

Synthesis and Characterization of 1,2-Benzenedimethoxy Substituted Novel Ball-Type and Mononuclear Metallo Phthalocyanines

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Summary: The phthalodinitrile derivative **1** was prepared by the reaction of 1,2-benzenedimethanol and 4-nitrophthalonitrile in dry DMF in the presence of K₂CO₃ by the common method of nucleophilic substitution of an activated nitro group in an aromatic ring. The template reaction of **1** with the corresponding metal salts gave the novel mono-nuclear ZnPc **2** and ball-type metallophthalocyanine LuPc₂ **3**.

In this study, we have used the “heating of the solid phase” method for the synthesis of novel ball-type LuPc₂ **3** phthalocyanines. Mono-nuclear ZnPc **2** phthalocyanine was prepared by reflux in solvent.

Mono and ball-type phthalocyanines were characterized by elemental analyses, FT-IR, ¹H NMR, ¹³C NMR, UV-vis and MALDI-TOF MS spectral data.

Key words: Ball-type phthalocyanine, zinc, lutetium

Introduction

Since the accidental synthesis of the first phthalocyanine in 1907, this class of compounds has continued to attract the attention of scientists. Phthalocyanines (Pcs) have been extensively studied as advanced materials due to their growing interest in many fields of technology and medical applications such as catalysis [1-5], solar cells functional material [6,7], photodynamic therapeutic agent [8-11], nonlinear optical limiting devices [12-14], gas sensors [15-21]. The central metal ion and peripheral substituents in phthalocyanines are two most important variables, so that the new synthesized derivatives of phthalocyanine become unlimited [22]. By changing these parameters, diverse functional phthalocyanines can be obtained [23-28]. Nevertheless, ball-type phthalocyanines are a new class of phthalocyanines, the first of which was reported in 2002 by the Tomilova's group [29-30]. This new type of phthalocyanines has four bridged substituents on the peripheral positions of each benzene ring of the two phthalocyanine units. [31-33].

The common method to synthesize substituted phthalocyanines is to prepare the phthalonitrile with required substituents, then synthesize the corresponding phthalocyanines by cyclotetramerization of the substituted phthalonitrile. In this work, we reported synthesis (see Scheme 1) and characterization of mononuclear zinc^{II} (**2**) and ball-type lutetium^{III} (**3**) phthalocyanines.

Results and Discussion

Scheme-1 shows the synthesis of the Pcs, **2** and **3**. Our starting material is compound **1** which can be obtained via a single step reaction of 1,2-benzene dimethanol with 4-nitrophthalonitrile (1:2) in dry DMF as the solvent in the presence K₂CO₃ as the base in a yield of 81%. Phthalocyanines **2** and **3** obtained from compound **1** demonstrated good solubility in common organic solvents such as acetone, chloroform, tetrahydrofuran (THF), DMF and DMSO. Melting points of the compounds **2** and **3** were found to be higher than 350 °C.

All of the new compounds were characterized by elemental analyses, FT-IR, ¹H-NMR, UV/Vis (Fig. 1) and MALDI-TOF MS (Fig. 2-4). spectroscopic techniques. The spectroscopic data of the new compounds were in accordance with the structures.

The IR spectra taken with KBr pellets showed a-CH₂ aliph. peak at 2927-2851 cm⁻¹ and an intense absorption attributable to C≡N at 2228 cm⁻¹ as single peak, Ar C=C peak at 1597 cm⁻¹ for compounds **1**. In addition, when compared with the IR spectrum of 4-nitrophthalonitrile, that of **1** confirmed the proposed structures by the disappearance of the arom-NO₂ bands 1530 cm⁻¹ and 1350 cm⁻¹. The appearance of an intense new absorption band at 1254 cm⁻¹ attributable to Ar-O-

