



Synthesis and characterization of new polyfluorinated dendrimeric phthalocyanines

Mukaddes Özçeşmeci, İbrahim Özçeşmeci, Esin Hamuryudan*

Department of Chemistry, Istanbul Technical University, Maslak TR34469, Istanbul, Turkey

ARTICLE INFO

Article history:

Received 29 April 2010

Accepted 23 June 2010

Available online 1 July 2010

Keywords:

Fluorinated
Phthalocyanines
Benzyloxy groups
Aggregation
Energy transfer

ABSTRACT

The synthesis of new polyfluorinated dendrimeric metallophthalocyanines (M = Zn, Ni, Co) bearing 3,5-bis(2',3',4',5',6'-pentafluorobenzyloxy)benzyloxy moieties (**2–4**) was achieved by cyclotetramerization of phthalonitrile derivative **1** in the presence of zinc, nickel or cobalt salts in DMF. All the target phthalocyanines were separated by column chromatography and their spectroscopic, fluorescence and energy transfer properties, and aggregation behavior were investigated in different solvents and at different concentrations in chloroform. The compounds were characterized by Fourier transform-infrared, fluorine, proton and carbon nuclear magnetic resonance, mass, ultraviolet–visible and fluorescence spectral data. The phthalocyanines (**2–4**) were extremely soluble in various organic solvents, such as tetrahydrofuran, acetone and dichloromethane.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) have a two-dimensional 18 π -electron conjugated system thereby allowing the incorporation of more than 70 different metal or non-metal ions into their inner core. Modifications in the macrocycle can be made either by introduction of different central ions or by substitution of functional groups at the peripheral sites of the ring. During recent decades, metal phthalocyanines have found widespread application not only as pigments and dyes but also as chemical sensors, liquid crystals, Langmuir–Blodgett films, catalysts, non-linear optical materials, optical data storage materials, carrier generation materials in near-IR and also in medicine [1–5]. For such applications, good solubility is preferred. A critical disadvantage of unsubstituted Pcs is their low solubility in organic solvents or water. By appropriate substitution with bulky or long-chain groups in the peripheral positions of the macrocycle, these compounds can be solubilized in common organic solvents, thus increasing the field of possible applications [6–14].

Redox-active d-metal (e.g. Fe, Mn, Co) phthalocyanines exhibit very high catalytic activity in the oxidation of thiols, hydrocarbons, hydroquinones, arenes and amines [15–18]. The most promising way to increase the first oxidation potential of phthalocyanine complexes is the introduction of electron-withdrawing substituents. It has been shown that halogenated metallo tetrapyrrole derivatives are very efficient catalysts for oxidation reactions under very mild conditions [19,20].

Fluorinated metal phthalocyanines and porphyrins currently receive a great deal of attention due to their interesting electron-transfer, photosensitizing properties, along with magnetic and thermal characteristics [21–24]. The presence of pentafluorophenyl groups on the macrocycle ring can increase the catalytic activity and stability [25]. Fluoro-substituted phthalocyanines are known for their high solubility, even in polar, aprotic solvents. The increased solubility may be due to fluorine, which has the highest electronegativity of all elements [26].

In our previous studies, we have reported the synthesis, electrochemical and spectroelectrochemical properties of symmetric and asymmetric phthalocyanines [27–33]. In this step, our aim has been to design new molecules with dendritic fluoro-substituents, enhancing their solubility in common solvents and at the same time prohibiting their aggregation. We report herein the synthesis, characterization, fluorescence and energy transfer properties of new readily soluble metal phthalocyanines with up to 40 fluorine-containing substituents on the periphery for the first time, and we also report on the effects of the substituents on the spectroscopic and aggregation properties of the phthalocyanine derivatives in different solvents and at different concentrations in chloroform.

2. Experimental

The IR spectra were recorded on a Perkin–Elmer Spectrum One-IR spectrometer and the electronic spectra were recorded on a Scinco Neosys-2000 double-beam ultraviolet–visible (UV–Vis) spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Cary eclipse fluorescence

* Corresponding author. Tel.: +90 2122856826; fax: +90 2122856386.
E-mail address: esin@itu.edu.tr (E. Hamuryudan).

spectrofluorimeter. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TÜBİTAK Marmara Research Centre. ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as an internal reference. ^{19}F NMR and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz NMR. Mass spectra were performed on Varian 711 and Bruker microflex LT MALDI-TOF MS mass spectrometers. All the reagents and solvents were of reagent grade quality obtained from commercial suppliers. All the solvents were dried and purified according to Ref. [34]. The homogeneity of the products was tested in each step by TLC (SiO_2). 4-Nitrophthalonitrile and 3,5-bis(pentafluorobenzyloxy)benzyl alcohol were synthesized according to published methods [35,36].

