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Synthesis and electrochemistry of metallophthalocyanines bearing {4-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]phenoxy} groups

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ABSTRACT

In this study, metallophthalocyanines **4**, **5**, **6** was carried out by the cyclotetramerization of 4-{3-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]phenoxy}phthalonitrile **3**. The synthesis of metallo derivatives [Zn(II), Co(II), Cu(II)] of phthalocyanines obtained from corresponding phthalonitrile derivative and in the presence of the anhydrous divalent metal salts ($Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$) was described. These phthalocyanines showed good solubility in organic solvents such as chloroform, tetrahydrofuran, DMSO and DMF. The newly synthesized Pcs were verified by IR, ^1H NMR, ^{13}C NMR, UV–vis and MS spectral data. The electrochemical properties of the zinc(II), copper(II) and cobalt(II) phthalocyanines were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The cobalt complex showed a metal based reduction process, while zinc phthalocyanines were giving ligand based electron transfer processes.

1. Introduction

Phthalocyanines (Pcs) have 18-π electron system, known as aromatic macrocyclic compounds, which don't occur in nature. They have attracted great interest for the first time since their accidental discovery in Scotland in 1928. Their considerable properties that include flexibility, thermal and chemical properties, photoconductivity and semiconductivity [1] have been of huge attention in research. In many fields, phthalocyanines have been remarkably used because of their magnificently industrial and technological properties such as for optical read-write discs [2], medical applications [3], chemical sensors in photocopying machines [4,5], solar cells for high energy batteries [6] and photocatalysis [7]. In recent years, especially metallophthalocyanines have been remarkably used photodynamic reagents for cancer therapy [8–11] because of their good singlet oxygen generation ability.

Low solubility of phthalocyanines in organic solvents and water restricts for the investigations of their chemical and physical behaviours in many fields [12]. It is synthesized soluble metal-free or metallophthalocyanines which linked long chain aliphatic groups, amide groups and carboxylic acid groups [13,14] or crown ether groups [15–19], etc. at the peripheral and non-peripheral positions of phthalocyanine ring. On the other hand, tetra-substituted Pcs are more soluble than octa-substituted Pcs due to the high dipole moment which derives from the unsymmetrical arrangement of the substituents at the periphery [20,21].

The chalcone moieties are of great interest and significance since this sub-unit is found in numerous natural compounds [22,23]. Therefore, intense efforts have been dedicated to the development of efficient methods for the synthesis of functionalized chalcones. They have attracted prominent current interest for several years because of their broad range of biological properties such as anticancer, antiinflammatory, antioxidant, cytotoxic, antimicrobial, analgesic and antipyretic [24]. Furthermore, chalcones are useful in various applications such as non-linear optics (NLO), electrochemical sensing, optical limiting, Langmuir films and photoinitiated polymerization [25–28].

Microwave assisted synthesis of phthalocyanines not only reduces chemical reactions times from hours to minutes but also improves reactions yield and their reproducibility [29–34]. The redox properties of phthalocyanines are critically related to most of their industrial applications. Redox process depend on various factors such as the type of metal, solvent, axial ligands and

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substituents. Cyclic voltammetry is the most widely used method to determine electrochemical properties in solution. Electrochemical properties of metallophthalocyanines have been intensively studied [35,36]. Electrochemical analyses of the newly synthesized metallophthalocyanine complexes are necessary to determine their possible applications in different electrochemical technologies such as chemical sensors, electrocatalysts and electrochromic materials. Therefore, we have synthesized, characterized and investigated the electrochemical properties of these novel metallophthalocyanine complexes substituted with (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one groups on peripherally position.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of 4-{4-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]phenoxy}phthalonitrile (**3**)