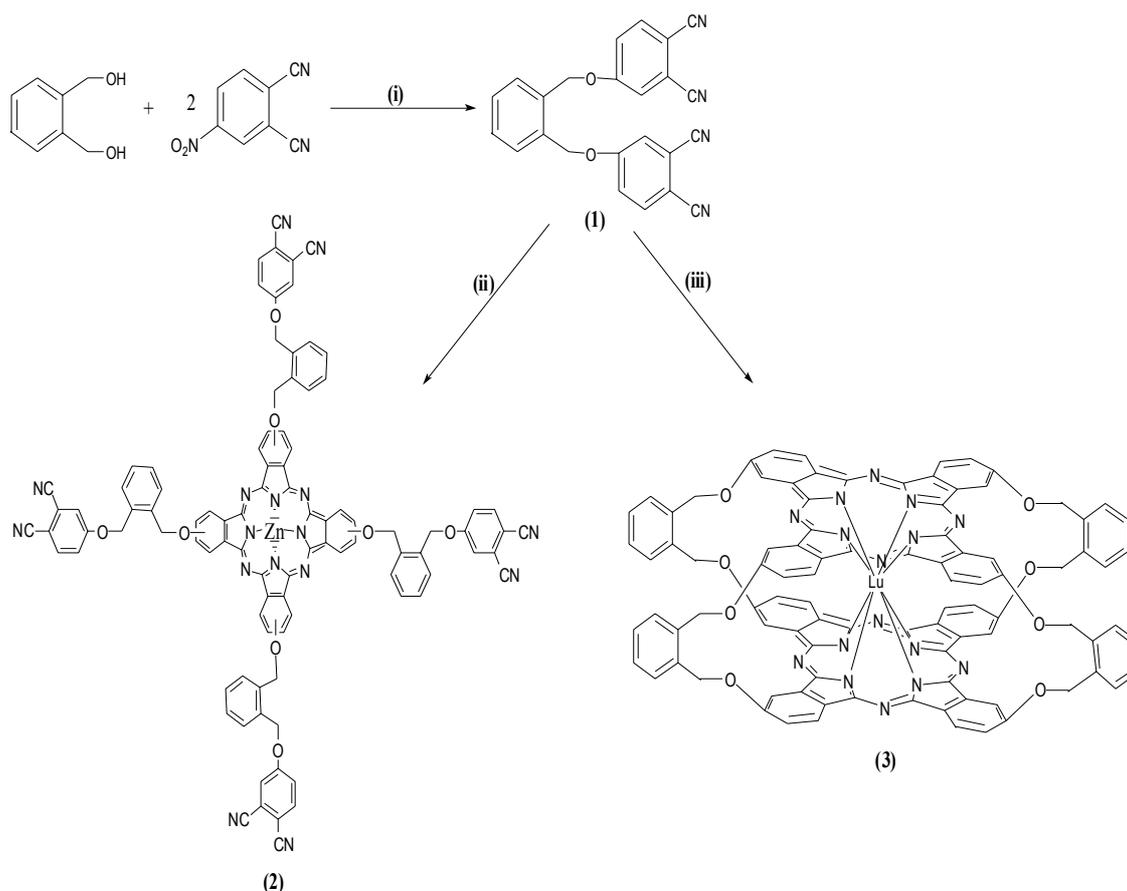
C. The IR spectrum of **2**₄ showed an intense absorption band at 2228 cm⁻¹ corresponding to the C≡N group. In addition, the IR spectrum of **3** show no C≡N vibrational peak at 2228 cm⁻¹ which was observed in the IR spectrum of **2**. In the IR spectrum of the Pc **3** showed Ar-O-C vibrational peak at 1248 cm⁻¹.

In the ¹H NMR spectrum of compound **1** (d-chloroform), the phenyl-protons appeared at 7.93-7.42 ppm as multiplet. The -OCH₂- protons appeared as a sharp singlet peak at 5.35 ppm. The spectra of Pc **2** and **3** were recorded in DMSO-d₆, and were similar to each other. The aromatic protons appeared at 8.32-7.44 ppm, and 7.85-7.24 ppm as well as OCH₂ protons at 5.35 ppm and 5.34 ppm respectively, in their ¹H NMR spectrum.

¹³C NMR (APT) spectra of the synthesized compounds were also in good correlation with the suggested structure. In the ¹³C NMR spectra of the

compound **2** and **3** which were taken in DMSO-d₆, the aromatic quarterner carbons appeared at 161.99-106.59 ppm, 162.87-129.11 ppm in positive region, and aromatic CH carbons at 136.22-120.95 ppm, 136.30-120.92 ppm in negative region, respectively. The peaks at 56.51 and 60.76 ppm in positive region indicated the presence of OCH₂ carbons in the compound **2** and **3**.

