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Novel phthalocyanines with pentafluorobenzyloxy-substituents

Mukaddes Selçukoğlu, Esin Hamuryudan*

Department of Chemistry, Technical University of Istanbul, Maslak 34469, Istanbul, Turkey

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Abstract

The synthesis of pentafluorobenzyloxy substituted metal-free phthalocyanine **4** was achieved by co-cyclotetramerization of 4-(2′,3′,4′,5′,6′-pentafluorobenzyloxy)phthalonitrile (**3**) with hydroquinone, whereas metallophthalocyanines (MPcs) **5–7** were synthesized in the presence of zinc, cobalt or nickel salts. The compounds were characterized by their elemental analyses, UV–vis, FT-IR, ^{1}H NMR, ^{19}F NMR and mass spectroscopic methods.

Keywords: Phthalocyanines; Fluorocarbons; 2,3,4,5,6-Pentafluorobenzyl alcohol; Zinc; Copper

1. Introduction

Phthalocyanines are well known colorants; besides their intense colour and efficient energy absorption, more remarkable properties have been discovered due to their 18π-electron conjugated system. On the other hand, phthalocyanines (Pcs) are also interesting compounds with increasing diverse industrial and biomedical applications including semiconductors, catalysts, chemical sensors, liquid crystals, nonlinear optics and electrochromic displays [1–4]. The exceptional chemical and physical properties of these compounds can be due to various substituents on the benzo rings. The range of solubility in phthalocyanines becomes very important for these applications, since many Pcs are poorly soluble in organic solvents and water. The solubility of Pcs can be enhanced by adding different kinds of substituents such as bulky or long chain alkyl, alkylthio or alkoxy groups at the periphery and axial positions of the phthalocyanine ring [5–13]. The most extensively investigated soluble substituted phthalocyanines are the tetra- and octasubstituted derivatives and tetrasubstituted ones exhibit usually a higher solubility [14]. The formation of constitutional isomers and the higher dipole moment of the tetrasubstituted phthalocyanines resulting from the unsymmetrical arrangement of the substituents in the periphery leads to a higher solubility of these systems [15].

Although phthalocyanines carrying electron-donating substituents have frequently been described, those with electron-withdrawing groups especially containing fluorine atoms have not been extensively studied [16–19]. Compared to unsubstituted parent metal phthalocyanines (Pcs), some of the metal complexes with multiple electron-withdrawing peripheral substituents are more stable and more active catalysts for a variety of hydrocarbon oxygenation reactions [20]. The high stability of the substituted metal complexes may be attributed to the electron-withdrawing substituents at the periphery of the macrocycle that cause a large increase in the ionization potential of the system and thus protect the catalyst from oxidative destruction [1,2,21].

The electrical properties of Pcs, which are known as semiconducting organic materials, can also be changed by introducing substituent groups effective on Pc π-electron ring. Among these introduction of electron donor and acceptor groups into the Pc ring can be mentioned [22]. Fluorinated metal phthalocyanines are currently receiving a great deal of attention due to their interesting electron-transporting characteristics [23,24].

While unsubstituted phthalocyanines exhibit p-type behaviour due to the doping with electron-accepting molecules, thin

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* Corresponding author. Tel.: +90 212 285 68 26; fax: +90 212 285 63 86.
E-mail address: esin@itu.edu.tr (E. Hamuryudan).

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films of some metal hexadecafluoro-phthalocyanines exhibit n-type behaviour [25]. These properties resulted in a number of studies aiming at different applications like photovoltaic cells, rectifying junction and gas sensors. Generally, fluoro-substituted phthalocyanines are known for their high solubility even in polar, aprotic solvents and become good electron donor for use as chemical sensors. The increased solubility may be due to fluorine, which has the highest electronegativity of all elements [18].

We have previously reported peripherally substituted symmetrical and unsymmetrical tetrapyrrole systems [26–29]. In the case of crown ethers as substituents, the molecules possess the capability of forming ion channels allowing the migration of alkali and alkaline-earth cations [30]. A consequence of incorporating a sulfanyl function on the periphery has been a shift of the Q band absorption to longer wave-lengths in the electronic spectra [31,32] and it is preferred for a number of applications such as far-IR absorbers and photosensitizers. The present paper reports, for the first time the synthesis and characterization of metal-free and metal phthalocyanines containing tetrakis-pentafluorophenoxy moieties on the periphery.

