Synthesis, characterization and thermal behaviour of novel phthalocyanines bearing chalcone groups on peripheral positions

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A new nickel, zinc, cobalt, copper and metal-free phthalocyanine was synthesized by nucleophilic aromatic substitution reaction of (E)-3-(3-hydroxyphenyl)-1-phenylprop-2-en-1-one with 4-nitrophthalonitrile and cyclotetramerisation of (E)-4-(3-(3-oxo-3-phenylprop-1-enyl)phenoxy) phthalonitrile. The new compounds were characterized by a combination of IR, ¹H NMR, ¹³C NMR, UV-Vis, elemental analysis and MS spectral data. The thermal stabilities of the phthalocyanine compounds were determined by thermogravimetric analysis.

Keywords: Phthalocyanine; Macrocyclic; Phthalonitrile; Chalcone; Thermogravimetric Analysis.

INTRODUCTION

Phthalocyanines (Pcs) form nowadays an important group of organic compounds that belong to the most studied subjects of organic functional materials [1]. However, although no phthalocyanines have been identified in the nature yet, they were some of the first macrocycles that were synthesized and used as model compounds to mimic the biologically important porphyrines [2, 3]. Microwave irradiation is an important improvement in the synthesis of metallophthalocyanines. The most important industrial application of phthalocyanines is the formation of colored complexes with metal cations that are used as highly stable pigments and dyes [4]. In recent years, the applications of metallophthalocyanine (MPC) complexes have expanded to areas such as photosensitizers in photodynamic therapy, photoconducting agents in photocopying machines and electrocatalysts. In addition, they can find commercial applications as: photovoltaic materials in solar cells [5-7], systems for fabrication of light emitting diodes (LED) [8, 9], liquid crystalline [10] and non-linear optical materials [11, 12], sensitizers for photodynamic (PDT) cancer therapy [13, 14], photoconductors in xerography [15], dyes at recording layers for CD-R and DVD-R optical storage discs [16], as well as diverse catalytic systems [17, 18].

In medicine, phthalocyanines have been found to have applications as phototoxic drugs for photodynamic therapy [19-22]. Chalcones belong to the largest class of plant secondary metabolites, which, in many cases, serve in plant defense mechanisms to counteract reactive oxygen species (ROS) in order to survive and prevent molecular damage and damage by microorganisms, insects, and herbivores. They are known to possess antioxidant character of different extents [23].

Closed shell diamagnetic ions such as Zn²⁺, Al³⁺ and Ga³⁺ give phthalocyanine complexes with both high triplet yields and long lifetimes of the excited triplet state. Thus, these complexes are expected to exhibit strong photochemical and photodynamic activities due to a higher efficiency in generating reactive oxygen species than porphyrins [19].

Some studies showed that a convenient route for the synthesis of metal-free phthalocyanine (H₂Pc) from phthalonitrile and metallophthalocyanines from phthalonitrile, phthalimide and phthalic anhydride using hexamethyldisilazane (HMDS). In spite of the potential utility of this approach, reaction times necessary for these reactions are very long at relatively high temperature. For example, the reaction times are 10-24 h at 100-150 ºC when metal-free phthalocyanine is synthesized from phthalonitrile, 10-48 h at 150 ºC when metallophthalocyanines are synthesized from phthalimide or phthalic anhydride and 10-12 h at 100-125 ºC in the case of phthalonitrile [24, 25].

Microwave-promoted organic reactions are well known as environmentally benign methods that can accelerate a great number of chemical processes. In particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [26].

In this article, we describe the synthesis and characterization of metal-free phthalocyanine 4 in 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) and n-
pentanol in a Schlenk tube under N₂ and metallophthalocyanines 5-8 by microwave irradiation.

