

SYNTHESIS AND CHARACTERIZATION OF METAL PHTHALOCYANINE COMPLEX USING CIPROFLOXACIN-SUBSTITUTED LIGAND

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ABSTRACT

In this research work, two metal complexes were synthesized from the prepared 4-nitrophthalonitrile ligand. It began with the cyclotetramerization of 4-(ciproxy) phthalonitrile in the presence of metals salt (cobalt and copper), which gave substituted metal phthalocyanine complexes. The formation of the synthesized compounds was confirmed by FT-IR spectrophotometry, Thermogravimetric Analyzer (TGA) and UV-VIS spectrophotometry. At a heating rate of 10 °C min⁻¹, TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer TGA-50 Instruments. Solubility of the compounds was confirmed in some common laboratory solvents (acetone, methanol, and DMF). The electronic spectra of copper phthalocyanine compound (CuPc) in DMF, showed intense Q absorption at 690 nm, the Q band absorption was observed at 678 nm for cobalt phthalocyanine (Copc). TGA results of the thermal stability of the phthalocyanine derivatives, when the phthalocyanine was heated up to 700 °C to determine the degradation temperature, showed that the phthalocyanines began to lose weight at 300 °C and 309 °C for Co and Cu phthalocyanine respectively. Therefore, it could be concluded that the synthesis of metal phthalocyanines complex using antibiotic as substituent was achieved and the complex synthesized in this study showed suitably high thermal stability.

Keywords: Ciprofloxacin, Phthalocyanine, Metal Complex, Ligand

INTRODUCTION

Phthalocyanine complexes refer to a class of coordination compounds that contain a central phthalocyanine ligand coordinated with a metal ion (Thakur *et al.*, 2021). Phthalocyanines are macrocyclic compounds with a structure similar to porphyrins and they are known for their intense colour and interesting electronic and optical properties (Cortes *et al.*, 2021). The central metal ion in phthalocyanine complexes can vary, but common choices include copper, nickel, cobalt, iron, and zinc (Zhao *et al.*, 2023). Phthalocyanines have a wide range of applications, such as catalysis, chemical sensors, dyes, pigments and colours, gas sensors, electrochromism, batteries, semiconductive materials, liquid crystals, nonlinear optics and photodynamic therapy (Eriyilmaz *et al.*, 2017). Since their discovery, phthalocyanines have been extensively used as colourants, but they also have been employed in different technological areas, such as photoconducting materials, light Light-Light-absorbing layers in recordable compact discs (CDs), photosensitizers in cancer therapy, and industrial catalysts (Gounden *et al.*, 2020). The word phthalocyanine was derived from the Greek word “naphtha”, meaning rock oil and

“cyanine”, meaning blue (Chohan, 2015). Sir Patrick Linstead in 1933 was the first to use this term to describe a new class of compound (Alharbi, 2014).

The properties and applications of phthalocyanine complexes can be tuned by modifying the structure of the ligand and the choice of the metal ion (Yang *et al.*, 2021). Researchers continue to explore and develop new phthalocyanine complexes with improved properties for various technological applications. Metallophthalocyanines complexes, have also attracted attention due to their structure rich in π -conjugation system owing to potential applications in various engineering and technological fields such as electronic devices (Yamada *et al.*, 2018), gas sensors (Yang *et al.*, 2021), static induction transistors (Namgoong *et al.*, 2018), and photoreceptor devices in laser beam printers and photocopiers (Korkmaz *et al.*, 2020). Additionally, certain derivatives of phthalocyanines have shown promising roles as photodynamic reagents for cancer therapy and other medical applications (Laskoski *et al.*, 2014). But, the poor solubility of metal phthalocyanine limits their applications. To solve this problem, introducing certain substituents at their peripheral ring (Lapok *et al.*, 2013) will be a promising way.

