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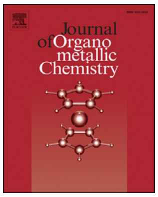

Preparation of aldehyde substituted phthalocyanines with improved yield and their use for Schiff base metal complex formation

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ABSTRACT

The context of this study is based on the synthesis of tetrakis[salicyoxy-salicyhydrazone] phthalocyaninato zinc(II) (**4**), with four salicylhydrazone ligating groups that are directly linked through oxygen bridges to the macrocyclic core, and its tri-nuclear Zn(II) Schiff base complex Bis[bis(salicyoxy-salicyhydrazone)zinc(II)]phthalocyaninato zinc(II) (**5**) starting from tetrakis(2-formylphenoxy)phthalocyaninato zinc(II) (**3**) which was obtained with an improved yield via de-protection of tetra acetal-substituted phthalocyanine tetrakis[2-(1,3-dioxolan-2-yl)phenoxy]phthalocyaninato]zinc(II) (**2**) in acetic acid/$FeCl_3$ system. The substituted zinc phthalocyanine (**2**) was prepared by the tetramerization of 4-[2-(1,3-dioxolan-2-yl) phenoxy] phthalonitrile (**1**) in the presence of the related metal salts. Complexion on the periphery to obtain trinuclear complex (**5**) has been performed through the reaction of the Schiff base substituted phthalocyanine (**4**) with the related zinc (II) salt in basic conditions in DMF. FT-IR, ^1H NMR, ^{13}C NMR, UV–Vis, ICP-OES and MS spectra were applied to characterize the prepared compounds. The fluorescence properties and quantum yields of the prepared complexes were investigated. The aggregation properties of the target phthalocyanines were also examined.

Introduction

Phthalocyanines (Pcs) with two-dimensional 18 π-electron conjugated system have been utilized in important functional materials in many fields [1]. Their architectural flexibility, high thermal, chemical and photochemical stability allow them to be used in wide spread applications [2–7]. High electron transfer abilities of metallophthalocyanines identified as “multipurpose synthetic electro-active materials” have been utilized in different fields of science and technology obtaining the desired physical and chemical properties. Owing to their useful properties, considerable efforts have been focused on the novel structures of metallophthalocyanines.

In recent years, many phthalocyanines bearing different substituents and containing different metal ions at their inner core have been synthesized. Functional substituted phthalocyanines are also of great importance for the development of further chemical reactions on Pc macrocycles [8–11]. Phthalocyanines containing reactive functional groups, such as crown ethers and amines having rich electron-donor units, have been interesting target for chemists due to bound metal ions for designing new molecular materials [12,13].

Because of the synthetic difficulties, there exist a few examples with the appended ligating group containing heteroatoms (N, S and O) for only sensing the metal ions as advanced materials [14,15].

Schiff base chemistry is a versatile tool in organic synthesis and it has played an important role in the development of coordination chemistry since it is all about the forming complexes with most transitions metals. They have wide applications in analytical chemistry, in medicine and in biological processes including antifungal, antibacterial and anticancer activities [16]. The extensive studies of these compounds have been conducted on the complexation with metals for the construction of new molecular materials due to their attractive biological, catalytical and physicochemical properties [17].

Hydrazones and their derivatives as a special group of compounds in Schiff base family, which are versatile ligands, offer a number of possibilities of different modes of coordination with transition metal ions. Hydrazone derivatives and their metal complexes are of interest for their various applications, such as fluorescent probe and fluorescence indicators [18]. In a few researches, Schiff base moieties and Schiff base-Zinc (Zn) complex attached to the phthalocyanine core have been reported starting

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from amine substituted phthalocyanine [19,20] and their fluorescence properties have been studied [21].

