Journal of Molecular Structure 927 (2009) 126–128

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and characterization of new metallophthalocyanines with four phenoxyacetamide units

M. Salih Ağırtaş *, M. Sait Izgi

Department of Chemistry, Faculty of Art and Science, Kafkas University, 36200 Kars, Turkey

ARTICLE INFO

Article history:
Received 1 January 2009
Received in revised form 3 March 2009
Accepted 3 March 2009
Available online 13 March 2009

Keywords:
Phthalocyanines
Template effect
Magnesium
Zinc
Phenoxyacetamide
Synthesis

ABSTRACT

N-(4-(3,4-dicyanophenoxy)phenyl)acetamide was obtained through the displacement reaction of 4-nitrophthalonitrile with 4-acetamidophenol. The zinc(II) Phthalocyanine**(4)** was prepared by the reaction of the *N*-(4-(3,4-dicyanophenoxy)phenyl)acetamide with $ZnCl_2$ in dimethyl formamide (DMF). Magnesium (II) and nickel (II) phthalocyanines (**5, 6**) were prepared by the reaction of the *N*-(4-(3,4-dicyanophenoxy)phenyl)acetamide with $MgCl_2$, $NiCl_2$ salts without solvents at 300 °C. This newness on the periphery increased solubility compared to the unsubstituted phthalocyanines. These metallophthalocyanines are soluble in DMF, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), DMF/water (1/1). The structures of target compounds were confirmed by elemental analyses, IR, ^1H NMR, UV–vis spectra.

1. Introduction

4-Acetamidophenol (paracetamol, acetaminophen) is one of the most widely used anti-pyretic, analgesic compounds currently available. The drug is metabolized mainly in the liver, and the several end products have no harmful effects [1–2]. Phthalocyanines and their derivatives display interesting electrical and electrochemical properties which are important for applications in nanotechnology [3], catalysis [4], as electrochromic substances [5], as liquid crystals [6], nonlinear optics [7], industrial dyes and pigments [8], optical data storage [9], chemical sensors [10], and photodynamic therapy [11–14]. In the last few years, phthalocyanines, particularly the aluminum and zinc derivatives have been intensively studied as second-generation photosensitizers for photodynamic therapy (PDT) of cancer [15–16]. The family of functional phthalocyanines has been an interesting target for the development of further chemical reactions on phthalocyanine complexes [17]. In this paper we have, in particular, combined these functional materials into a single compound via synthetic methodology to obtained soluble phthalocyanines. Substituent groups have been previously used for the synthesis of phthalocyanines and a few references on the topic are available [18–22].

In the present paper we reported on the synthesis and characterization of the new metallophthalocyanines bearing four phenoxyacetamide substituents.

2. Experimental

Electronic spectra were recorded on a Perkin Elmer Lambda 25 UV/vis and Thermo Electron Corporation spectrophotometers. Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr pellets. ^1H NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer with tetramethylsilane as internal standard. Elemental analyses results were found in good agreement with calculated values. The starting material **2** was synthesized according to published procedures [23]. All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [24] the solvents were stored over molecular sieves (4 Å).

2.1. N-(4-(3,4-dicyanophenoxy)phenyl)acetamide (3)

4-Acetamidophenol (1.51 g, 0.01 mol) was dissolved in dimethyl formamide (DMF) (25 cm^3) under nitrogen and 4-nitro-1,2-dicyanobenzene (1.73 g, 0.01 mol) was added. After stirring for 15 min at room temperature, finely ground anhydrous potassium carbonate (5.2 g, 0.038 mol,) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 26 h. Then the mixture was

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* Corresponding author. Tel.: +90 474 212 11 32x3121; fax: +90 474 2122706.
E-mail address: salihagirtas@hotmail.com (M.S. Ağırtaş).

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doi:10.1016/j.molstruc.2009.03.011

poured into 400 ml ice–water, and precipitate was filtered off, washed with water and dried. The residue was recrystallized from ethanol.