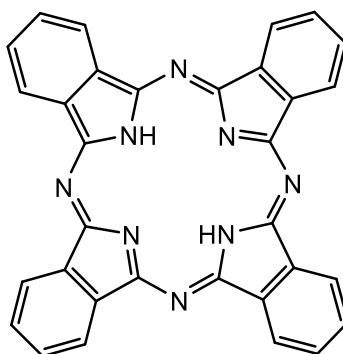


Figure 1: Chemical structure of phthalocyanine

MATERIALS AND METHODS

All reactions were performed under argon atmosphere. 1,8-diazabicyclo [5.4.0] -undec7-ene (DBU), cobalt and copper, were obtained from Merck and Glycerol solution, was procured from Sigma-Aldrich and used as obtained without further purification. The spectral analysis of complex was carried out after the synthesis as FT-IR spectrum of the samples was recorded on an FT-IR spectrophotometer (Perkin Elmer). UV-Vis spectra were recorded on a T80+UV/VIS spectrophotometer. At a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, TGA was conducted under Argon using a SHIMADZU thermogravimetric analyzer TGA-50 Instruments.

Synthesis of Cobalt phthalocyanine

Phthalonitrile (0.40 g) [0.9 mmol] was added to 10mL of glycerol and stirred, 0.100g (0.401mmol) of cobalt acetate and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) [4 drops] was added, stirred and heated at a reflux temperature under an argon atmosphere for 24 hr. After cooling to room temperature, the reaction mixture was precipitated by dropwise addition to distilled water (200 mL). The product was collected by filtration, washed with distilled water and dried. The compound was purified by dissolving in 3.0 mL of sulphuric acid and stirred, it was precipitated in distilled water, vacuum filtered and washed several time with distilled water until the pH of the water was neutral. A green product obtained was dried and weighed.

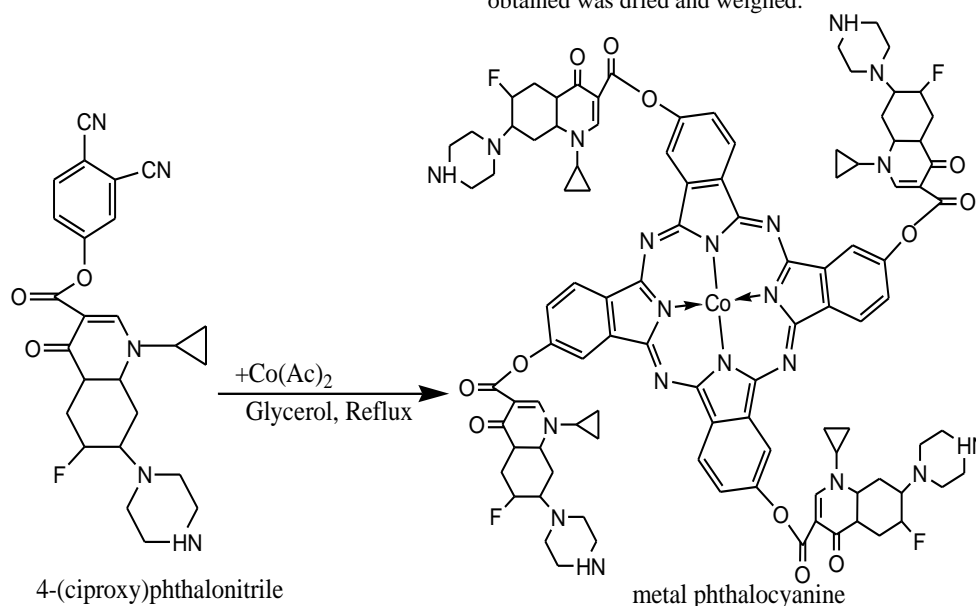


Figure 2: Synthesis of cobalt phthalocyanine complex

Synthesis of Copper phthalocyanine

Phthalonitrile (0.40 g) [0.9 mmol] was added to 10ml of Glycerol and stirred, 0.100g (0.055mmol) copper acetate and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) [4 drops] was added, stirred and heated at a reflux temperature under an argon atmosphere for 24 hr. After cooling to room temperature, the reaction mixture was precipitated by

dropwise addition to distilled water (200 ml). The product was collected by filtration, washed with distilled water and dried. (Touaiti *et al.*, 2017). The compound was purified by dissolving in 3.0 ml of sulphuric acid and stirred, it was precipitated in distilled water, vacuum filtered and washed several time with distilled water until the pH of the water was neutral. A greenish product obtained was dried and weighed.