We report herein, the synthesis and characterization of compound **5**, displaying a suitable combination of salicyhydrazone Zn complexes. Phthalocyanine may allow new functionalized materials in which two Zn(II) complexes are directly linked through oxygen bridges to the phthalocyanine core. The importance of this new type of phthalocyanine may be regarded as a complementary system with excellent building block potential [22]. We have examined the chemical reactivity of tetra (2-formylphenoxy) substituted Zn–Pc **3** with salicylhydrazide to give four Schiff's base groups bearing phthalocyanine **4** at the peripheral positions as the first example of the similar species of the phthalocyanines, starting from aldehyde substituted phthalocyanine. We also report on the effect of substituents on the spectroscopic and aggregation properties of Zinc phthalocyanine derivatives in DMSO. Fluorescence properties of these compounds were also investigated.

Experimental

Chemicals and instruments

Salicylhydrazide has been obtained by reaction of methylsalicylate and hydrazine hydrate according to the published literature [23]. Zinc chloride ($ZnCl_2$) was dried over 120 °C and used as anhydrous. The deuterated chloroform ($CDCl_3$) for NMR spectroscopy and the following chemicals were obtained from Sigma–Aldrich; hexane, methanol (MeOH), *N*,*N*-dimethylaminoethanol (DMAE), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), acetic acid (AcOH), dichloromethane (CH_2Cl_2), *n*-pentanol and $FeCl_3.6H_2O$. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers. All solvents were stored over molecular sieves (4 Å) after they dried and purified as described by Perrin and Armarego [24]. Oxygen free inert atmosphere was supplied by argon through dual-bank vacuum-gas manifold system. Thin-Layer chromatography (TLC) was performed using silica gel 60-HF_{254} as an adsorbent. Column chromatography was performed with silica gel (Merck grade 60) and the size exclusion chromatography with Bio-beads gel (SX-1).) Melting points (m.p.) were determined using a Barnstad-Electrotermel 9200 apparatus and were left as uncorrected. Electronic spectra were recorded on a Shimadzu UV-2600 Pc-spectrophotometer with quartz cell of 1 cm. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrophotometer equipped with Perkin Elmer UATR-TWO diamond ATR and corrected by applying the atr-correction function of Perkin Elmer Spectrum software. Bruker 400 spectrometer in Atatürk University was used to record ^1H and ^{13}C NMR spectra and the measurements were performed at 70 °C. For Maldi-TOF spectra, the experiments were carried out using a Bruker microTOF (Germany) in Gebze Institute of Technology. The compounds were ionized in the positive electro-spray ionization ion source (ESI+) of the mass-spectrometer. Compound **5** (5.3 mg) was leached by HNO_3 at 170 °C for 1 h. The zinc content of **5** in the dissolved mixture was determined using external standard with A Spectro Arcos inductively coupled plasma-optical emission (ICP-OES) (SPECTRO Kleve, Germany).

Synthesis

*4-(2-(1,3-Dioxolan-2-yl) phenoxy) phthalonitrile (**1**)*

The preparation of **1** has been performed in our earlier studies and reported recently [25].

*Tetrakis[2-(1,3-dioxolan-2-yl)phenoxy)]phthalocyaninato zinc(II) (**2**)*

In a standard schlenk tube, 4-(2-(1,3-dioxolan-2-yl)phenoxy) phthalonitrile (500 mg, 1.71 mmoL) (**1**) was dissolved in DMAE (2 mL). $ZnCl_2$ as metal salt as (58.48 mg, 0.43 mmoL) and DBU (2 drops) were added to the solution. The reaction mixture was purged by argon at room temperature and heated up to 140 °C for 6 h. After cooling to the room temperature, the reaction mixture was precipitated by adding methanol (15 mL). The precipitate was collected by centrifugation, washed several times with ethanol and water to dissolve any unwanted organic impurity and any unreacted metal salt and dried. Further purification of the phthalocyanine was performed by size exclusion chromatography on Bio-beads gel (SX-1). The crude product was put onto the column and eluted with CH_2Cl_2, and the collected phases were concentrated on a rotary evaporator and re-precipitated with methanol. The desired pure ZnPc (**2**) was obtained as a green solid. Yield 0.250 g, 47%. m.p. > 300 °C. FT-IR (UATR-TWO™) ν max/cm^{-1}: 3064 (Ar, C–H), 2922–2852 (Aliph., C–H), 1605 (C=N), 1585 (Ar, C=C), 1470–1335 (Aliph., C–C), 1230 (Ar–O–Ar), 1073 (C–O–C). UV–Vis (DMSO): λ_{max} (nm) (log ε) 681 (5.24), 613 (4.51), 357 (4.79). ^1H NMR (DMSO-d_6) δ (ppm): 8.92–8.71 (m, 4H, ArH), 8.42–8.35 (d, 4H, ArH), 7.87–7.81 (m, 4H, ArH), 7.72–7.43 (m, 16H, ArH), 6.48–6.38 (t, 4H, AlipH), 4.22–4.02 (m, 16H, AlipH). ^{13}C NMR (DMSO-d_6) δ (ppm): 159.37, 155.27, 139.91, 139.76, 133.11, 133.02, 131.46, 131.39, 130.44, 128.67, 128.58, 125.01, 124.17, 124.12, 123.41, 120.89, 120.79, 120.65, 120.44, 120.11, 119.94, 119.81, 110.78, 110.71, 99.39, 99.33, 65.57. MS (MALDI-TOF): *m*/*z* 1235 $[M + 3]^+$.