The Pcs show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300-400nm (Soret band) and the other in the visible portion between 600-700nm (Q band). In the UV/VIS spectra in solution, the characteristic Q-bands of **2** and **3** were observed at 681 and 682 nm as single bands with high intensities in the visible region (Fig. 1). These characteristic absorptions are due to the π→π* transitions of conjugated 18π electron systems. The Soret bands for **2** and **3** occurred at 348 and 354 nm, respectively.



Scheme-1: i) K₂CO₃, DMF, Ar, 70 °C; (ii), Zn(AcO₂)₂.2H₂O, DMF, Ar; (iii), Lu(AcO₂)₃.H₂O, DBU, Ar, 300 °C.

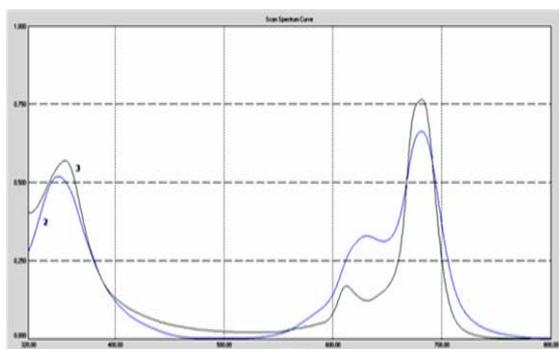


Fig. 1: UV-vis spectra of **2** ($5.10 \times 10^{-6} \text{M}$, in DMF) and **3** ($1.23 \times 10^{-5} \text{M}$, in DMF).

MALDI-MS spectra of compound **1** were recorded in α -cyano-4-hydroxycinnamic acid with better intensity than the other novel MALDI matrices. For the high resolution spectrum, reflectron mode positive ion MALDI-MS spectrum was recorded. For $\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}_2$ **1** compound, only sodiated adduct ion peak was observed (Fig. 2). This data show that sodium affinity of the compound in the gas phase is really higher than the proton affinity of the compound.

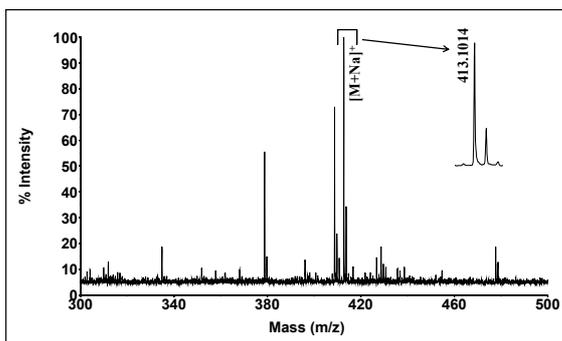


Fig. 2. Positive ion and reflectron mode MALDI-TOF-MS spectrum of $\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}_2$ **1** in α -cyano-4-hydroxycinnamic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots. Inset spectrum shows expanded molecular mass region of the complex.

For all complexes, MALDI-MS spectra were recorded in 2,5-dihydroxybenzoic acid with better intensity than the other conventional MALDI matrices and MALDI-MS spectra are given in Fig. 3 and Fig. 4 for $\text{C}_{96}\text{H}_{56}\text{N}_{16}\text{O}_8\text{Zn}$ **2** and $\text{C}_{96}\text{H}_{56}\text{N}_{16}\text{O}_8\text{Lu}$ **3**, respectively. In the case of $\text{C}_{96}\text{H}_{56}\text{N}_{16}\text{O}_8\text{Zn}$ **2** complex, mainly protonated molecular ion peak was observed. Isotopic mass distribution of the experimental and theoretical of the protonated ion of this complex peaks were compared each other and it was noticed that the peaks for experimental and

theoretical were overlapped each other perfectly. Also monoisotopic peak mass for the experimental and the theoretical values were found to be the very close each other. This shows the mass accuracy between the theoretical and also experimental monoisotopic mass for this complex. On the other hand, no more signal on MALDI-MS mass spectra were observed representing any impurities. All the observation described that the complex was synthesized perfectly in desired manner. (Fig. 3).

