



Microwave-assisted synthesis, electrochemistry and spectroelectrochemistry of amphiphilic phthalocyanines



Emre Güzel^{a,b}, Atif Koca^c, Ahmet Gül^a, Makbule Burkut Koçak^{a,*}

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

^b Department of Chemistry, Sakarya University, TR54187 Serdivan, Sakarya, Turkey

^c Chemical Engineering Department, Marmara University, 34722 Göztepe, Istanbul, Turkey

ARTICLE INFO

Article history:

Received 1 October 2014

Received in revised form 19 November 2014

Accepted 25 November 2014

Available online 18 December 2014

Keywords:

Metallophthalocyanines

Hexadeca-substitution

Amphiphilic

Microwave irradiation

Electrochemistry

Spectroelectrochemistry

ABSTRACT

Novel hexadeca-substituted metallophthalocyanines (M = Cu, Ni, In) carrying eight hexyloxy groups on non-peripheral positions together with four chloro and four *p*-sulphonylphenoxy groups on peripheral positions have been synthesized by using microwave irradiation. All newly synthesized amphiphilic phthalocyanine complexes have been characterized by using elemental analysis, Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, mass and UV–vis spectroscopy techniques. The electrochemical behavior of the phthalocyanines was investigated by cyclic voltammetry and square wave voltammetry on a platinum-working electrode. While all complexes gave common phthalocyanine ring-based electron transfer processes, changing the metal center especially affected the aggregation and chemical stabilities of the complexes during the redox reactions. Aggregation tendency of copper phthalocyanine was also studied in methanol and no aggregation was observed in the concentration range from 2×10^{-6} to 12×10^{-6} mol dm⁻³.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) and their metallated congeners have attracted considerable interest in recent years because of their unique optical, electronic, catalytic and structural properties [1–4]. Traditionally, phthalocyanines have been used as dyes and pigments [4] but recently they have found wide applications in the different scientific and technological areas [1] such as catalysis [5], liquid crystals [6,7] chemical sensors [1,8], photodynamic therapy of cancer [9] solar energy conversion [10] nonlinear optics [3,11] optical data storage [12] and semiconductors [13].

Because of the π stacking (aggregation) between planar macrocycles, unsubstituted phthalocyanines are insoluble or slightly soluble in common organic solvents and water, thereby limiting their applications. Adding functional substituents on the periphery (β) or nonperiphery (α) of the macrocycles and axial substituents at the metal ion enhances their solubility in various solvents, since these substituents increase the distance between the 18- π electron conjugated systems of Pcs and make solvation applicable. While peripheral or nonperipheral substitution with alkyl, alkoxy, alkylthio, phenoxy, ester groups of different chain

lengths or macrocyclic groups leads to phthalocyanine products soluble in nonpolar solvents [14–22], the incorporation of carboxyl, sulfonyl or amino groups results in water-soluble metallophthalocyanine derivatives [23–27]. However, the solubility in water can be accomplished only within certain pH ranges with these substituents. By quaternizing amino or aza groups of the substituents, products soluble in water over a wide pH range were obtained [28–33].

The solubility, electronic and spectroscopic properties of the phthalocyanines do not only depend on the size and nature of the substituents but also depend on their positions (*i.e.*, non-peripherally, peripherally and axially). Placing electron-donating substituents at the nonperipheral positions (1, 4, 8, 11, 15, 18, 22 and 25) of the phthalocyanine ring result in a shift of the Q-band toward the near-IR region. Substitution at the more sterically crowded non-peripheral positions reduces aggregation tendencies more than substitution at peripheral positions [1,34,35]. Axial ligands in MPCs are also useful in preventing or minimizing intermolecular interactions which result in aggregation in solution [36]. It has long been known that tetrasubstituted phthalocyanines are more soluble than the corresponding octa-substituted Pcs with identical substituents due to the formation of four constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [32,33,37].

