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Synthesis and properties of some novel soluble metallophthalocyanines containing the 3-triflurومethylphenyoxy moiety

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Abstract

Some new tetrakis(3-trifluoromethylphenoxy)phthalocyanine complexes with cobalt, nickel or zinc were synthesized and their structures were confirmed by IR, UV–vis, ^{1}H NMR and elemental analysis. These compounds are soluble in weakly and medium polar solvents, but their solubility in strong polar solvents such as DMF and DMSO is fairly low. It was found that the introduction of trifluoromethylphenoxy subtituents greatly affected their spectroscopic properties. The redox peaks of cyclic voltammograms possess good symmetric characteristics, indicating that they are good electron donors, and their electrochemical process is quasireversible with the introduced fluorine group.

Keywords: Phthalocyanine derivatives; Trifluorophenoxy substituent; Synthesis; Solubility; UV–vis spectra; Electrochemical property

1. Introduction

For many years, phthalocyanine compounds (Pcs) have been widely used in the area of organic pigments and dyestuffs. Besides the application in traditional area, Pcs have recently been used as optical storage media in compact discs and as photoconducting medium in photocopying machines [1]. Their exceptionally high thermal and chemical stability have provoked research in other fields [2], including photocatalysis, electrocatalysis and as chemical sensors, semiconductors, nonlinear optical (NLO) devices, photodynamic therapy (PDT) [3–6]. The solubility of Pcs becomes very important for these applications, since many Pcs are poorly soluble in organic solvents and water, because Pcs are both large and flat, which make the molecules stack easily.

In order to improve the solubility of Pcs, it is important to reduce its stacking propensity. The solubility of Pcs can be enhanced by introducing different kinds of solubility-enhancing substituents at the peripheral and axial positions of the Pcs ring. For example, the introduction of lipophilic alkyl, alkoxy, phenoxy [7,8] groups makes it impossible for Pcs to form dimers because of steric hindrance, which thus makes the Pcs more soluble in organic solvents. The introduction of carboxy

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[9] or sulfonyl [10] groups in peripheral positions provide water-soluble products; peripherally substituted Pcs were widely investigated recently [1–10]. Although phthalocyanines carrying electron-donating substituents have frequently been described, those with electron-withdrawing groups have not been extensively studied, especially those containing fluorine atoms. Recently, several workers [3,5,11] reported the syntheses and properties of some fluoroalkoxy substituted Pcs. In the case of electron-withdrawing peripheral fluorine substituents, Pcs can dissolve even in polar, aprotic solvents and become good electron donors for use as chemical sensors. This paper concerns some new phthalocyanine derivatives substituted by the 3-trifluoromethylphenoxy group (Fig. 1); their spectral and electrochemical properties are also discussed.

2. Experimental

2.1. Materials and methods of characterization

4-Nitrophthalonitrile was prepared and purified according to the methods described in the literature [12]. Other reagents were commercially available and were used without further purification unless otherwise noted. All solvents were of reagent grade and were dried over a 4A molecular sieve and were distilled before use.

All melting points were determined using a Yanaco Mp-500. Elemental analyses were carried out using a Perkin-Elmer2400 analyzer, IR spectra were measured in KBr on a PARAGN1000 FT-IR spectrometer and electronic spectra were recorded on a LAMBDA20/2.0 spectrometer. ^1H NMR was obtained in $CDCl_3$ using a Gemini-2000 analyzer (300MHz, Varian Ltd.).

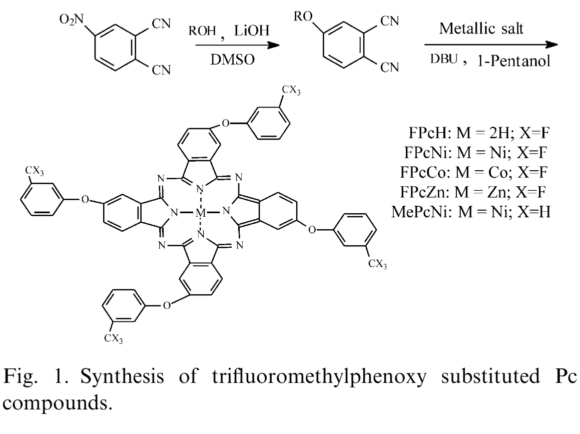

Fig. 1. Synthesis of trifluoromethylphenoxy substituted Pc compounds.