EXPERIMENTAL

All reactions were carried out under dry nitrogen atmosphere using standard Schlenk techniques. The IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer, using potassium bromide pellets. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl₃, and chemical shifts are reported (δ) relative to Me₄Si as internal standard. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. UV-visible absorption spectra were measured by a Unicam UV-visible spectrometer. Melting points were measured on an Electrothermal apparatus. Domestic oven (Arçelik MD 823, 350 W) was used for all syntheses of phthalocyanines. A Seiko II Exstar 6000 thermal analyzer was used to record the DTA curves under nitrogen atmosphere with a heating rate of 20 °C min⁻¹ in the temperature range of 30 to 900 °C using platinum crucibles. Domestic oven was used for all syntheses of phthalocyanines.

Synthesis of (E)-4-(3-(3-oxo-3-phenylprop-1-enyl)phenoxy)phthalonitrile (3)

(E)-3-(3-hydroxyphenyl)-1-phenylprop-2-en-1-one (1) [31]. (1 g, 4.46 mmol) was dissolved in dry DMF (15 ml) under N₂ atmosphere and 4-nitrophthalonitrile (2) (0.773 g, 4.46 mmol) was added to the solution. After stirring for 10 min finely ground anhydrous K₂CO₃ (3.07 g, 22.3 mmol) was added portionwise within 2 h under efficient stirring. The reaction mixture was then stirred under N₂ at 50 °C for 72 h. Then the solution was poured into ice-water (100 ml) and was stirred in the course of 1 day. The solid product was filtered, washed with water and dried in vacuo over P₂O₅. The obtained green solid was recrystallized from ethanol. Yield: 1.19 g (76 %), mp: 132 °C; ¹H NMR (CDCl₃, 200 MHz) δ: 8.02-7.10 (m, Ar-H, olefinic C-H); ¹³C NMR (CDCl₃, 200 MHz) δ: 190.29, 161.66, 154.34, 143.05, 138.07, 137.97, 135.80, 133.43, 131.53, 129.00, 128.79, 126.65, 123.84, 122.61, 121.89, 121.76, 120.25, 117.98, 109.43, 115.58, 115.14; IR (KBr) ν: 3076, 2927-2846, 1665, 1577, 1473, 1436, 1330, 1236, 1147, 1093, 1017, 977, 772, 689; MS (ES⁺) m/z: 350 [M⁺]. Anal. calcd for C₂₃H₁₄N₂O₂: C 78.84, H 4.03, N 8.00; found C 78.54, H 4.06, N 8.02.

Preparation of metal-free phthalocyanine (4)

(E)-4-(3-(3-oxo-3-phenylprop-1-enyl)phenoxy)phthalonitrile (3) (300 mg, 0.86 mmol), DBU (five drops) and dry n-pentanol (4 ml) were added in a Schlenk tube. The mixture was heated and stirred at 160 °C for 24 h under N₂. Thereafter the reaction mixture was cooled to 30 °C and precipitated by adding ethanol. The solid product was filtered and washed with ethanol. The green solid product was chromatographed on silica gel with chloroform/methanol (9:1) as an eluent. Yield: 48 mg (16 %), UV-vis (chloroform) λmax: 705(2.85), 669(2.79), 642(2.45), 605(2.25), 396(2.35), 341(2.68) nm; ¹H NMR (CDCl₃, 200 MHz) δ: 7.73-6.72 (m, Ar-H, olefinic C-H); ¹³C NMR (CDCl₃, 100 MHz) δ: 176.12, 172.22, 172.74, 163.30, 162.42, 157.28, 154.46, 146.21, 134.14, 131.12, 130.86, 127.94, 126.42, 124.31, 123.64, 122.89, 118.26, 116.42, 114.18; IR (KBr) ν: 3426, 3060, 2923-2853, 1662, 1571, 1464, 1376, 1269, 1119, 852, 750, 692; MS (ES⁺) m/z: 1404 [M⁺]. Anal. calcd for C₉₀H₅₇N₂₀C₈: H 4.13, N 7.98, found C 78.62, H 4.11, N 7.96.