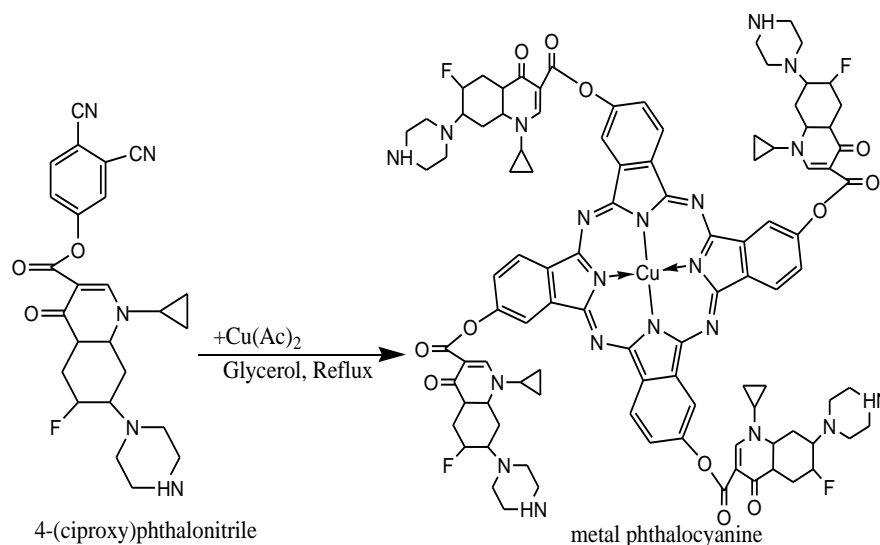


Figure 6: Synthesis of Copper Phthalocyanine Complex

RESULTS AND DISCUSSION

Cyclotetramerization of the phthalonitrile derivative was carried out in a high-boiling solvent (glycerol). A few drops of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as a strong base and metals salt at reflux temperature under an argon atmosphere afforded the synthesis of the phthalocyanine complexes, the compounds were confirmed by FT-IR, UV-Vis spectra and TGA. The most important proof of the

cyclotetramerization of nitrile groups was the absence of the $\text{-C}\equiv\text{N}$ vibrations at 2230cm^{-1} for phthalocyanine compounds in IR spectra of the substituted metal phthalocyanine compounds.

Synthesis and Characterization of Cobalt Phthalocyanine
Cobalt phthalonitrile as given in Figure 4 was synthesized using 4-phthalonitrile and cobalt acetate in glycerol solutions.

