

Synthesis of New Manganese (II) and Lanthanum (III) Tetrasubstituted Phthalocyanine

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Abstract: To synthesized and evaluate the variation of the properties of phthalocyanines with both the position of the substituents and the type of metal used for coordination, tetrasubstituted manganese, and lanthanum, phthalocyanines bearing 7-hydroxycoumarin as substituents were synthesized by the cyclotetramerization reaction of the synthesized 1,3-diiminoisoindoline. The structures of the synthesized compounds were characterized by a combination of ¹H NMR, UV-Vis, and FT-IR spectrophotometry.

Keywords: Phthalocyanine, 1,3-diiminoisoindoline, 7-hydroxycoumarin, Thermal analysis

1. Introduction

Phthalocyanines (Pcs) are symmetrical 18 π -electron aromatic macrocycles, closely related to the naturally occurring porphyrins [1]. Phthalocyanines are chemically and thermally stable compounds which can host more than seventy different metal ions in the central cavity [2]. Since their discovery, phthalocyanines have been extensively used as colorants, but more recently they have been employed in different technological areas, i.e. as photoconducting materials, light absorbing layers in recordable CDs, photosensitizers in cancer therapy, and industrial catalysts [3]. Despite the huge number of actual applications, further research is still in dispensable since many other future applications are envisaged. The physical properties and the process ability required for technological applications can be chemically tuned by changing the peripheral substituents and/or the central metal [4]. The possibility of designing and synthesizing unsymmetrically substituted Phthalocyanines may enhance the technological applications of phthalocyanines, i.e. within the field of second-order nonlinear optics. Other feasible chemical manipulation is the alteration of the Phthalocyanine skeleton, that leads to various Phthalocyanine analogues, such as subphthalocyanines, three-quarter phthalocyanines and expanded azaporphyrins. More recently, the construction of multinuclear and multicomponent Phthalocyanine-based systems is attracting much attention owing to their potential capability of performing complex functions, for example as molecular switches and solar cells, among others. The preparation of these complex systems requires the use of modern synthetic methodologies [5].

The approach in this study focused on the synthesis of inorganic macrocyclic compound (metallated Phthalocyanine) by encapsulating Mn and La metals inside the void and cage space of phthalocyanine bearing 7-hydroxycoumarin substituents on the non-peripheral positions using synthesized 1,3-diiminoisoindoline compound as precursor. Atomic absorption and thermal stability of the new synthesized compound was also investigated.

2. Materials and Methods

2.1 Materials

All reactions were performed under Argon atmosphere. 7-Hydroxy coumarin and 1,8-diazabicyclo [5.4.0] -undec-7-ene (DBU), were received from Merck. 3-Phthalonitrile from AFG scientific, $Mn(Ac)_2 \cdot 4H_2O$, and $LaCl_3$, anhydrous dimethylformamide (DMF), Glycerol solution, were obtained from Sigma-Aldrich and used as received without further purification. Other chemicals used were reagent grade.

2.2 Apparatus

Melting points of the compounds were determined with Griffin MFB-590.

¹H spectra were taken using Bruker Ultra-shield 400 MHz with $DMSO-d_6$ as solvents and tetramethylsilane as an internal standard. Transmission FT-IR spectrum of the samples were recorded on an FT-IR spectrophotometer (Perkin Elmer); solid substances were ground with KBr and pressed to pellets. UV-Vis spectra were recorded on a T80+UV/VIS spectrophotometer. At a heating rate of $10^\circ C \text{ min}^{-1}$, TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer TGA-50 Instruments.

2.3 Synthesis

2.3.1. Synthesis of 3-(2-OXO-2H-Chromen-7-YLOXY) 1,3 Diiminoisoindoline

To a solution of phthalonitrile 1.275 g (4.423 mmol) in dry methanol (100 mL) was added sodium methoxide 0.139 g (2.576 mmol). Anhydrous ammonia was bubbled through the solution under reflux. The course of the reaction was followed by FT-IR spectroscopy, monitoring the $C \equiv N$ peak at 2230 cm^{-1} . After the completion of the reaction, the ammonia inlet was closed, and the volume of the reaction mixture was reduced to 10 ml under reduced pressure. The mixture was precipitated with distilled water (100 ml), and the solid was filtered off washed and dried. Yield: 1.108 g 74 %, M.P: $128^\circ C$, ¹H NMR (400 MHz, $DMSO-d_6$, δ ,

ppm): 6.50-8.5 (m, 8H, Ar-H+H₂,3). FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$: Ar-CH (2921) C=C (1473) C=O (1619) C-O-C (1249).