Nickel (II) phthalocyanine (5)

A mixture of (E)-4-(3-(3-oxo-3-phenylprop-1-enyl)phenoxy)phthalonitrile (3) (200 mg, 0.57 mmol), anhydrous metal salt NiCl₂ (18.5 mg, 0.14 mmol), and 2-(dimethylamino)ethanol (3 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off and dried in vacuo over P₂O₅. The obtained green solid product was purified by column chromatography on silica gel with chloroform/methanol (5:1) as an eluent. Yield: 69 mg (33 %), UV-vis (chloroform) λmax: 678(2.88), 653(2.51), 436(2.57), 353(2.21) nm; ¹H NMR (CDCl₃, 200 MHz) δ: 7.90-6.32 (m, Ar-H, olefinic C-H); ¹³C NMR (CDCl₃, 100 MHz) δ: 199.44, 173.32, 168.71, 162.03, 156.41, 143.80, 142.99, 139.73, 138.06, 133.21, 128.79, 125.60, 124.29, 122.86, 119.99, 113.81, 113.08, 112.27, 111.86, 110.24, 107.59; IR (KBr) ν: 3060, 2927-2846, 1665, 1577, 1473, 1446, 1330, 1236, 1147, 1093, 1017, 977, 772, 689; MS (ES⁺) m/z: 1460 [M⁺]; Anal. calcd for Cₙ₀H₅₇N₂₀O₈Ni: C 75.60, H 3.83, N 7.67; found C 75.63, H 3.81, N 7.69.

Zinc (II) phthalocyanine (6)

A mixture of (E)-4-(3-(3-oxo-3-phenylprop-1-enyl)phenoxy)phthalonitrile (3) (200 mg, 0.57 mmol), anhydrous metal salt Zn(CH₃COO)₂ (29 mg, 0.14 mmol), and 2-(dimethylamino)ethanol (3
ml) was irradiated in a microwave oven at 175 °C, 350 W for 6 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off and dried in vacuo over P2O5. The obtained green solid product was purified from the column chromatography on silica gel with chloroform-methanol (6:1) as an eluent. Yield: 107 mg (51 %), UV-vis (chloroform) λmax: 682(3.12), 651(2.45), 400(2.99), 353(3.16) nm; 1H NMR (CDCl3, 200 MHz) δ: 7.98-6.87 (m, Ar-H, olefinic C-H); 13C NMR (CDCl3, 100 MHz) δ: 186.44, 174.23, 171.02, 166.88, 161.54, 157.44, 151.13, 146.97, 141.85, 132.72, 130.16, 129.58, 128.78, 124.88, 121.42, 120.13, 119.17, 118.42, 110.02, 105.00; IR (KBr) ν: 3061, 2927-2851, 1664, 1578, 1484, 1393, 1314, 1236, 1179, 1089, 1045, 977, 880, 773; MS (ES+) m/z: 1467 [M+1]+; Anal. calcd for C92H56N8O8Zn: C 75.26, H 3.82, N 7.63; found C 75.24, H 3.86, N 7.62.

RESULTS AND DISCUSSION

Synthesis of (E)-4-(3-(3-oxo-3-phenylprop-1-enyl)phenoxy) phthalonitrile 3 was carried out by the reaction of 4-nitrophthalonitrile (2) and (E)-3-(3-hydroxyphenyl)-1-phenylprop-2-en-1-one (1) in the presence of K2CO3 in dry DMF. Final purification of the phthalonitrile derivative 3 by recrystallization afforded 3 with satisfactory elemental analysis and mass spectral data. In the 1H-NMR spectrum of the phthalonitrile derivative 3, the OH group of compound 1 disappeared as expected. The disappearance of OH and the presence of C≡N functional group at 2227 cm\(^{-1}\) in the IR spectrum of compound 3 confirmed the formation of the desired compound 3. The 13C-NMR spectrum of the phthalonitrile derivative 3 indicated the presence of nitrile carbon atoms at 115.58, 115.14 (C≡N) ppm.