Cyclic voltammograms were carried out using a Model 273A Potentiostad-Galvanostat analyzer (EG&G PARC) at room temperature in DMF containing a 0.1 mol dm^{-1} solution of tetrabutylanmonium perchlorate (TBAP) as supporting electrolyte. The working and counter electrodes were platinum wires and the reference electrode was a saturated calomel electrode (SCE); the diameter of the working electrode was 3 mm. Before measurement, the solution was deoxygenated by nitrogen gas bubbling for ten minutes.

2.2. Synthesis of 4-(3-trifluoromethylphenoxy)-phthalonitrile (I)

4-Nitrophthalonitrile (3.46 g, 0.02 mol) and 3-trifluoromethylphenol (3.16 g, 0.02 mol) were dissolved in 100 ml dry dimethylsulphoxide (DMSO) at room temperature. In a nitrogen atmosphere, the reaction mixture was stirred and 1.00 g (0.041 mol) of anhydrous lithium hydroxide was added over 3 h. The mixture was then stirred for 48 h. The reactant was slowly added into rapidly stirred water (400 ml) with the temperature kept below 15 °C. After the suspension had settled for 8 h, the product was collected by vacuum filtration and washed with water until the filtrate became neutral. The crude product was recrystallized twice from methanol yielding large needles and gave 3.93 g (68%) of the product: mp 103–104 °C. IR (cm^{-1}): 3075–3000 (Ar, H), 2230 (C≡N), 1920, 1590, 1485, 1450, 1420, 1400 (C-F), 1320 (C-F), 1250 (Ar-O-Ar), 1200, 1130, 925, 755, 850. ^1H NMR ($CDCl_3$): δ 7.78–7.64 (m, 3H, H-$Ar(CN)_2$), δ 7.30 (m, 4H, H-$ArCF_3$). Elemental analysis: ($C_{15}H_7F_3N_2O$, FW 288) Calc: C 62.51, H 2.45, N 9.72; Found: C 62.38, H 2.51, N 9.66.

In order to compare the properties of the trifluoromethyl analogues with those not containing fluorine, the intermediate (4-(3-methylphenoxy)-phthalonitrile, II) of tetrakis(3-methylphenoxy)-phthalocyaninanickel (NiPcMe) was also synthesized using the method described for the preparation of I. Yield 65%, mp 84–85 °C. IR (cm^{-1}): 3085–3000 (Ar, H), 2985, 2940 2233 (C≡N), 1563, 1535, 1493, 1310, 1300, 1255 (Ar-O-Ar), 1165, 1129, 1092, 973, 853, 705. ^{1}H NMR ($CDCl_3$): δ 7.72–7.60 (m, 3H, H-Ar(CN)$_2$), δ 7.06 (m, 4H, H-ArCH$_3$), δ2.36 (s, 3H,-CH$_3$). Elemental analysis: ($C_{15}H_{10}N_2O$, FW 234) Calc: C 76.91, H 4.30, N 11.96; Found: C 76.48, H 4.22, N 12.04.

2.3. Preparation of tetrakis(3-trifluoromethylphenoxy)phthalocyaninanickel (NiPcF)

Phthalonitrile I (1.0 g, 3.5 mmol), 1-pentanol (20 ml) and 1,8-diazalicyclo[5.4.O]undec7-lne (DBU) (1.5ml) were mixed and homogenized. The mixture was stirred at 50 °C for 10 min in a nitrogen atmosphere and then 0.1g (0.8 mmol) of anhydrous nickel chloride was added. The suspension was slowly brought to boiling over 2 h and then refluxed for 40 h. The reactant was cooled to 60 °C and 50 ml of methanol was added. The deep blue product was filtered, washed with hydrochloric acid (5%, 150 ml) and then methanol (2×100 ml). The crude product was extracted with methanol in a Soxhlet extractor and purified by column chromatography (silica gel, toluene). The blue fraction was collected, evaporated under vacuum and dried in vacuo at 100 °C. Yield: 0.69 g (71%), deep blue powder. IR (cm^{-1}): 1610, 1592, 1491, 1450, 1414 (C-F), 1327 (C-F), 1282, 1245 (Ar-O-Ar), 1168, 1121, 1062, 1010, 960, 910, 895, 824, 792, 696, 654. ^{1}H NMR ($CDCl_3$): δ 7.2–7.55 (m, 28, Ar-H). Elemental analysis: ($C_{60}H_{28}F_{12}N_8NiO_4$, FW 1210) Calc: C 59.48, H 2.33, N 9.25; Found: C 59.38, H 2.36, N 9.13.