The yield was 2.40 g (86, 6%). mp 236 °C. Calcd. for $C_{16}H_{11}N_3O_2$: C, 69,31; H, 4.00; N, 15.15%. Found: C, 69.35; H, 3.97; N, 15.13%. IR spectrum (cm^{-1}): 3296, 3068, 2227, 1666, 1611, 1592, 1557, 1493, 1309, 1247, 1197, 855, 846, 524. ^1H NMR (DMSO-d_6) δ, ppm: 8.04 (NH), 7.71–7.11 (Ar–H), 2.33 (CH_3).

2.2. Tetrakis [(phenoxyacetamide)-phthalocyaninato] zinc (4)

Compound[1] (0.138 g, 0.498 mmol) and $ZnCl_2$ (0.017 g) were dissolved in 1.5 mL of DMF. The reaction mixture was refluxed under nitrogen for 22 h. The product was precipitated by adding water. The precipitate was filtered and washed with water. The product was washed with $CHCl_3$, toluene, diethyl ether and dried. Compound **4** is soluble in THF, DMF, DMSO and DMF/water.

The yield of **4**: 0.085 g (58.6%). Calcd. for $C_{64}H_{44}N_{12}O_8Zn$: C, 65.45; H, 3.78; N, 14.31%. Found C, 65.40; H, 3.85; N, 14.28%. IR spectrum (cm^{-1}):3275, 1653, 1607, 1540, 1506, 1474, 1223, 1090, 1044, 945, 837, 746. UV–vis (DMF) λ_{max} nm (log ε): 355(3.86), 612(3.53), 679(4.24). ^1H NMR (DMSO-d_6) δ, ppm: 8.58 (NH), 7.80–7.02 (Ar–H), 2.83–2.12 (CH_3 protons).

2.3. Tetrakis [(phenoxyacetamide)-phthalocyaninato] magnesium (5)

Compound **1** (0.138 g, 0.498 mmol) and $MgCl_2 \cdot 6H_2O$ (0.020 g) were powdered in a quartz crucible and heated in a sealed glass tube for 7 min under nitrogen at 300 °C. After cooling to room temperature, a green-colored reaction product was obtained. The product was washed with EtOH, $CHCl_3$, and ethyl acetate. DMF (2 mL) was added to the residue in order to dissolve the product. The reaction mixture was precipitated by adding EtOH. The precipitate was filtered and washed with EtOH. Compound **5** is soluble in THF, DMF, DMSO and DMF/water.

The yield of **5**: 0.020 g (14.3%). Calcd. for $C_{64}H_{44}N_{12}O_8Mg$: C, 67.82; H, 3.91; N, 14.83%. Found C, 67.86; H, 3.95; N, 14.79%. IR spectrum (cm^{-1}):3393, 1654, 1506, 1314, 1233, 1084, 1043, 946,834,751. UV–vis (DMF) λ_{max} nm (log ε): 353(4.28), 614(3.76), 679(4.33). ^1H NMR (DMSO-d_6) δ, ppm: 7.79(NH), 7.67–7.13(Ar–H), 2.49–2.04(CH_3 protons).