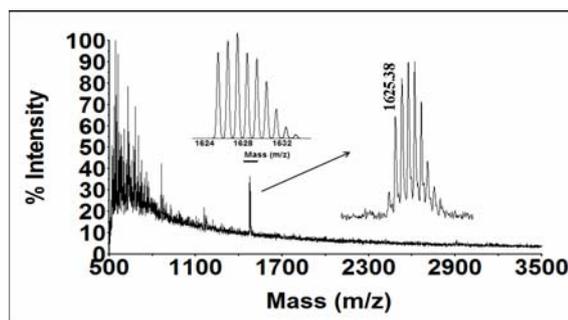


Fig. 3. Positive ion and reflectron mode MALDI-TOF-MS spectrum of $\text{C}_{96}\text{H}_{56}\text{N}_{16}\text{O}_8\text{Zn}$ **2** in α -2,5-dihydroxybenzoic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots.

For the complex **3** only linear mode MALDI-MS spectra were obtained. This shows that this complex is not more stable under the mass spectrometric conditions. However, linear mode MALDI-MS of this complex was acquired and also protonated ion mass was overlapped exactly with the protonated ion mass of this complex calculated theoretically. These observations show that the complex was synthesized correctly in the desired manner (Fig. 4).

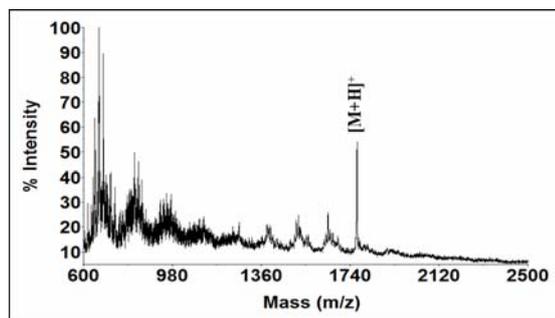


Fig. 4: Positive ion and linear mode MALDI-TOF-MS spectrum of $\text{C}_{96}\text{H}_{56}\text{N}_{16}\text{O}_8\text{Lu}$ **3** in α -2,5-dihydroxybenzoic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots.

In conclusion, we have described the synthesis and spectral characterization of two new phthalocyanines with 1,2-benzenedimethoxy substituents on the periphery.

Experimental

All solvents (reagent grade) and the starting materials were acquired from Sigma–Aldrich and were used without purification. IR spectra were recorded on a Ati Unicam Mattson 1000 Series FT-IR spectrometer (KBr pellets). UV-vis spectra were recorded with a Shimadzu UV-1700 spectrometer. Elemental analyses were performed by the LECO CHNS 932. ¹H-NMR and ¹³C NMR spectra were recorded at 400 MHz on a Bruker 400 spectrometer at room temperature using tetramethylsilane (TMS) as the internal standart. All MALDI-TOF-Mass spectra were acquired on a Voyager-DETM PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra were recorded in linear and reflectron modes using positive mode with average of 100 shots.

Synthesis of (1,2-benzene-dimethoxy) diphthalonitrile (1)

1,2-benzenedimethanol (1.38 gr, 10 mmol) and 4-nitrophthalonitrile (3.46 gr, 20 mmol) were added with stirring to dry dimethylformamide (DMF, 20 mL). After they were dissolved, anhydrous K₂CO₃ (4.14 gr, 30 mmol) was added to the mixture for over a period of 2 h with efficient stirring. The reaction mixture was stirred at 70 °C for 24 h. Reaction was monitored by TLC. Then, The reaction mixture was poured into 200 mL of cold water and it was stirred for 15 min. The precipitate was filtered off, flushed several times with cold water. The crude product was dried on air. The pale yellow solid was soluble in ethanol, acetone, chloroform, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Yield: 3.15 gr (81%). m.p. 130 °C.

IR (KBr): ν (cm⁻¹) 2927-2851 (aliph-CH₂); 2228 (C \equiv N); 1597 (Ar- C=C); 1254 (Ar-O-C). ¹H NMR (400MHz, CHCl₃-d): δ , ppm 7.93-7.42 (m, Ar-H), 5.35 (s, O-CH₂). Anal. Calc.(%) for C₂₄H₁₄N₄O₂: C, 73.77; H, 3.59; N, 14.34. Found: C, 74.03; H, 3.30; N, 14.43%. MS (MALDI-TOF) m/z : 413 [M+Na]⁺.