Other phthalocyanines were prepared using the method described for NiPcF. Tetrakis(3-trifluoromethylphenoxy)phthalocyanine (H_2PcF) (yield, 47%). IR (cm^{-1}): 3293 (N-H), 3080–3000, 1610, 1592, 1491, 1476, 1449, 1397 (C-F), 1328 (C-F), 1282, 1252 (Ar-O-Ar), 1169, 1121, 1090, 1010, 937, 825, 743, 654. Elemental analysis: ($C_{60}H_{30}F_{12}N_8O_4$, FW 1154) Calc: C 62.40, H 2.62, N 9.70; Found: C 62.48, H 2.57, N 9.65.

Tetrakis(3-methylphenoxy)phthalocyaninanickel (NiPcMe) (yield, 65%). IR (cm^{-1}): 2980–2870, 1611, 1590, 1487, 1477, 1417, 1245 (Ar-O-Ar), 1182, 1124, 1081, 1015, 963, 830, 768, 750, 702. Element analysis: ($C_{60}H_{40}N_8NiO_4$, FW 994) Cal: C 72.38, H 4.05, N 11.25; Found: C 72.35, H 4.09, 11.22.

Tetrakis(3 - trifluoromethylphenoxy)phthalocyaninacobalt (CoPcF) (yield, 42%). IR (cm^{-1}): 1654, 1610, 1591, 1490, 1449, 1408 (C-F), 1326 (C-F), 1281, 1234 (Ar-O-Ar), 1168, 1123, 1062, 975, 909, 825, 793, 696, 654. Element analysis: ($C_{60}H_{28}CoF_{12}N_8O_4$, FW 1211) Cal: C 59.47, H 2.33, N 9.25; Found: C 59.44, H 2.23, N 9.15.

Tetrakis(3 - trifluoromethylphenoxy)phthalocyaninazinc (ZnPcF) (yield, 51%). IR (cm^{-1}): 1654, 1609, 1489, 1449, 1396 (C-F), 1327 (C-F), 1282, 1231, 1170, 1124, 1064, 949, 918, 897, 794, 697, 656. Element analysis: ($C_{60}H_{28}F_{12}N_8O_4Zn$, FW 1216) C 59.15, H 2.32, N 9.20; Found: C 59.10, H 2.31, N 9.18.

3. Results and discussion

3.1. Synthesis

Nucleophilic substitution of 3 (or 4)-nitrophthalonitrile has been used to synthesis 3 (or 4)-alkoxy (or phenoxy) substituted phthalonitrile [2,10]. The reaction is usually catalyzed by K_2CO_3 in dimethlsulfoxide (DMSO). According to the literature [12], we used LiOH as the catalyst in DMSO and found the yield was moderate. The peripherally substituted Pcs were prepared from the phthalonitrile derivative and corresponding anhydrous metal chloride (or acetate), catalyzed by DBU in anhydrous solvent of 1-pentanol. The reaction conditions were mild and the yield was much higher than that obtained using other methods; however, the yield was found to depend on the central metal ion. The shortcoming of this method was that the reaction time was very long. This procedure yields a mixture of 4 geometric isomers with a 3-trifluoromethlphenoxy group at the 2- or 3-position of each ring in the phthalocyanine molecule. The isomers were not separated by chromatography. Elemental analysis and spectroscopic dada (IR, ^{1}HNMR and UV–VIS) confirmed the assigned structures of the compounds.

3.2. Solubility

It is anticipated that the introduction of a trifluoromethlphenoxy group into the peripheral

Table 1
Visible absorption data of the compounds in THF

Compound	Concentration (mol dm^{-1}×10^{-6})	Wavelength (nm)/ molar absorbtivity (log ε)	
H_2PcF	10.23	696 (5.13), 661 (5.09)	603 (4.50)
	1.27	696 (5.20), 662 (5.19)	603 (4.56)
	0.51	696 (5.19), 660 (5.15), 638 (4.69)	603 (4.50)
CoPcF	10.65	660 (5.09),	598 (4.50)
	1.32	663 (5.15),	603 (4.56)
	0.53	661 (5.06),	597 (4.42)
NiPcF	21.40	667 (5.00),	603 (4.64)
	1.71	667 (5.29),	602 (4.62)
	0.80	668 (5.35),	602 (4.67)
NiPcMe	11.05	669 (5.08),	606 (4.54)
	1.13	669 (5.36),	605 (4.73)
	0.55	670 (5.24),	603 (4.58)
ZnPcF	11.13	671 (5.40),	606 (4.64)
	1.42	672 (5.48),	606 (4.68)
	0.57	668 (5.50),	606 (4.77)

position of phthalocyanines will impart high solubility in organic solvents. The increased solubility might be due to the higher solubility of fluoroalky-substituted dyes in organic polar solvents [13] and the steric hindrance of peripheral 3-trifluoromethlphenoxy substituents makes it impossible to form dimers of the MPcF (M = H, Ni, Co, Zn) molecules (see Fig. 1). The MPcF shows high solubility in weakly and medium polar solvents such as benzene, toluene, chloroform, ethyl acetate and tetrahydrofuran (THF), but its solubility decreases in strongly polar solvents such as DMSO and DMF. The solubility of MPcF is also affected by the central metal ions; NiPcF shows a lower solubility than those of CoPcF and ZnPcF in polar solvents, but their solubility has not much difference in less polar solvents. In the case of the introduced fluorine group, NiPcF is more soluble in polar solvents than is NiPcMe, this finding coinciding with that reported in the literature [3].