* Corresponding author. Tel.: +90 212 285 69 64; fax: +90 212 285 63 86.
E-mail address: mkokak@itu.edu.tr (M.B. Koçak).

Phthalocyanine derivatives exhibit maximum absorption in the red/far-red range between 600 and 800 nm, and have a great penetration into the tissues and a long triplet lifetime, and high singlet oxygen quantum yields. Closed shell diamagnetic ions such as Zn^{2+} , Al^{3+} , Ga^{3+} , In^{3+} and Si^{4+} , give phthalocyanine complexes with both high triplet yields and long lifetimes which are useful for PDT studies. Among these compounds, amphiphilic phthalocyanines are the most promising photosensitizers [38–40]. Sulfonated phthalocyanines with diamagnetic ions in the inner core have attracted considerable attention as second-generation photosensitizers for treatment of malignant tumors by photodynamic therapy (PDT) in the recent decades [40,41].

Rapid synthesis of phthalocyanines with microwave irradiation has attracted much attention in recent years with respect to long reaction times and very high temperatures required in traditional synthetic routes to phthalocyanines [42,43]. For this response, in a recent work, we have described microwave-assisted synthesis and *in vitro* PDT activity of a new hexadeca substituted zinc phthalocyanine bearing *p*-sulphonylphenoxy groups on peripheral positions [26]. In the present paper, to ensure the continuity of our previous studies, we have aimed to synthesize a new class of phthalocyanines with hexyloxy groups in non-peripheral and *p*-sulphonylphenoxy and chloro groups in peripheral positions and to investigate their electrochemical and spectroelectrochemical properties.

2. Experimental

2.1. Chemicals and instrumentation

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Scinco S-3100 spectrophotometer. 1H -NMR spectra were recorded on Agilent VNMRS 500 MHz and the spectrum was referenced internally by using the residual solvent resonances ($\delta = 2.49$ ppm for DMSO- d_6 and $\delta = 7.26$ for $CDCl_3$ in 1H NMR). Mass spectra were measured on a Micromass Quatro LC/Ultima LC-MS/MS spectrometer. Single mode reactor (CEM DISCOVER SP) were used for microwave heating. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC. The solvents were stored over molecular sieves. 4-(2-chloro-4,5-dicyano-3,6-bis(hexyloxy)phenoxy)benzenesulfonic acid (**1**) was prepared according to reported procedure [26].

2.2. Electrochemical, in situ spectroelectrochemical and in situ electrocolorimetric measurements

All electrochemical measurements were carried out with Gamry Reference 600 potentiostat/galvanostat. A three-electrode configuration was utilized with a Pt disc working electrode (surface area: 0.071 cm^2), a Pt wire counter electrode and saturated calomel reference electrode (SCE). Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dimethylsulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3} .

An OceanOptics QE65000 diode array spectrophotometer was used for UV-vis absorption spectra and chromaticity diagram measurements. *In situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of quartz thin-layer spectroelectrochemical cell consisting a Pt tulle working electrode, a Pt wire counter electrode, and a SCE reference electrode. *In situ* electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement

mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell.

2.3. Synthesis

2.3.1. General procedures for phthalocyanine derivatives

Reaction: A mixture of **1** (0.100 g, 0.187 mmol), 0.235 mmol anhydrous metal salts [$NiCl_2$, 0.030 g; $CuCl_2$, 0.031 g; $InCl_3$, 0.050 g] and an catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in *n*-pentanol (2 mL) was irradiated with microwave (300 W) at 140°C in a sealed glass tube for 25 min under a nitrogen atmosphere. **Work up:** after cooling to room temperature, the green mixture was precipitated by adding diethyl ether and it was filtered. 5.0 mL of acetic acid was poured into the product and it was stirred for 15 min and again precipitated with diethyl ether. **Purification:** (If different it is indicated.) the purification of the crude product was performed in two steps: first, column chromatography by using silica gel as stationary phase and methanol as eluent. Then preparative chromatography was applied by using silica gel as stationary phase and 2/3 DCM/ethanol as eluent giving pure compounds as an isomeric mixture. **Solubility:** extremely soluble in methanol, ethanol, DMF and DMSO.

