyanines; Regioselective nucleophilic aromatic substituents; Hexylthio

1. Introduction

Since their synthesis in the early 1930, phthalocyanines (Pcs) are known as excellent functional materials. Metallophthalocyanines have attracted a great deal of interest due to their high colouring property, extremely high thermal stability, chemical resistivity, electrical conductivity, photoconductivity and catalytic activity [1–6].

Their utility derives, in part from the ease with which their properties (solubility, electronic absorption, fluorescense, self-assembly etc.) can be modified through synthetic manipulation. Specificity in the applications of phthalocyanines can be introduced by modification of the benzenoid substituents or variation in the central metal ion [7–9]. Substituents provide the prime means of solubilizing the ring system in either aqueous media or in organic solvents and offer a useful way of tuning the wavelength of the visible region absorption band [10–17].

The electrical properties of phthalocyanines, that is well known as semiconducting organic materials, can also be changed by introducing electron donor or acceptor groups as substituents into the Pc π-electron ring [18–20]. Fluorinated metal phthalocyanines form a class of coordination compounds which are currently receiving a great deal of attention due to their interesting electron transporting characteristics [21,22]. Also, fluorocarbons exhibit increased thermal stability, hydrophobicity, lipophobicity, chemical resistance and decreased intermolecular attractive forces in comparison to their hydrocarbon analogues [23,24]. It has been reported that the position and number of pentafluorophenyl groups on the macrocycle ring has a marked effect on the stability and catalytic activity [25,26].

Reaction of various nucleophiles with *meso*-tetra(pentafluorophenyl)porphyrine led to the selective replacement of the *para*-fluorine substituents of the starting porphyrin in high yields. The *para*-fluoro group is known to be reactive toward nucleophilic substitution reactions. The substitution regioselectivity was always quite high only at the *para*-fluorine of the pentafluorophenyl groups [27–33].

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We have recently described the synthesis of metal phthalocyanines which contain tetra-pentafluorobenzyloxy moieties on the periphery [34]. Various functionalized polyhalogeno compounds are prepared by regioselective substitution of the *para*-fluorine atoms by several nucleophiles such as primary and secondary amines, alkoxides and thiols [27,31,35]. The present paper reports the synthesis and characterization of some new metal phthalocyanines containing four covalently attached hexylthio-groups on the periphery of the tetrakis(pentafluorophenyl) moieties by regioselective substitution reactions. These new compounds have been characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{19}F NMR, UV−vis and mass spectral data.

2. Experimental

IR spectra were recorded on a Perkin−Elmer Spectrum One FT-IR spectrometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as internal reference. ^{19}F NMR spectra were recorded on a Varian Unity Inova 470 MHz NMR. Mass spectra were performed on Varian 711 mass spectrometer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. All solvents were dried and purified according to Ref. [36]. The homogeneity of the products was tested in each step by TLC (SiO_2). 4-Nitrophthalonitrile and 4-(2′,3′,4′,5′,6′-pentafluorobenzyloxy)phthalonitrile (**1**) were synthesized according to published methods [37,34].