(2*E*)-1-(4-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (**1**) (1 g, 3.18×10^{-3} mol) was dissolved in dry DMF (0.010 L) and 4-nitrophthalonitrile (0.55 g, 3.18×10^{-3} mol) was added under nitrogen atmosphere. To this reaction mixture finely ground anhydrous potassium carbonate (1.31 g, 9.54×10^{-3} mol) was added in 8 portions every 15 min. The reaction mixture was stirred under N_2 at 50 °C for 4 days. Then the solution was poured into ice-water (100 g). Solid product was filtered, washed water and dried in vacuo over P_2O_5. The crude product **3** was crystallized from ethanol. Yield: 0.70 g (50%), mp: 151–153 °C. IR (KBr pellet), ν_{max}/cm^{-1}: 3071 (Ar–H), 2939–2840 (Aliph. C–H), 2232 (C≡N), 1663, 1580, 1504, 1420, 1319, 1280, 1249, 1127, 1001, 957, 832, 754, 666, 608, 524. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8 Hz, 2H, Ar–H), 7.78 (d, J = 8 Hz, 2H, Ar–H), 7.75 (s, 1H, Ar–H), 7.64 (t, J = 8 Hz, 1H, Ar–H), 7.40 (d, J = 16 Hz, 1H, α-H), 7.34 (bt, 1H, Ar–H), 7.28 (d, J = 16 Hz, 1H, β-H), 6.88 (s, 2H, Ar–H), 3.92 (s, 6H, O–CH_3), 3.90 (s, 3H, O–CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.87, 161.26, 154.17, 153.54, 146.16, 140.97, 135.57, 130.98, 129.96, 126.08, 124.68, 121.79, 121.71, 120.58, 120.35, 117.79, 115.26, 114.85, 109.41, 106.01, 61.00, 56.30, 56.24 MS (ES^+), (m/z): 459 $[M + H_2O + H]^+$.

2.1.2. Synthesis of zinc(II) phthalocyanine (**4**)

A mixture of 4-{3-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]phenoxy}phthalonitrile **3** (0.25 g, 0.57×10^{-3} mol), anhydrous $Zn(CH_3COO)_2$ (53×10^{-3} g, 0.29×10^{-3} mol) and 2-(dimethylamino)ethanol (0.0025 L) 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 P_2O_5. The obtained green solid product was purified from the column chromatography which is placed aluminium oxide using only chloroform:methanol (100:3) as solvent system. Yield: 0.115 g (44%). IR (KBr tablet) ν_{max}/cm^{-1}: 3068 (Ar–H), 2933–2835 (Aliph. C–H), 1660, 1578, 1465, 1432, 1317, 1275, 1234, 1124, 1088, 1043, 1000, 826, 795, 746. ^{1}H NMR (400 MHz, $CDCl_3$)(δ: ppm): 7.77–7.71 (m, 16H, Ar–H), 7.62–7.53 (m, 12H, Ar–H), 7.36–7.31 (m, 8H, Ar–H), 6.86 (m, 8H, Ar–H), 3.92 (m, 24H, O–CH_3), 3.79 (m, 12H, O–CH_3). UV–vis (chloroform): λ_{max}, nm (log ε): 349 (4.90), 615 (4.16), 680 (4.83). MALDI-TOF-MS m/z: 1826 $[M + H]^+$.

2.1.3. Synthesis of cobalt(II) phthalocyanine (**5**)

The reaction was carried out by the compound **4** procedure using compound **3** (0.2 g, 0.45×10^{-3} mol) anhydrous $CoCl_2$ (30×10^{-3} g, 0.23×10^{-3} mol) and 2-(dimethylamino)ethanol (0.002 L). The obtained green solid product was chromatographed on preparative silicagel plate with chloroform:methanol (100:5) as eluents. Yield: 0.1 g (49%). IR (KBr tablet) ν_{maxs}/cm^{-1}: 3065 (Ar–H), 2924–2852 (Aliph. C–H), 1661, 1579, 1503, 1462, 1377, 1320, 1275, 1241, 1126, 1098, 1001, 828, 752. UV–vis (chloroform): λ_{max}, nm (log ε): 334 (5.13), 611 (4.32), 672 (4.69). MALDI-TOF-MS m/z: 1819 $[M + H]^+$.