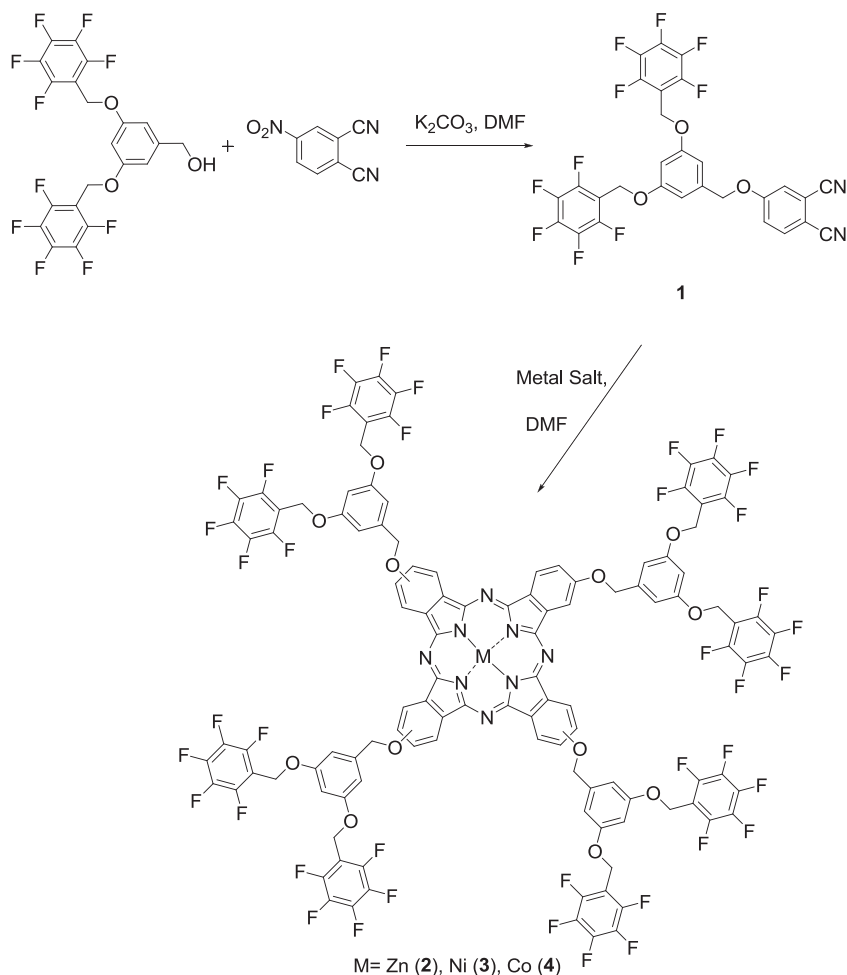
2.1. 4-[3,5-Bis(2',3',4',5',6'-pentafluorobenzyloxy)-benzyloxy]phthalonitrile (**1**)

3,5-Bis(2',3',4',5',6'-pentafluorobenzyloxy)benzyl alcohol (1.446 g, 2.890 mmol) and 4-nitrophthalonitrile (0.500 g, 2.890 mmol) were dissolved in 15 mL of dry DMF. Anhydrous K_2CO_3 (0.800 g, 5.780 mmol) was added portion wise for over 2 h and the mixture was stirred vigorously at room temperature under N_2 for 24 h. Then the solution was poured into ice-water (200 mL). The residue that formed was filtered off, washed with water several times until the filtrate was neutral, and then with cold methanol, and dried *in vacuo*. A pale beige product was purified by chromatography

on silica gel using hexane/chloroform (100:1) to give phthalonitrile derivative (**1**) (Scheme 1). Yield: 0.977 g (54%). Elemental analysis, *Anal. Calc.* for $\text{C}_{29}\text{H}_{12}\text{F}_{10}\text{N}_2\text{O}_3$: C, 55.60; H, 1.93; N, 4.47. Found: C, 55.83; H, 2.05; N, 4.62%. IR $\nu_{\text{max}}/\text{cm}^{-1}$: 2964–2855 (alkyl CH), 2227 ($\text{C}\equiv\text{N}$), 1255 ($\text{C}-\text{O}-\text{C}$). ^1H NMR (CDCl_3), (δ , ppm): 7.73 (d, H, Ar-H), 7.26 (d, H, Ar-H), 7.22 (s, H, Ar-H), 6.65 (s, 2H, Ar-H), 6.56 (s, H, Ar-H), 5.11 (s, 6H, CH_2). ^{19}F NMR (CDCl_3), (δ , ppm): -144.8 (d(d), 4F, *o*-fluorine), -154.6 (t, 2F, *p*-fluorine), -163.8 (m, 4F, *m*-fluorine). ^{13}C NMR (CDCl_3), (δ , ppm): 161.69 (aromatic C-O), 159.84 (aromatic C-O), 147.03 (aromatic C-F), 146.03 (aromatic C), 145.02 (aromatic C-F), 137.79 (aromatic C-F), 135.51 (aromatic C-H), 120.15 (aromatic C-H), 119.89 (aromatic C-H), 117.86 (aromatic C), 115.69 ($\text{C}\equiv\text{N}$), 115.34 ($\text{C}\equiv\text{N}$), 109.92 (aromatic C-H), 108.20 (aromatic C), 107.17 (aromatic C-H), 102.39 (aromatic C-H), 70.75 (OCH_2), 57.88 (OCH_2). MS (ESI⁺), (*m/z*): 626.50 [*M*]⁺.

2.2. {2,9(10),16(17),23(24)-Tetrakis-[3,5-bis(2',3',4',5',6'-pentafluorobenzyloxy)benzyloxy]phthalocyaninato}metal derivatives (**2–4**)

A mixture of compound **1** (0.300 g, 0.480 mmol) and 0.125 mmol anhydrous metal salt (zinc acetate 0.023 g, cobalt chloride 0.0163 g or nickel chloride 0.0163 g) and dry DMF (1.5 mL) was placed under nitrogen atmosphere in a standard sealed tube. The reaction mixture was heated and stirred at 150 °C under N_2 for 48 h. After cooling to room temperature, the green mixture that formed was poured into ice-water (100 mL).



Scheme 1. The synthesis of phthalonitrile derivative **1** and phthalocyanine complexes **2–4**.

Download English Version:

<https://daneshyari.com/en/article/1338808>

Download Persian Version:

<https://daneshyari.com/article/1338808>

[Daneshyari.com](https://daneshyari.com)