*2.1. 4-(2′,3′,5′,6′-Tetrafluoro-4′-hexylthio-benzyloxy) phthalonitrile (**2**)*

4-(2′,3′,4′,5′,6′-Pentafluorobenzyloxy)phthalonitrile (**1**) (1 g, 3.085 mmol) and hexanethiol (0.364 g, 3.085 mmol) were added successively with stirring to dry DMF (15 ml). After they were dissolved, finely ground anhydrous K_2CO_3 (0.639 g, 4.628 mmol) was added portionwise over 2 h. The reaction mixture was stirred under nitrogen at 30 °C for 20 h. Then the solution was poured into icewater (200 ml). The precipitate was filtered off, washed first with water until the filtrate was neutral and then extracted with chloroform (3 × 100 ml); the chloroform extracts were combined, dried over $MgSO_4$, and the solvent was removed at reduced pressure. The residue was washed several times with hexane and finally with diethyl ether. Purification of the product was accomplished by column chromatography with silica gel using methanol/chloroform (1:100) as eluent. Yield: 0.63 g (48%); m.p. 65 °C; IR, ν (cm^{-1}): 2957−2858 (alkyl CH), 2232 (C≡N), 1250 (C−O−C); ^{1}H NMR ($CDCl_3$-*d*): δ: 7.72 (d, H, Ar−H), 7.32 (s, H, Ar−H), 7.25 (d, H, Ar−H), 5.22 (s, 2H, CH_2), 2.96 (t, 2H, SCH_2), 1.52 (m, 2H, $SCCH_2$), 1.32 (m, 2H, CCH_2C), 1.26 (m, 4H, CCH_2C) 0.86 (t, 3H, CH_3). Anal. Calcd for $C_{21}H_{18}F_4N_2OS$: C, 59.71; H, 4.29; N, 6.63. Found: C, 59.58; H, 4.25; N, 6.47%.

*2.2. 2,9/10, 16/17, 23/24-Tetrakis[(2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy)phthalocyaninato]zinc(II) (**3**)*

A mixture of 0.200 g (0.473 mmol) of phthalonitrile derivative (**2**) and 0.022 g (0.119 mmol) of anhydrous $Zn(CH_3COO)_2$ in 2 ml of anhydrous DMF was heated and stirred at 150 °C for 3 days under N_2 in a sealed tube. The dark green mixture was cooled to room temperature and diluted with ethanol/water (1:1) mixture until the crude product precipitated. The precipitate was filtered off and washed several times with hot water and ethanol to remove unreacted materials and dried *in vacuo*. Finally, the green precipitate was chromatographed on silica gel with chloroform/ethylacetate (1:4) as eluent. Yield: 0.039 g (19%); m.p. > 200 °C; IR, ν (cm^{-1}): 2946−2857 (alkyl CH), 1271 (C−O−C); ^{1}H NMR ($CDCl_3$-*d*): δ: 7.64−7.30 (m, 12, Ar−H), 5.17 (s, 8H, CH_2), 3.01 (m, 8H, SCH_2), 1.66 (m, 8H, $SCCH_2$), 1.33 (m, 8H, CCH_2C), 1.24 (m, 16H, CCH_2C), 0.92 (t, 12H, CH_3); ^{19}F NMR (acetone-d_6):δ: −143.1 ppm (d-*o*-fluoro), −160.5 ppm (q-*m*-fluoro); UV−vis λ_{max} (nm) (log ε) in $CHCl_3$: 356 (4.35), 685 (4.53); MS (FAB) *m*/*z*: 1753.05 $[M]^+$. Anal. Calcd for $C_{84}H_{72}F_{16}N_8O_4S_4Zn$: C, 57.48; H, 4.13; N, 6.38. Found: C, 57.23; H, 4.07; N, 6.26%.

*2.3. 2,9/10, 16/17, 23/24-Tetrakis[(2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy)phthalocyaninato]nickel(II) (**4**)*