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 spectrometer. Mass spectra were performed on Ultima Fourier Transform and 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. [33]. The homogeneity of the products was tested in each step by TLC (SiO_2). 4-Nitrophthalonitrile was prepared according to a report procedure [34].

2.1. *4-(2′,3′,4′,5′,6′-Pentafluorobenzyloxy)phthalonitrile (**3**)*

2,3,4,5,6-Pentafluorobenzyl alcohol (**1**) (1.44 g, 5.78 mmol) and 4-nitrophthalonitrile (**2**) (1 g, 5.78 mmol) were added successively with stirring to dry DMF (7 ml). After they were dissolved, anhydrous K_2CO_3 (1.6 g, 11.56 mmol) was added portionwise for 2 h and the mixture was stirred vigorously at 30 °C for 48 h under nitrogen. Then the solution was poured into icewater (200 ml). The precipitate formed was filtered off, washed first with water until the filtrate was neutral and then with EtOH and dried in vacuo. Purification of the product was accomplished by column chromatography with silica gel using methanol/chloroform (1:100) as eluent. Yield: 0.96 g (51%); m.p. 137 °C; IR, ν (cm^{-1}): 3083 (Ar–H), 2970–2890 (alkyl CH), 2233 (C≡N), 1250 (C–O–C); ^{1}H NMR (acetone-d_6) δ: 8.06 (d, H, Ar–H), 7.79 (s, H, Ar–H), 7.58 (d, H, Ar–H), 5.52 (s, 2H, CH_2); Anal. Calcd. for $C_{15}H_5F_5N_2O$: C, 55.55; H, 1.54; N, 8.64. Found: C, 55.12; H, 1.47; N, 8.35%.

2.2. *Metal-free phthalocyaninate (**4**)*

A mixture of 0.200 g of compound **3** (0.617 mmol) and 0.120 g (1.100 mmol) of freshly sublimed hydroquinone was heated and stirred at 135 °C for 24 h under N_2. The dark green mixture was cooled to room temperature, and diluted with water until the crude product completely precipitated. The precipitate was filtered off and washed several times with hot water and then with hot EtOH. The green product was isolated on a silica gel column with acetone/toluene (1:2). Yield: 0.042 g (27.5%); m.p > 200 °C; IR, ν (cm^{-1}): 3290 (NH), 3058 (aryl CH), 2957–2891 (alkyl CH), 1209 (C–O–C); ^{1}H NMR (d-$CDCl_3$) δ: 7.68–6.56 (br s, 3H, Ar–H), 5.31 (s, 2H, CH_2), −9.7 (br s, 4H, NH); UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 343 (4.75), 663 (4.75), 701 (4.95); MS (FAB) *m/z*: 1299 [M + 1]; Anal. Calcd. for $C_{60}H_{22}F_{20}N_8O_4$: C, 55.47; H, 1.69; N, 8.62. Found: C, 55.23; H, 1.56; N, 8.48%.

2.3. *Zinc(II) phthalocyaninate (**5**)*

A mixture of 0.200 g of **3** (0.617 mmol) and 0.028 g (0.154 mmol) of anhydrous $Zn(CH_3COO)_2$ in 2 ml of anhydrous DMF was heated and stirred at 150 °C for 30 h under N_2. 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. Finally, the green precipitate was chromatographed on silica gel with acetone/toluene (1:2) as eluent. Yield: 0.070 g (33.2%); m.p. > 200 °C; IR, ν (cm^{-1}): 3083 (aryl CH), 2950–2890 (alkyl CH), 1217 (C–O–C); ^{1}H NMR (acetone-d_6) δ: 8.03 (d, H, Ar–H), 7.80 (s, H, Ar–H), 7.59 (d, H, Ar–H), 5.53 (s, 2H, CH_2); ^{19}F NMR (acetone-d_6) δ: −142.4 ppm (*o*-fluoro), −151.2 ppm (*p*-fluoro), −154.5 ppm (*m*-fluoro); UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 351 (4.80), 678 (5.12); Anal. Calcd. for $C_{60}H_{20}F_{20}N_8O_4Zn$: C, 52.88; H, 1.46; N, 8.22. Found: C, 52.75; H, 1.31; N, 8.04%.