*Tetrakis (2-formylphenoxy)phthalocyaninato zinc(II) (**3**)*

The cleavage reaction of **2** (222 mg, 0.18 mmoL) was performed in acetic acid (5 mL)/$FeCl_3$ (catalytic amount) system using THF (5 mL) to solve the phthalocyanine before adding cleavage regents. The reaction solution was stirred at 75 °C for 3 days and at room temperature for following 3 days. The resulting mixture was precipitated with water, and the precipitate was collected by centrifugation. The crude product was washed several times with ethanol and water to remove any unwanted organic impurity and acidic residue, and then it was dried under vacuum. Further purification of the prepared phthalocyanine was performed by size exclusion chromatography on Bio-beads gel (SX-1) using CH_2Cl_2 as the eluent. The desired pure product **3** was collected by the re-precipitation with methanol after rotary evaporation of the collected organic eluent phases as blue-green solid. Yield 160 mg, 84%. m.p. > 300 °C. FT-IR (UATR-TWO™) ν max/cm^{-1}: 3070–3025 (Ar, C–H), 2922–2754 (O=C–H), 1685 (–C=O), 1597 (C=N), 1577 (C=C), 1468–1388 (C–C), 1228 (Ar–O–Ar), UV–Vis (DMSO): λ_{max} (nm) (log ε) 680 (5.30), 613 (4.56), 357 (4.85). ^1H NMR (DMSO-d_6) δ (ppm): 10.82–10.72 (m, 4H, CHO), 8.89 (m, 1H, ArH), 8.78 (m, 1H, ArH), 8.50 (m, 1H, ArH), 8.42 (m, 1H, ArH), 8.11–7.7.99 (m, 5H, ArH), 7.90–7.80 (m, 9H, ArH), 7.64–7.40 (m, 10H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 189.65, 176.98, 173.80, 164.56, 163.17, 159.70, 158.32, 158.05, 156.27, 151.98, 147.85, 139.68, 137.06, 133.75, 133.00, 131.53, 129.38, 129.30, 127.67, 127.46, 124.95, 124.76, 124.36, 120.98, 120.33, 120.12, 117.65, 112.26. MS (MALDI-TOF): *m*/*z* 1059 $[M + 1]^+$.

*Tetrakis[salicyoxy-salicyhydrazone] phthalocyaninato zinc(II) (**4**)*

A solution of salicylhydrazine (76 mg, 0.5 mmoL) in dry THF (10 mL) was added to a solution of tetrakis(2-formylphenoxy)-phthalocyaninato]zinc(II) (**3**) (130 mg, 0.122 mmoL) in THF (10 mL) and the mixture was heated up to 70 °C for 4 h. After cooling to the room temperature, the solvent was evaporated to 1/10 of the initial volume of the reaction mixture, and then it was precipitated by adding methanol/water (v/v: 1/1). The crude product was collected by filtration as green solid and washed successively with cold