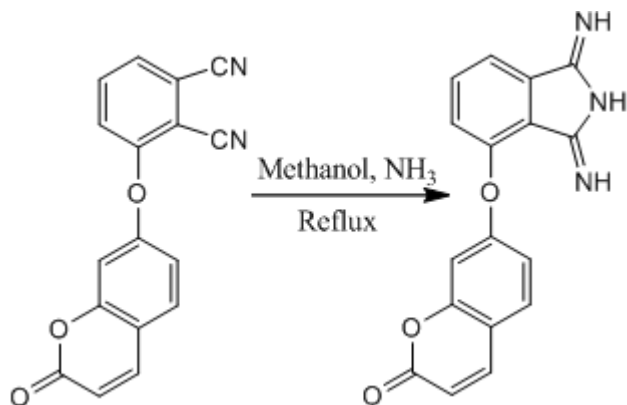


Figure 2.1: Synthesis of 1,3-diiminoisoindoline

2.3.2.1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin] Manganese (II) Pthalocyanine.

1,3-diiminoisoindoline (0.200 g, 0.655 mmol), Manganese(II) acetate $\text{Mn}(\text{OAc})_2$ (0.0736g, 0.300 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) in DMF/Glycerol (10 mL) was stirred and heated at reflux temperature under an argon atmosphere for 24 hours. After cooling to room temperature, the reaction mixture was precipitated by adding it drop wise into distilled water (100ml). The product was precipitated, collected by filtration, purified and washed with distilled water. The green product was dried and weight. Yield: 0.146g, 18%. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$: Ar-CH (2929) C=C (1599) C=O (1727) C-O-C (1274).

Scheme 2.2: Synthesis of Manganese phthalocyanine

2.3.3.1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin] Lanthanum (III) Pthalocyanine.

1,3-diiminoisoindoline (0.170g, 0.557 mmol), lanthanum (III) Chloride LaCl_3 (0.063 g, 0.257 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) in DMF/Glycerol (10 mL) was stirred and heated at reflux temperature under an argon atmosphere for 24 hours. After cooling to room temperature, the reaction mixture was

precipitated by adding it dropwise into distilled water (100ml). The crude product was precipitated, collected by filtration, purified and washed with distilled water. The green product was dried and weight. Yield: 0.145gr, 20%, M.P: 342°C. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$: Ar-CH (2974) C=C (1611) C=O (1710) C-O-C (1245).

Scheme 2.3. synthesis of Lanthanum phthalocyanine

3. Result and Discussion

Phthalonitrile derivative was obtained through the nucleophilic substitution reaction between 3-nitro phthalonitrile and 7-Hydroxycoumarin at 80°C under Argon

atmosphere in dry DMF in the presence of K_2CO_3 as a base with 62% yield. This reaction has been used in the preparation of a variety of ether or thioether substituted phthalonitriles [6,7]. The 1,3-diiminoisoindoline derivative was also obtained as stated in the procedure above.

Cyclotetramerization of the 1,3-diiminoisoindoline derivative in a high-boiling solvent Glycerol in the presence of a few drops 1,8-diazabicyclo [5.4.0]undec-7-ene DBU as a strong base and anhydrous Metals at reflux temperature under an Argon atmosphere afforded the synthesized phthalocyanines. The route for the synthesis of 1,3-diiminoisoindoline and Phthalocyanine compounds were shown above. The characterization of the compounds was carried out by, FT- IR, ¹H NMR, UV-vis spectra and TGA. The compounds structures were confirmed by the results of these analyses.

The most important proof of the cyclotetramerization of nitrile groups is the absence of the $-C\equiv N$ vibrations at 2230 cm^{-1} for Phthalocyanines compounds in FT-IR spectra of the substituted Phthalocyanine compounds.

The ground state electronic spectra are especially useful to identify the structure of the phthalocyanines. Generally, UV-Vis spectra of phthalocyanines show typical electronic spectra with two strong absorption bands known as Q and B bands. The Q band in the visible region at ca. 600–750 nm is attributed to the $\pi-\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring and the B band in the UV region at 300–400 nm [8, 9]. The ground state

electronic absorption spectra of the non-peripherally tetra-substituted phthalocyanine complexes showed monomeric behavior evidenced by a single (narrow) Q band, typical of nonaggregated metallophthalocyanine complexes in DMF.