2.4. Tetrakis [(phenoxyacetamide)-phthalocyaninato] nickel (6)

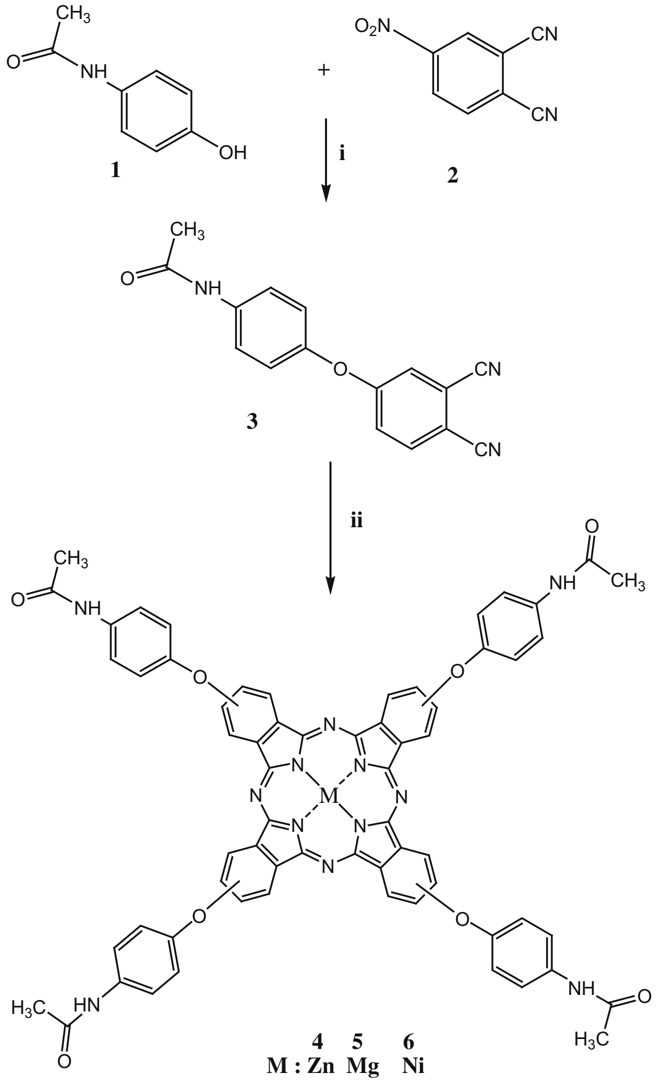
Compound **1** (0.138 g, 0.498 mmol) and $NiCl_2$ (0.017 g) were powdered in a quartz crucible and heated in a sealed glass tube for 5 min under nitrogen at 300 °C. After cooling to room temperature, a green-colored reaction product was obtained. The product was washed with EtOH, hot EtOH, and THF. DMF (2 mL) was added to the residue in order to dissolve the product. The reaction mixture was precipitated by adding ethyl acetate. The precipitate was filtered and washed with ethyl acetate. Compound **6** is soluble in THF, DMF, DMSO and DMF/water.

The yield of **6**: 0.021 g (14.5%). Calcd. for $C_{64}H_{44}N_{12}O_8Ni$: C, 65.82; H, 3.80; N, 14.39%. Found C, 65.83; H, 3.84; N, 14.35%. IR spectrum (cm^{-1}): 3421, 1607, 1506, 1473, 1406, 1317, 1238, 1121, 1093, 1060, 958, 839, 518. UV–vis (DMF) λ_{max} nm (log ε): 331(4.07), 629 (4.00), 672 (4.07).

3. Results and discussion

We reported on the preparation of a new phthalonitrile derivative (**3**) and conversion to metallophthalocyanines (**4–6**) that are soluble in solvents such as THF, DMSO, DMF (dimethyl formamide) and DMF/water (1/1). For this, the synthesis of *N*-(4-(3,4-dicyanophenoxy)phenyl)acetamide **3** was based on the reaction of 4-acetamidophenol with 4-nitrophthalonitrile (DMF in the presence of K_2CO_3 as base, at room temperature for 26 h) [23,25]. The phthalocyanine **4** was obtained by the reaction compound **3** with $ZnCl_2$ in DMF. The phthalocyanine **5, 6** were obtained by the reaction compound **3** with metal salts ($MgCl_2 \cdot 6H_2O$, $NiCl_2$) under nitrogen at 300 °C (Scheme 1). While compound **4** was obtained by high yield in DMF, **5, 6** compounds were not obtained by the reaction **3** with $MgCl_2 \cdot 6H_2O$, $NiCl_2$ in DMF. However, compounds **5, 6** were obtained directly from the reaction of phthalonitrile derivative with the appropriate metal salts. The effect of different metal ions differed in solvent under the same conditions. Thus, optimum reaction conditions of each metallophthalocyanine could be changed by solvent and the template effect. So, high yield of compound **4** can be attributed to the template effect of zinc. In this study, we tried the synthesis of phthalocyanines both with solvent and without solvent. We cited the best yielded results in the paper. For compound **4** the best results were obtained with solvent, whereas for compounds **5, 6** the best results were obtained without solvent.