2.4. *Nickel(II) phthalocyanine (**6**)*

A mixture of 0.200 g of **3** (0.617 mmol) and 0.020 g (0.154 mmol) of anhydrous $NiCl_2$ in 1 ml of anhydrous DMF was heated and stirred at 150 °C for 20 h under N_2. The dark green mixture was cooled to room temperature, and diluted with 50% ethanol/water mixture until the crude product precipitated. The precipitate was filtered off and washed several times with hot water. Finally, the green precipitate was washed in EtOH under reflux and dried. This green crude product was chromatographed on silica gel and eluted with acetone/toluene (1:2). Yield: 0.038 g (18%); m.p. > 200 °C; IR, ν (cm^{-1}): 3083 (aryl CH), 2950–2890 (alkyl CH), 1219 (C–O–C); ^{1}H NMR (acetone-d_6) δ: 8.06–7.57 (s, 3H, Ar–H), 5.52 (d, 2H, CH_2); UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 332 (3.98), 672 (4.19); Anal. Calcd. for

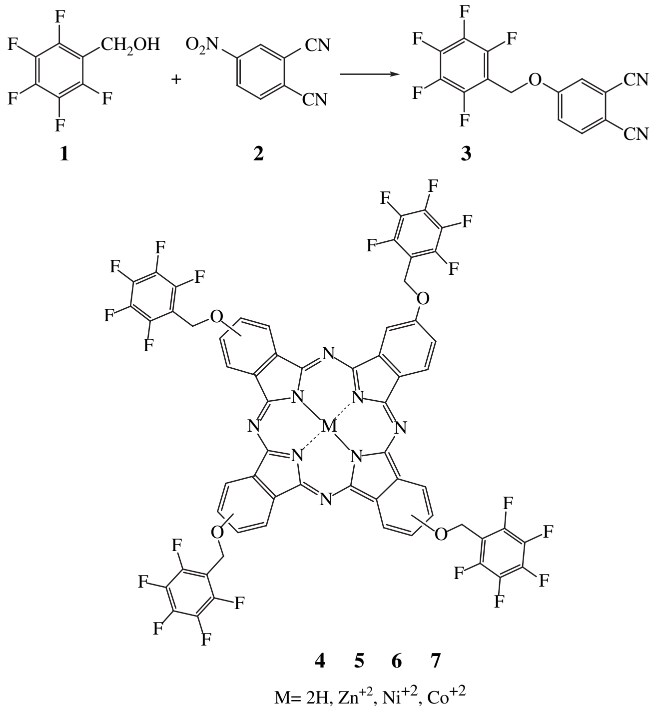
$C_{60}H_{20}F_{20}N_8O_4Ni$: C, 53.14; H, 1.47; N, 8.26. Found: C, 53.06; H, 1.40; N, 8.12%.

*2.5. Cobalt(II) phthalocyanine (**7**)*

A mixture of 0.200 g of compound **3** (0.617 mmol) and 0.020 g (0.154 mmol) of anhydrous $CoCl_2$ in 4 ml of anhydrous ethylene glycol was heated and stirred at 180 °C for 5.5 h under N_2. After cooling to room temperature, ethanol (4 ml) was added in order to precipitate the product. The dark green product was filtered off and washed several times with hot water and then with hot EtOH and finally with diethyl ether. This green crude product was chromatographed on silica gel and eluted with acetone/toluene (1:2). Yield: 0.044 g (21%); m.p. > 200 °C; IR, ν (cm^{-1}): 3083 (aryl CH), 2950–2890 (alkyl CH), 1218 (C–O–C) cm^{-1}; UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 319 (4.40), 669 (4.34); MS (FAB) m/z: 1356 [M + 1]; Anal. Calcd. for $C_{60}H_{20}F_{20}N_8O_4Co$: C, 53.14; H, 1.47; N, 8.26. Found: C, 52.97; H, 1.39; N, 8.18%.