The electronic spectra of Manganese, and Lanthanum-phthalocyanine compounds (MnPc, and LaPc) in DMF/Glycerol (3:1) are given in figure (3.1 and 3.3) below. The UV-Vis absorption spectra of MnPc, and LaPc, in DMF showed intense Q absorption at 690nm.

The electronic absorption transitions of these compounds are strongly dependent on the type of the substituent (withdrawing or donating groups) as well as the type of the metal ion and its position (in the centre or on non-peripheral position) [10].

The thermal stability of the compound derivative was checked by TGA. The Phthalocyanine were heated to 700°C to determine their degradation temperature. The temperatures at which the phthalocyanine began to exhibit weight loss were 318°C , and 350°C , for MnPc, and LaPc, respectively. It could, therefore, be concluded that the Metal Phthalocyanines prepared in this study showed suitably high thermal stability and can be used to prepare dyes for various applications.

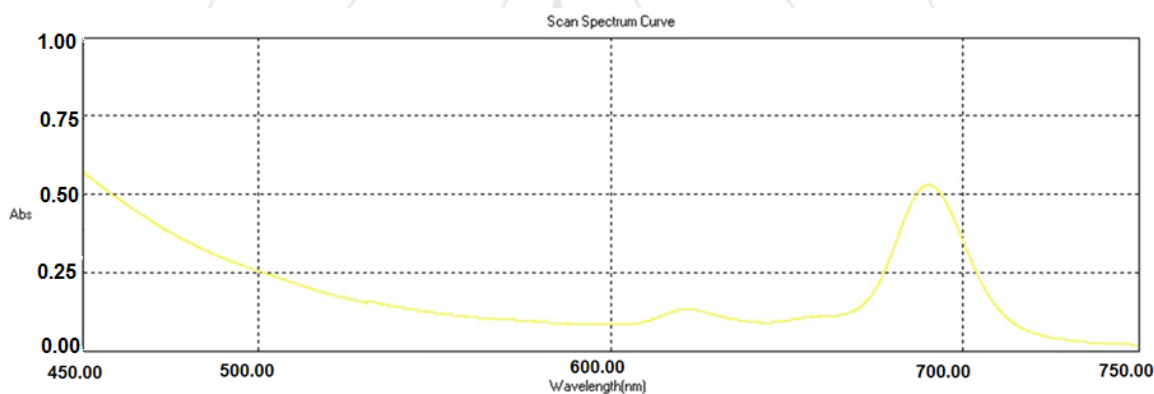