3.3. Absorption spectrum

The characteristic UV–vis absorption spectra of the compounds are shown in Table 1; there are usually two peaks for phthalocyanine derivatives, one (600–630 nm) representing the absorption of the aggregate of the molecules, and the other one (660–700 nm) representing the absorption of the monomeric molecule. The hydrogen Pc (H_2PcF) showed the expected Q band splitting at around 680 nm, and the split is about 30 nm, in accordance with the data of other substituted Pcs, [5,12]. The λ_{max} of the fluorinated compound (NiPcF) was slightly shifted to shorter wavelengths compared with NiPcMe, due to the

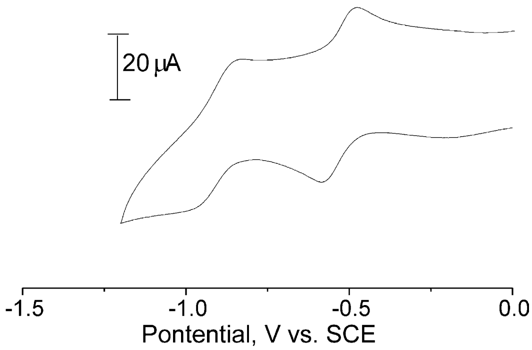

Fig. 2. Cyclic voltammogram of H_2PcF at 50 mv s^{-1} ($C = 4.62\times10^{-4}$ mol dm^{-1}).

Table 2
Reduction and oxidation potential of the compounds

Compound	Potential V (vs SCE)			
	Reduction		Oxidation	
H_2PcF	−0.9646,	−0.5857	−0.8531,	−0.4892
CoPcF	−0.9247,	−0.2812	−0.5360,	−0.0680
NiPcF	−0.8356,	−0.3439	−0.6475,	−0.2016
NiPcMe		−0.3629[a]		−0.559[a]
ZnPcF	−0.8264		−0.7356	

[a] Irreversible peak.

electron-withdrawing effect of the fluorine atoms in the phenoxy substituents. Compared with H_2PcF, the λ_{max} of the metallo Pcs moved to shorter wavelengths and decreased in the order ZnPcF, NiPcF, CoFcF, because of the difference in the electron-withdrawing ability of the central metal ion. The effect of dilution on the spectrum of these compounds is shown in Table 1. An increase in concentration resulted in a decline of the λ_{max} and the molar absorption coefficient possibly due to a strong tendency of the phthalocyanine molecules to dimerise at high concentration.

3.4. Electrochemical character

The cyclic voltamamogram (CV) of H_2PcF is shown in Fig. 2. The reduction and oxidation potentials of all Pcs from their CVs are summarized in Table 2. The redox peaks are in totally symmetry, which proves that MPcF is a good electron donor. It also can be concluded that the electrochemical process is quasireversible, except in the case of NiPcMe. The electrons are added to the orbital of the phthalocyanine ring or central metal depending on the redox potential [9]. According to the literature [9,14], the cathodic waves in each CV can be proposed as follows: the first is the reduction of the ring π-system ($\mathrm{Pc}/\mathrm{Pc}^{-}$) while the second is the reduction of $\mathrm{Pc}^{-}/\mathrm{Pc}^{2-}$. The potentials for both reductions are affected by the respective substituent and the central metal in the ligand. Trifluoromethylphenoxy is an electron-withdrawing group, and so is expected to reduce the electron charge in the phthalocyanine ring and the first reduction potential of its derivatives is higher than that of methylphenoxy (NiPcMe −0.3629, NiPcF −0.3439). The reduction potential of H_2PcF is negative, compared with the metallophthalocyanines (CoPcF, NiPcF, ZnPcF); because the metallic ions draw the electrons away from the phthalocyanine ring. With the difference of the electron-withdrawing ability of the central metal, the reduction potential of CoPcF is lower than that of NiPcF, ZnPcF, while NiPcF's is lower than that of ZnPcF.

4. Uncited references

[13,14]

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