3. Results and discussion

The key reactant for the preparation of phthalocyanines carrying oxy-bridged pentafluorophenoxy moieties is the cyano compound **3** which has been synthesized through base-catalyzed aromatic nitro displacement of 4-nitrophthalonitrile with pentafluorobenzyl alcohol (Scheme 1). The reaction is catalyzed by K_2CO_3 in dimethylformamide (DMF). This reaction has been used in the preparation of a variety of ether- or thioether-substituted phthalonitriles [35–37]. Conversion of **3** into phthalocyanine was accomplished through the usual cyclotetramerization reactions in the presence of a reductant and/or metal salt, i.e. hydroquinone was used to obtain the metal-free derivative **4**, while the metal salt [$Zn(OAc)_2$, $NiCl_2$ or $CoCl_2$] and a suitable solvent, such as DMF or ethylene glycol were required for the metal phthalocyanines **5**, **6** and **7**. The tetra-substituted phthalocyanines obtained by the cyclotetramerization of mono-substituted phthalonitrile derivatives naturally exist as four structural isomers [1], but the isolation and characterization of all four of them are hardly possible [1,38,39]. Our attempts to separate these isomers by chromatographic techniques in this study have been unsuccessful. Characterization of the products involved combination of elemental analysis and spectroscopic data (UV–vis, FT-IR, ^1H NMR, ^{19}F NMR and mass spectroscopy). Spectral investigations for all the new products were consistent with the assigned structures (Scheme 1).



Scheme 1.

The IR spectrum of **3** clearly indicates the presence of CN groups by the intense stretching bands at 2233 cm^{-1}. In the ^1H NMR analysis of **3** in deuterated acetone, the aromatic protons appear as a multiplet at 8.06–7.58 ppm and CH_2 protons of pentafluorobenzyl moieties at 5.52 ppm.

Cyclotetramerization of the dinitrile derivative was confirmed by the disappearance of the sharp C≡N vibration at 2233 cm^{-1}. The IR spectra of phthalocyanines **5**–**7** are very similar with the exception of the metal-free **4** showing an NH stretching band at 3290 cm^{-1} due to the inner core imino group. ^1H NMR investigations of phthalocyanines have provided the characteristic chemical shifts for the structures expected. The NH protons in the inner core of the metal-free phthalocyanine are also very well characterized by the ^1H NMR which shows a peak at δ −9.7 ppm as a result of the 18π-electron system of the phthalocyanine ring. The ^1H NMR spectra of metal-free (**4**), zinc(II) (**5**) and nickel(II) (**6**) phthalocyanines are almost identical, the only difference being the disappearance of the broad NH protons of **4**.

^{19}F NMR spectroscopy has been a very useful technique for investigating the fluorinated compound. ^{19}F NMR spectrum of ZnPc (**5**) showed three multiplets at −142.4 ppm, −151.2 ppm and −154.5 ppm, respectively, relative to the fluorine atoms in the *ortho*, *para* and *meta* positions of the phenyl substituents.

In the FAB mass spectra of compounds **4** and **7**, the presence of the characteristic molecular ion peaks at $m/z = 1299$ (**4**) and 1356 [M + 1] (**7**) confirmed the proposed structure.

The phthalocyanines **4**–**7** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–400 nm (B band) arising from the deeper π-levels → LUMO transition and the other in the visible part of the spectrum around 600–700 nm (Q band) attributed to the π–π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{-2} ring. Tetra-substitution with oxygen or sulfur bridged groups causes a shift of the intense Q band to longer wavelengths when compared with the unsubstituted derivatives [30,40,41]. On the other hand, 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 [16,18].

The metal-free phthalocyanine **4** showed the expected Q band splitting around 680 nm, and the split is about 40 nm, in accordance with the data of other substituted Pcs. The λ_{max} value of the fluorinated compounds [**4–7**] were slightly shifted to the shorter wavelengths. Compared with H_2Pc, the λ_{max} of the MPcs moved to shorter wavelengths and decreased in the order ZnPc, NiPc, CoPc, due to the nature of the central metal ion [16].

It is important to mention here that for certain technological applications solubility of phthalocyanines is important. It is well known that a mixture of different Pc compounds of similar structure is more soluble than a pure Pc material, due to disruption of aggregation phenomena [19]. The solubility of MPcs is also affected by the type of central metal ions and by the peripheral substituents. In case of electron-withdrawing peripheral fluorine substituents, phthalocyanines show a high solubility even in polar, aprotic organic solvents [16,42]. In parallel with the findings reported for the earlier examples of fluorinated phthalocyanine derivatives, the most obvious feature of newly synthesized phthalocyanines **4–7** is their solubility in various solvents such as toluene, chloroform, THF and acetone. Consequently, phthalocyanines reported here can be proposed as active for catalytic and photosensor applications in homogeneous media.

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