2.1.4. Synthesis of copper(II) phthalocyanine (**6**)

The reaction was carried out by the compound **4** procedure using compound **3** (0.2 g, 0.45×10^{-3} mol) anhydrous $CuCl_2$ (30×10^{-3} g, 0.23×10^{-3} mol) and 2-(dimethylamino)ethanol (0.002 L). The obtained green solid product was chromatographed on preparative silicagel plate with chloroform:methanol (100:5) as eluents. Yield: 0.105 g (51%). IR (KBr tablet) ν_{max}/cm^{-1}: 3065 (Ar–H), 2928–2836 (Aliph. C–H), 1661, 1579, 1503, 1432, 1419, 1313, 1275, 1242, 1185, 1124, 1051, 952, 828, 796, 747. UV–vis (chloroform): λ_{max}, nm (log ε): 338 (5.16), 622 (4.21), 682 (4.61). MALDI-TOF-MS m/z: 1824 $[M + H]^+$.

3. Results and discussion

3.1. Syntheses and characterization

Starting from (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxy phenyl)prop-2-en-1-one **1** and 4-nitrophthalonitrile **2**, the general synthetic route for the synthesis of new metallophthalocyanines are given in Scheme 1. The synthesis of peripheral substituted phthalonitrile derivative **3** is based on the reaction of (2*E*)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one with 4-nitrophthalonitrile (in dry DMF and in the presence of dry K_2CO_3 as base, at 50 °C in 96 h). The metallophthalocyanines **4**–**6** were obtained by the anhydrous metal salts [$Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$] in 2-(dimethylamino)ethanol by microwave irradiation. The structures of the target compounds were confirmed using IR, ^{1}H NMR, ^{13}C NMR and MS spectral data. The characterization data of the new compounds are consistent with the assigned formula.

The IR spectra of the phthalonitrile compound **3** clearly indicate the presence of C≡N group by the intense stretching bands at 2232 cm^{-1}. The ^{1}H NMR spectra of phthalonitrile compound **3** were recorded in $CDCl_3$. In the ^{1}H NMR spectrum of compound **3**, OH group of (2*E*)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one disappeared as expected. In the ^{1}H NMR spectrum of **3** the aromatic protons appear at 7.97 (d), 7.78 (d), 7.75 (s), 7.64 (t), 7.34 (bt), 6.88 (s) ppm. In the ^{13}C NMR spectrum of compound **3** indicated the presence of nitrile carbon atom at δ = 115.26, 120.58 ppm. In the mass spectra of phthalonitrile compound **3**, the molecular ion peak was observed at m/z 459 $[M + H_2O + H]^+$.

The IR spectrum of the zinc phthalocyanine **4**, cobalt phthalocyanine **5** and copper phthalocyanine **6** clearly indicates the cyclotetramerization of the phthalonitrile derivatives **3** with the disappearance of the C≡N peaks at 2232 cm^{-1}. The IR spectra of ZnPc, CoPc and CuPc are also very similar. ^{1}H NMR spectrum of compound **4** the aromatic protons appeared at 7.77–7.71, 7.62–7.53, 7.36–7.31, 6.86 ppm, aliphatic CH_3 protons at 3.92, 3.79 ppm. ^{1}H NMR measurement of the cobalt and copper phthalocyanines **5**–**6** were precluded owing to its paramagnetic nature. The mass spectra of tetra-substituted phthalocyanines **4**, **5** and **6** confirmed the proposed structure, with the molecular ion being easily identified at 1826 $[M + H]^+$, 1819 $[M + H]^+$ and 1824 $[M + H]^+$ respectively.

The metal-free and metallophthalocyanine complexes exhibit distinctive electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other one in the visible region at 600–700 nm (Q band) [37]. UV–Vis spectra of metallophthalocyanines **4**–**6** in chloroform displayed an intense single Q band absorption of $\pi \rightarrow \pi^*$ transitions around 672–682 nm. The maximum absorption band of ZnPc