The metal-free phthalocyanine 4 was synthesized by heating a mixture of phthalonitrile derivative 3, DBU and dry n-pentanol in a Schlenk tube. The IR spectrum of the metal-free phthalocyanine 4 shows 3426 cm\(^{-1}\) (N-H) vibrations. The disappearance of the C≡N stretching vibration in the IR spectrum of phthalonitrile derivative 3 suggested the formation of compound 4. In the 1H-NMR spectrum of this compound 4 the inner core protons of Pe-2H could not be observed due to strong aggregation of molecules [27]. The mass spectrum of this compound at (m/z): 1404 [M+1]+ supports the proposed formula for this structure. The elemental analysis confirmed the structure of compound 4 (Fig. 1). The transition metal complexes were prepared from the phthalonitrile derivative 3 and the corresponding metal salt by microwave irradiation in 2-(dimethy lamino) ethanol at 175°C, 350 W. The IR spectra of the metal-free compound 4 and the metallophthalocyanine compounds 5-8 are very similar. The significant difference is the presence of (N-H) vibrations of the inner phthalocyanine core which are assigned to a weak band at 3426 cm\(^{-1}\) in the metal-free molecule. These bands disappear in the spectra of the metallophthalocyanine complexes. The disappearance of the C≡N stretching vibration in the IR spectra of compound 3 suggested the formation of compounds 5-8. The NMR characteristics of the nickel compound 5 and zinc-compound 8.
the compound 6 were similar to those of the precursor dicyano compound 3 and the metal-free phthalocyanine compound 4. In the mass spectrum of Ni, Zn, Co and Cu phthalocyanines, the presence of molecular ion peaks at (m/z): 1460 [M]⁺, 1467 [M+1]⁺, 1460 [M+1]⁺, 1466 [M+1]⁺ respectively, confirmed the proposed structures (Fig. 1). The elemental analyses of the metallophthalocyanines 5-8 were satisfactory.

The UV-vis absorption spectra of compounds 4-8 in chloroform at room temperature are shown in Figs. 2 and 3. In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at about 300-350 nm related to the B band and the other in the visible region at 600 -700 nm related to the Q band. The split Q bands in compound 4, which are characteristic for metal-free phthalocyanines, were observed at λmax = 705, 669 nm, respectively. These intense Q bands indicate monomeric species, as species with D₂h symmetry show two intense absorption bands around 700 nm [28]. Such split Q band absorptions are due to the π→π* transition from the HOMO to the LUMO of the phthalocyanine ring related to the fully conjugated 18π electron system. The presence of strong absorption bands in compound 4 in the near UV region at λmax = 341 nm also shows Soret region B bands which have been ascribed to the deeper π→π* levels of LUMO transitions [29].

The thermal behaviour of the metallophthalocyanines were investigated by TG/DTA. Although the thermal stabilities of phthalocyanines are well known, the phthalocyanine compounds are not stable above 292 ºC. The initial and main decomposition temperatures are given in Table 1. The initial decomposition temperatures decreased in the order: 8>6>7>5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>Initial decomposition temperature in ºC</th>
<th>Main decomposition temperature in ºC</th>
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<tr>
<td>5</td>
<td>Ni</td>
<td>292</td>
<td>336</td>
</tr>
<tr>
<td>6</td>
<td>Zn</td>
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<td>Cu</td>
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Fig. 1. Synthesis of metal-free phthalocyanine and metallophthalocyanines
ConclusiOn

In this work, we describe the synthetic procedure and characterization of new metal-free and metallophthalocyanines. A dinitrile monomer was synthesized by nucleophilic aromatic substitution of (E)-3-(3-hydroxyphenyl)-1-phenylprop-2-en-1-one onto 4-nitrophthalonitrile.

The newly developed methods for the synthesis of phthalocyanine are easier, more economical, and less time-consuming. The microwave energy facilitates the synthesis. In addition, the thermal properties of the new phthalocyanines were examined by thermogravimetric analysis. Phthalocyanines are known as compounds of high thermal stability. So this property enables the use of phthalocyanines as technological materials.

References