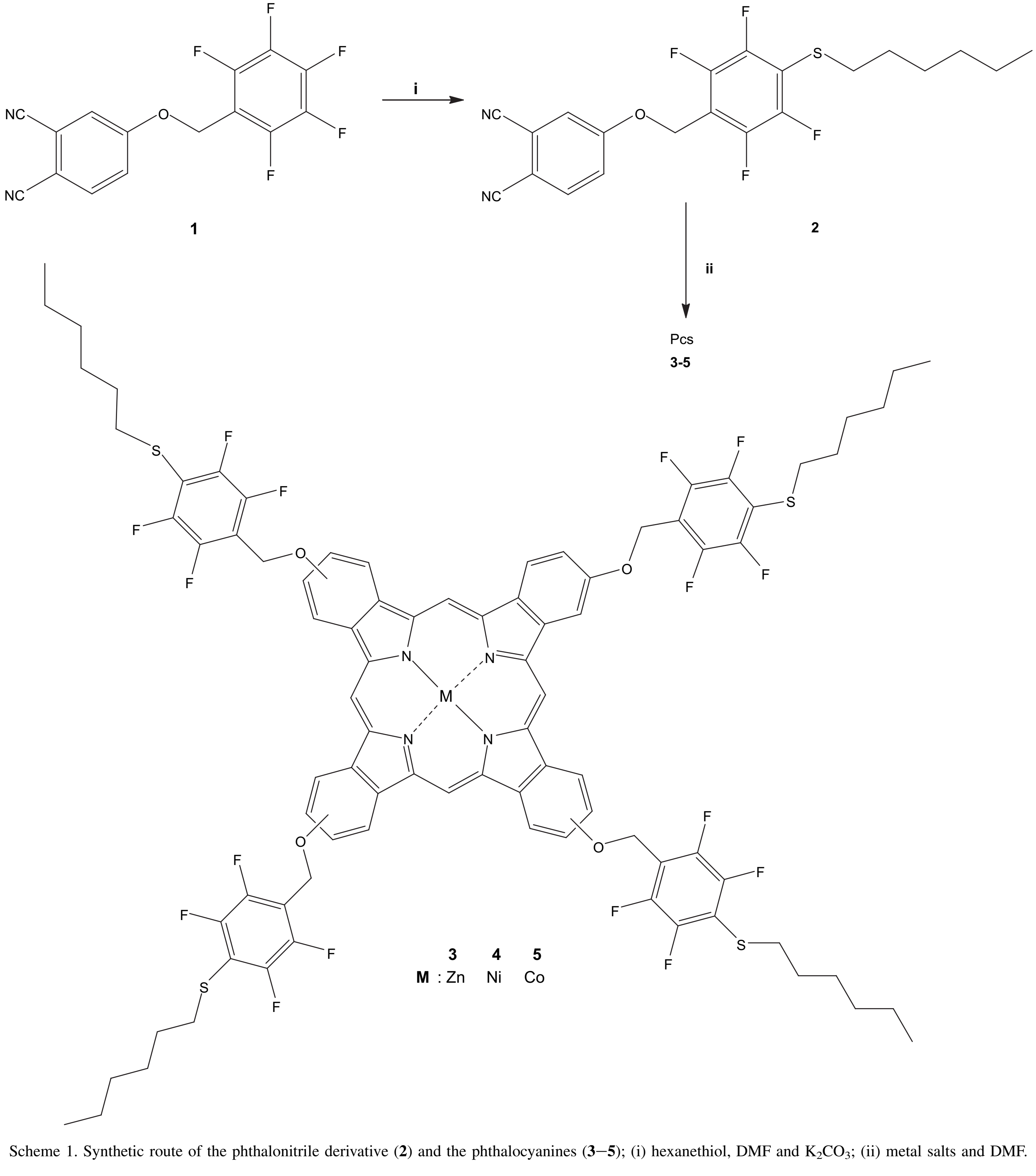
A mixture of 0.400 g (0.946 mmol) of compound **2** and 0.030 g (0.238 mmol) of anhydrous $NiCl_2$ in 1 ml of anhydrous DMF was heated and stirred in a sealed tube at 150 °C for 24 h under N_2. The resulting green suspension was cooled to room temperature and poured into icewater (100 ml). It was filtered off and washed several times with hot water and ethanol and then dried *in vacuo*. This green crude product was isolated by silica gel column chromatography with chloroform/ethylacetate (1:4) as an eluent. Yield: 0.124 g (17%); m.p. > 200 °C; IR, ν (cm^{-1}): 2950−2862 (alkyl CH), 1271 (C−O−C); ^{1}H NMR ($CDCl_3$-*d*): δ: 7.57−7.23 (m, 12H, Ar−H), 5.15 (s, 8H, CH_2), 2.97 (m, 8H, SCH_2), 1.65 (m, 8H, $SCCH_2$), 1.30 (m, 8H, CCH_2C), 1.19 (m, 16H, CCH_2C), 0.91 (t, 12H, CH_3); UV−vis λ_{max} (nm) (log ε) in $CHCl_3$: 340 (4.43), 675 (4.53); MS (FAB) *m*/*z*: 1747.37 $[M]^+$. Anal. Calcd for $C_{84}H_{72}F_{16}N_8NiO_4S_4$: C, 57.70; H, 4.15; N, 6.41. Found: C, 57.51; H, 4.05; N, 6.20%.