Figure 3.1: UV spectrum of Manganese (II)phthalocyanine

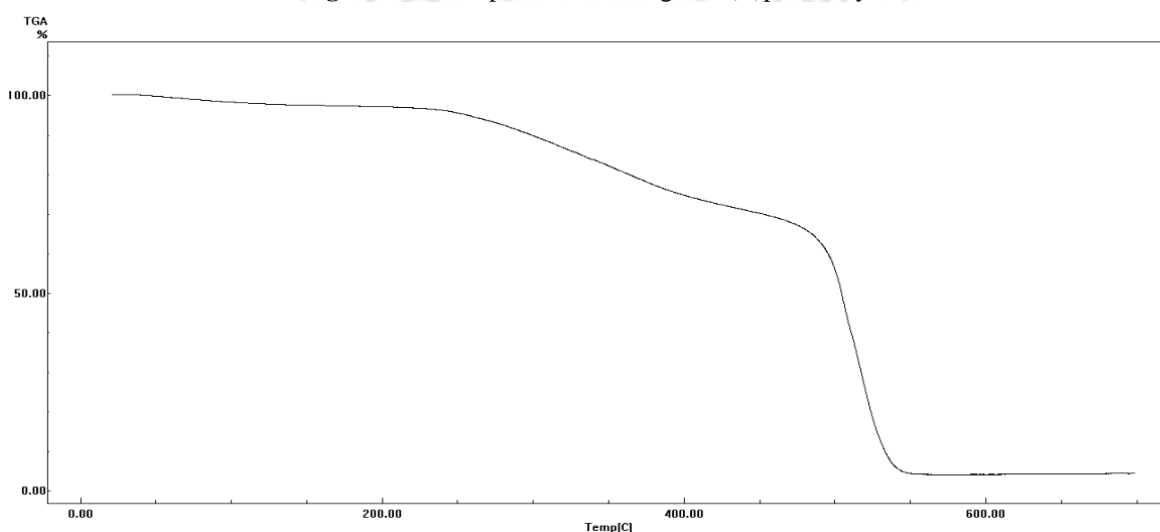


Figure 3.2: TGA of Manganese Phthalocyanine

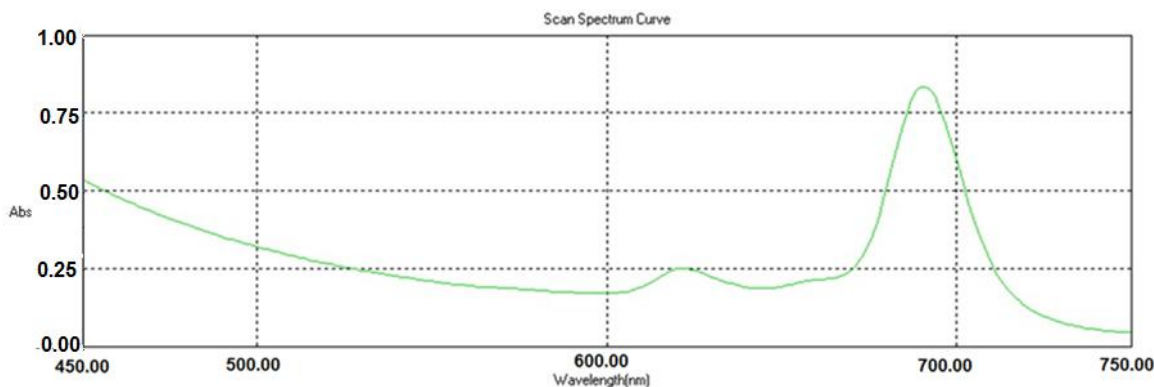


Figure 3.3: UV spectrum of Lanthanum(III)phthalocyanine

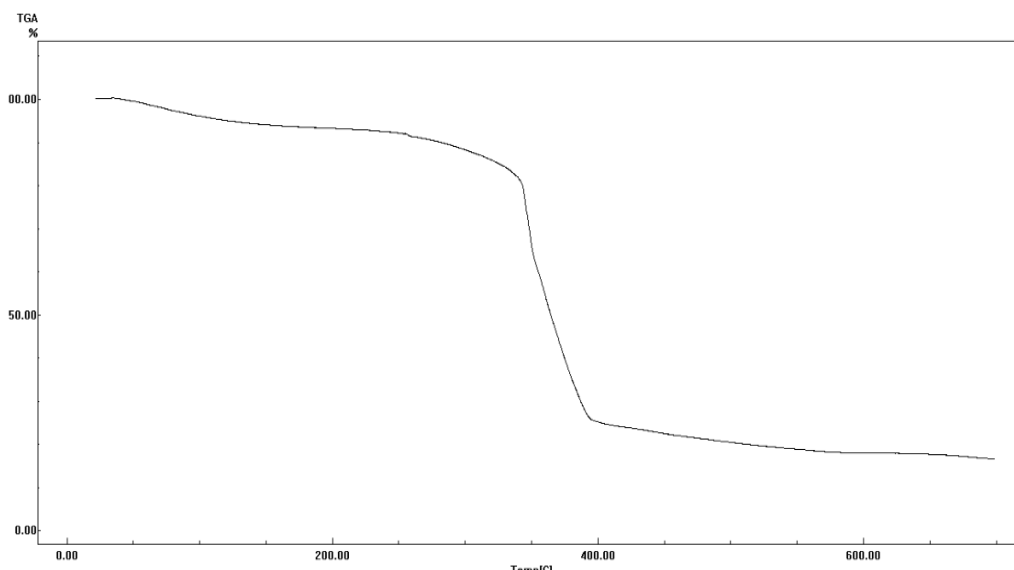


Figure3.4: TGA of Lanthanum Phthalocyanine

4. Conclusion

In conclusion, the present work describes the synthesis and characterization of metal phthalocyanines bearing 7-Hydroxy coumarin substituents on the non-peripheral positions, these new complexes were characterized by Electronic absorption spectra, FT-IR spectroscopy and thermal stability. The synthesized phthalocyanine complexes show partial solubility in some organic solvents. such as, THF, DMF and DMSO, the degradation temperature of the compounds were determined and the results shows the synthesized phthalocyanine compounds exhibits a suitably high thermal stability and can be used for various applications.

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