Spectral data of the newly synthesized compounds are consistent with the proposed structures. Comparison of the IR spectral data



Scheme 1. Synthesis of compounds **3–6**. Reagents and conditions: (i) K_2CO_3, N_2, DMF, rt, 26 h; (ii) $ZnCl_2$, N_2, DMF, reflux temperature, 22 h; $MgCl_2 \cdot 6H_2O$, N_2 300 °C,7 min; $NiCl_2$, N_2, 300 °C, 5 min.

Table 1
UV–vis data for the phthalocyanines.

Compound	Solvent	λ_{max}/nm (logε/dm^3 mol^{-1} cm^{-1})
4	DMF	679 (4.24), 612 (3.53), 355 (3.86)
5	DMF	679 (4.33), 614 (3.76), 353 (4.28)
6	DMF	672 (4.07), 629 (4.00), 331 (4.07)

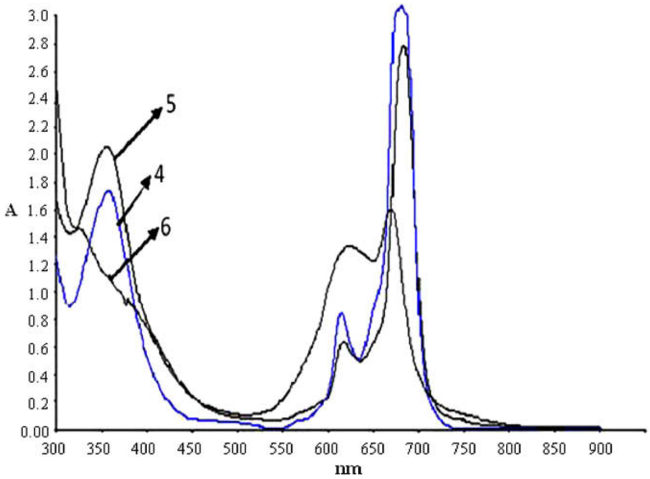


Fig. 1. Electronic spectra of **4–6** in DMF.

clearly indicated the formation of compound **3**, the appearance of new absorption bands at 3296 cm^{-1}(NH), 2227 cm^{-1}(C$\equiv$N), 1611–1557 cm^{-1}(C$=$C), 1247 cm^{-1}(Ar—O—Ar). After conversion of the compounds **3** into the phthalocyanines (**4–6**), the sharp peak for the C$\equiv$N vibration around 2227 cm^{-1} disappeared.

The ^{1}H NMR spectrum of **3** exhibited NH at 8.04, aromatic protons (Ar—H) at 7.71–7.11 ppm, at 2.33 ppm (CH$_3$). The ^{1}H NMR spectra of phthalocyanines **4–6** were almost identical except for small shift and in good correlation with the structures of the synthesized compounds.

The phthalocyanines **4–6** show typical electronic spectra with two strong absorption regions (Table 1), one of them in the UV region at about 300–350 nm (B band) and the other in the visible part of the spectrum around 600–700 nm (Q band). The UV–vis spectra of the phthalocyanine **4–6** in DMF showed characteristic Q band absorptions between 679–672 nm, which were attributed to the $\pi \rightarrow \pi*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands (B) in UV region at 355–331 nm were observed due to transition from the deeper π levels to the LUMO [26,27] (Fig. 1).

4. Conclusion

N-(4-(3,4-dicyanophenoxy)phenyl)acetamide was synthesized and used as a key compound for the preparation and characterization of novel metallophthalocyanines (Zn, Mg Ni,) with phenoxyacetamide substituents. All phthalocyanines (**4**–**6**) exhibited good solubility in THF, DMF, DMSO and DMF/water (1/1). Thus, choice of the most suitable substituent can be made based on solubility and membrane compatibility characteristics. In conclusion the novel Pcs reported in this study can be considered as efficient candidates in the case of photosensitizers used in photodynamic therapy.

Acknowledgements

The authors acknowledge Osman Ucuncu for his help in running the NMR and IR spectra, and Research Fund of the Kafkas University.

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