*2.4. 2,9/10, 16/17, 23/24-Tetrakis[(2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy)phthalocyaninato]cobalt(II) (**5**)*

A mixture of 0.300 g (0.710 mmol) of compound **2** and 0.023 g (0.179 mmol) of anhydrous $CoCl_2$ in 1 ml of anhydrous DMF was heated and stirred at 150 °C for 20 h under N_2 in a sealed tube. After cooling to room temperature, ethanol (6 ml) was added in order to precipitate the product. The dark green product was filtered off, washed several times with hot water and then with hot EtOH and finally with MeOH. The pure phthalocyanine derivative was obtained by column chromatography on silica gel using chloroform/ethylacetate (1:4) mixture as eluent. Yield: 0.114 g (21%); m.p. > 200 °C; IR, ν (cm^{-1}): 2957–2875 (alkyl CH), 1271 (C–O–C); UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 326 (4.22), 674 (4.42); MS (FAB) *m*/*z*: 1748.69 $[M]^+$. Anal. Calcd for $C_{84}H_{72}Co\ F_{16}N_8O_4S_4$: C, 57.69; H, 4.15; N, 6.41. Found: C, 57.49; H, 4.11; N, 6.18%.

3. Results and discussion

The synthesis of substituted phthalocyanines starts generally with the preparation of the corresponding phthalonitrile precursors. The synthesis of the target metallophthalocyanines (**3–5**) undertaken in this work is shown in Scheme 1. The synthesis begins with 4-(2′,3′,4′,5′,6′-pentafluorobenzyloxy)phthalonitrile (**1**) since the *para*-fluoro group is known to be reactive



Scheme 1. Synthetic route of the phthalonitrile derivative (**2**) and the phthalocyanines (**3–5**); (i) hexanethiol, DMF and K_2CO_3; (ii) metal salts and DMF.

toward nucleophilic substitution reaction. The substitution regioselectivity was always quite high only at the *para*-fluorine of pentafluorophenyl moieties. 4-(2′,3′,4′,5′,6′-Pentafluorobenzyloxy)phthalonitrile (**1**) was converted to compound **2** in DMF containing K_2CO_3 as a base at 30 °C for 20 h under nitrogen atmosphere, afforting **2** in 48% yield [38–40].

Cyclotetramerization of the dinitrile compound **2** in the presence of anhydrous metal salts [$Zn(CH_3COO)_2$, $NiCl_2$ or $CoCl_2$] gave the desired metallophthalocyanines **3–5**. The green products were isolated by column chromatography on silica gel with chloroform/ethylacetate (1:4) as eluent. The elemental analysis results of the starting materials and the phthalocyanines show good agreement with the calculated values. All phthalocyanines **3–5** are soluble in a number of solvents such as chloroform, dichloromethane, acetone, THF etc. Characterization of the products involved a combination of methods including FT-IR, elemental analysis, UV–vis spectroscopy, ^{1}H NMR and ^{19}F NMR and mass spectroscopy.

The IR spectral data clearly indicated the formation of compound **2** with the presence of alkyl-thio groups by the intense stretching bands at 2957–2858 cm^{-1} and the strong absorption vibration at 2232 cm^{-1} corresponding to the CN groups disappearance after their conversion to the metallophthalocyanines **3–5**. The IR spectra of **3–5** showed similar characteristics.