Synthesis of [2,10,16,24-tetrakis(1,2-benzene dimethoxy)phthalocyaninato zinc(II)] (2)

A well-powdered mixture of compound 1 (1 gr, 2.56 mmol) and Zn(OAc)₂·2H₂O (0.12 gr,

0.64 mmol) were refluxed in dry dimethylformamide (DMF, 10 mL) under argon for 24h. The reaction mixture was cooled down to room temperature and the undissolved salt was removed by filtration. Then the reaction mixture was poured into water (100mL) and stirred. The resulting precipitate was filtered and washed with water. After the product was washed with ethanol, acetone and chloroform. The blue-green solid was soluble in DMF, DMSO and THF(partially). Yield: 0.25gr (24%). Mp >350 °C.

IR (KBr) : ν (cm⁻¹) 3060-2921 (aliph-CH₂); 2228 (C \equiv N); 1600 (Ar- C=C); 1226 (Ar-O-C). ¹H NMR (400MHz, DMSO-d₆): δ , ppm 8.32-7.44 (m, Ar-H), 5.35 (s, O-CH₂). UV-Vis (DMF), λ_{max} , nm(log ϵ): 681(5.11), 631(4.81), 348(5.00). Anal. Calc.(%) for C₉₆H₅₆N₁₆O₈Zn : C, 70.81; H, 3.44; N, 13.77. Found : C, 70.03; H, 4.30; N, 13.43%. MS (MALDI-TOF) m/z : 1628 [M+H]⁺.

Synthesis of [2,10,16,24-(tetrakis benzyl)-bisphthalocyaninato- lutetium(III)] (3)

A well-powdered mixture of compound 1 (0.3 gr, 0.768 mmol) and lutetium(III)acetate (0.07 gr, 0.192 mmol) were heated in a sealed glass tube at the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), under argon atmosphere, at 300 °C for 15 min. After cooling to room temperature, the crude product was soluble in hot DMF and precipitated by water (100mL). After filtration, the product was washed with water, ethanol, chloroform and acetone. The dark green compound was soluble in DMF and DMSO. Yield: 0.07gr (21%). Mp >350 °C.

IR (KBr) : ν (cm⁻¹) 2928-2851 (aliph-CH₂); 1599 (Ar- C=C); 1248 (Ar-O-C). ¹H NMR (400MHz, DMSO-d₆): δ , ppm 7.85-7.24 (m, Ar-H), 5.34 (s, O-CH₂). UV-Vis (DMF), λ_{max} ,nm (log ϵ): 682 (4.79), 612 (4.13), 354 (4.67). Anal. Calc.(%) for C₉₆H₅₆N₁₆O₈Lu :C, 66.40; H, 3.26; N, 12.90. Found : C, 66.83; H, 3.48; N, 13.21%. MS (MALDI-TOF) m/z : 1737.54 [M+H]⁺.

MALDI sample preparation

MALDI matrix, α -cyano-4-hydroxycinnamic acid (ACCA) was prepared in THF:water mixture in 1:1, v/v ratio at a concentration of 10 mg/mL. MALDI sample for 1 was prepared by mixing sample solutions (0.5 mg/mL in tetrahydrofuran:water mixture:DMSO, 1:1:0.01 v/v) with the matrix solution (1:10 v/v) in a 0.5 mL eppendorf micro tube. Finally 0.5 μ L of this mixture was deposited on the sample plate, dried at room temperature and then

analyzed. MALDI matrix, α -2,5-dihydroxybenzoic acid was prepared in DMSO:ACN:H₂O mixture in 1:1:1, v/v/ ratio at a concentration of 20 mg/mL and acidified with trifluoroacetic acid (0.1%). MALDI samples for **2** and **3** were prepared by mixing sample solutions (2 mg/mL in DMSO:ACN:H₂O mixture in 1:1:1, v/v/v ratio containing 0.1% trifluoroacetic acid) with the matrix solution (1:10 v/v) in a 0.5 mL eppendorf micro tube. Finally 1.0 μ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

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