2.3.2. 2,9(10), 16(17), 23(24)-tetra-chloro1,4,8,11,15,18,22,25-octahexyloxy 3,9(10), 16(17), 23(24)-tetra-(4-sulfonylphenoxy) phthalocyaninatonicel(II) (**2**)

Yield: 0.090 g. 22%. m.p. $> 200^\circ\text{C}$, FT-IR, cm^{-1} 2945, 2935, 2872 (R-H), 1232, 1248 (R-O-Ar), 1544 (Ar); UV-vis λ_{max} (nm) methanol: 702, 339; 1H -NMR (250 MHz, DMSO- d_6): δ , ppm 7.60 (8H, b), 7.00 (8H, b), 4.74 (16H, b), 2.08–0.76 (88H, m), MALDI-TOF-MS m/z : 2221 $[M+Na]^+$. Anal. calc. for $C_{104}H_{124}N_8Cl_4O_{24}S_4Ni$ calculated %: C, 56.81; H, 5.68; N, 5.10; found %: C, 56.77; H, 5.76; N, 5.22.

2.3.3. 2,9(10), 16(17), 23(24)-tetra-chloro1,4,8,11,15,18,22,25-octahexyloxy 3,9(10), 16(17), 23(24)-tetra-(4-sulfonylphenoxy) phthalocyaninatocopper(II) (**3**)

Yield: 0.103 g. 25%. m.p. $> 200^\circ\text{C}$, FT-IR, cm^{-1} 2965, 2934, 2877 (R-H), 1240, 1246 (R-O-Ar), 1544 (Ar). UV-vis λ_{max} (nm) methanol: 704, 317; MALDI-TOF-MS m/z : 2204 $[M+H]^+$. Anal. calc. for $C_{104}H_{124}N_8Cl_4O_{24}S_4Cu$ calculated %: C, 56.68; H, 5.67; N, 5.08; found %: C, 56.98; H, 5.72; N, 5.16.

2.3.4. 2,9(10), 16(17), 23(24)-tetra-chloro1,4,8,11,15,18,22,25-octahexyloxy 3,9(10), 16(17), 23(24)-tetra-(4-sulfonylphenoxy) phthalocyaninatoindium(III) chloride (**4**)

Yield: 0.051 g. 12%. m.p. $> 200^\circ\text{C}$, FT-IR, cm^{-1} 2927, 2940, 2875 (R-H), 1232, 1240 (R-O-Ar), 1534 (Ar); UV-vis λ_{max} (nm) methanol: 337, 720. 1H -NMR (250 MHz, DMSO- d_6): δ , ppm 7.64 (8H, b), 7.06 (8H, b), 4.98 (16H, b), 2.13–0.81 (88H, m), MALDI-TOF-MS m/z : 2467 $[M-Cl+matrix+Na]^+$ (as a matrix α -cyano-4-hydroxycinnamic acid). Anal. calc. for $C_{104}H_{124}Cl_4InN_8O_{24}S_4$ calculated %: C, 54.53; H, 5.46; N, 4.89; found %: C, 53.98; H, 5.36; N, 4.96.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the phthalonitrile derivative bearing two hexyloxy groups on non-peripheral positions and *p*-sulfonylphenoxy and chloro groups on peripheral positions **1** was carried out by using the procedure previously presented [26]. Scheme 1 shows the synthetic procedure for the target amphiphilic phthalocyanine derivatives. Cyclotramerization of dinitrile derivative **1** in the

Download English Version:

<https://daneshyari.com/en/article/1440816>

Download Persian Version:

<https://daneshyari.com/article/1440816>

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