^{1}H NMR spectrum of **2** exhibited the characteristic chemical shifts for the structures expected. In the ^{1}H NMR spectrum of **2** in $CDCl_3$, the aromatic protons belonging to cyano substituted benzene appear as multiplet at δ: 7.72–7.25 ppm. The singlet at δ: 5.22 ppm belongs to CH_2 protons of pentafluorobenzyl moieties. The aliphatic protons of the side chains of **2** exhibited the $-SCH_2$ protons at 2.96 ppm, $-CH_3$ at the end of the chain at 0.86 ppm, $-C-CH_2-C-$ protons at 1.52–1.26 ppm. A common feature of the ^{1}H NMR spectra of the Pcs (**3** and **4**) is the broad absorptions when compared with that of the cyano derivatives.

^{19}F NMR spectrum of ZnPc (**3**) showed two multiplets, relative to the fluorine atoms in *ortho* and *meta* positions of the phenyl substituents at −143.1 ppm and −160.5 ppm, respectively. The ^{19}F NMR spectrum of this reaction product did not show any signal corresponding to the *para*-fluorine atoms of the parent phthalonitrile, leading to the conclusion that the reaction reached completion and that the product was substituted with hexylthio group.

A close investigation of the mass spectra of the dinitrile (**2**) derivatives and phthalocyanines **3**, **4**, **5** confirmed the proposed structures. In the FAB mass spectra of compounds **3–5**, the presence of the characteristic molecular ion peaks at *m/z*: 1753, 1747 and 1748, respectively.

Electronic spectra are especially important to establish the structure of the all phthalocyanines **3–5**. UV–vis spectra of phthalocyanine core is dominated by two intense bands, the Q band around 600–700 nm and the B band in the near UV region at about 300–400 nm, both correlated to $\pi-\pi^*$ transitions. UV–vis spectra of metallophthalocyanines (**3–5**) in $CHCl_3$ exhibited intense single Q band absorption around 674–685 nm and B bands around 326–356 nm (Fig. 1). The Q band position of the perfluorinated complex was slightly shifted to shorter wavelengths compared with non-fluorinated phenoxy substituted compounds, due to the electron-withdrawing effect of the fluorine atoms in the phenoxy substituents [34]. An important feature of the phthalocyanines **3–5**, when compared with that of the 4-(2′,3′,4′,5′,6′-pentafluorobenzyloxy) substituted analog [34] is their electronic spectrum. Substitution of the electron-withdrawing fluorine with the electron-donating thiol results in a 7–5 nm red shift in the Soret band.

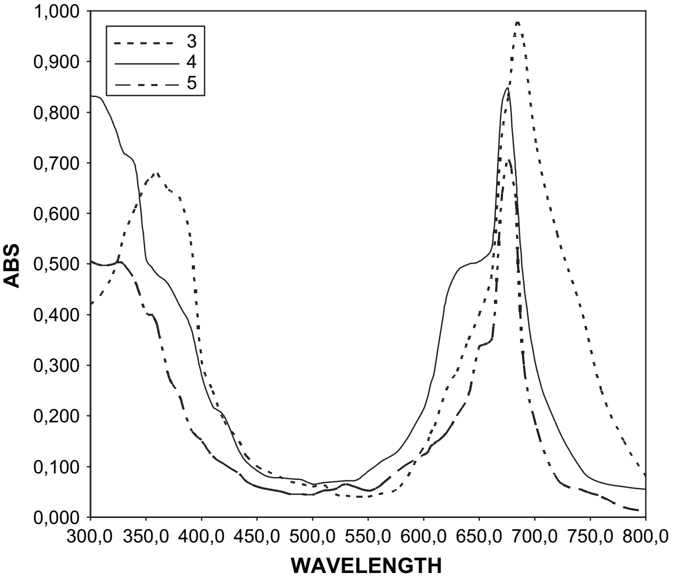


Fig. 1. UV–vis spectra for the phthalocyanines **3–5** in chloroform (2.5×10^{-5} mol dm^{-3}).

4. Conclusions

In the present work, new metallophthalocyanines substituted with four *para*-hexylthio-tetrafluoro-phenoxy groups were described. These compounds show high solubility in solvents of differing polarity from ethanol to acetone, chloroform, hexane. Hexylthio-substitution resulted with a red shift of Q band maxima in these phthalocyanines. These materials deserve further research on their catalytic and photoelectric properties.

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