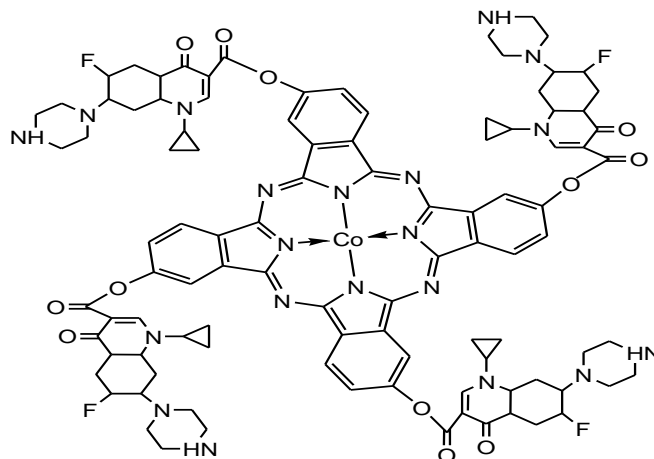


Figure 4: Cobalt phthalocyanine

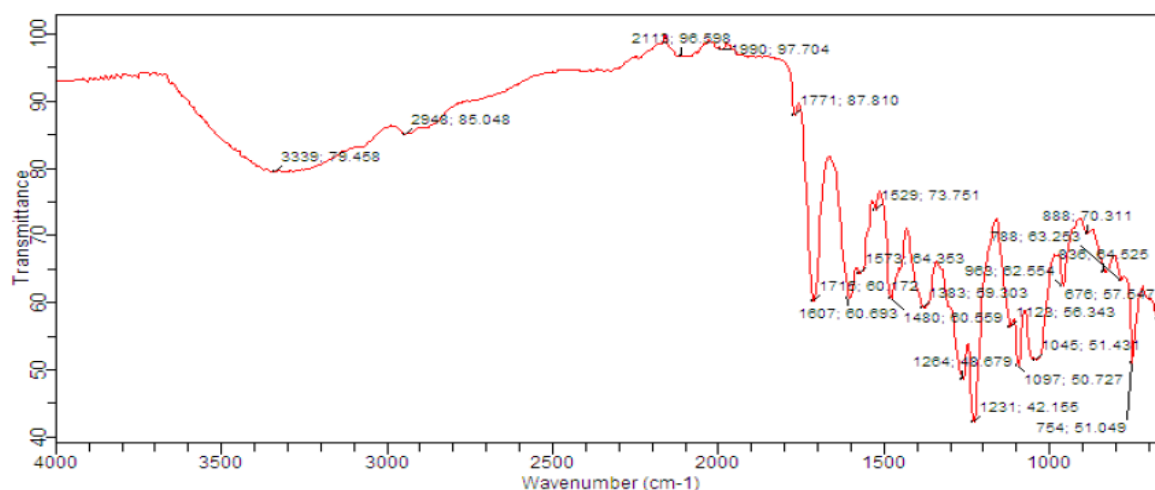


Figure 5: FT-IR of cobalt phthalocyanine

Table 1. FT-IR results of cobalt phthalocyanine

S/N	Frequency (cm^{-1})	Bond Vibration
1	2948	Ar-CH
2	1716	C=O
3	1607	C=C
4	1231	C-O

The synthesized CoPc compound showed intense Q band at 677 nm, in the UV-VIS spectrum obtained in DMF solvent, this is attributed to $\pi\text{-}\pi^*$ transition from the highest occupied

molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 610 nm.

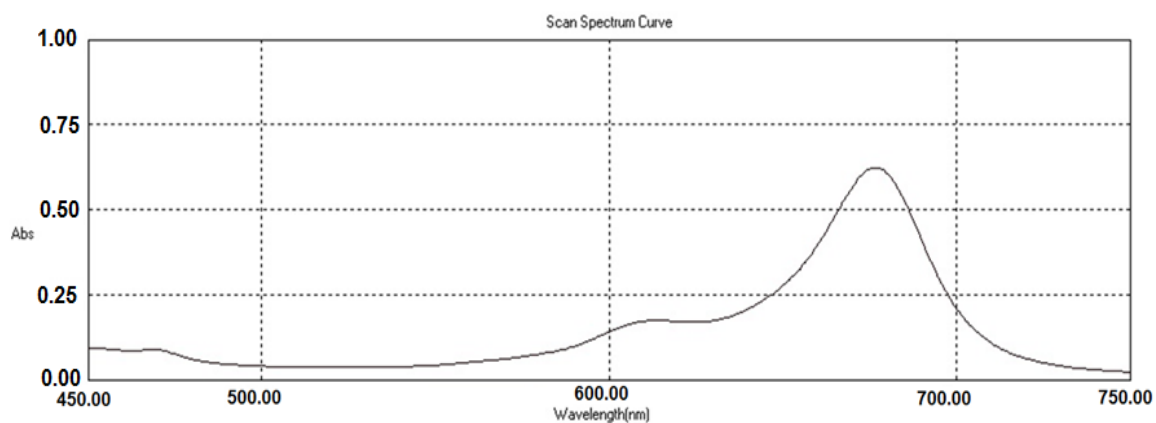


Figure 6: UV spectrum of cobalt phthalocyanine

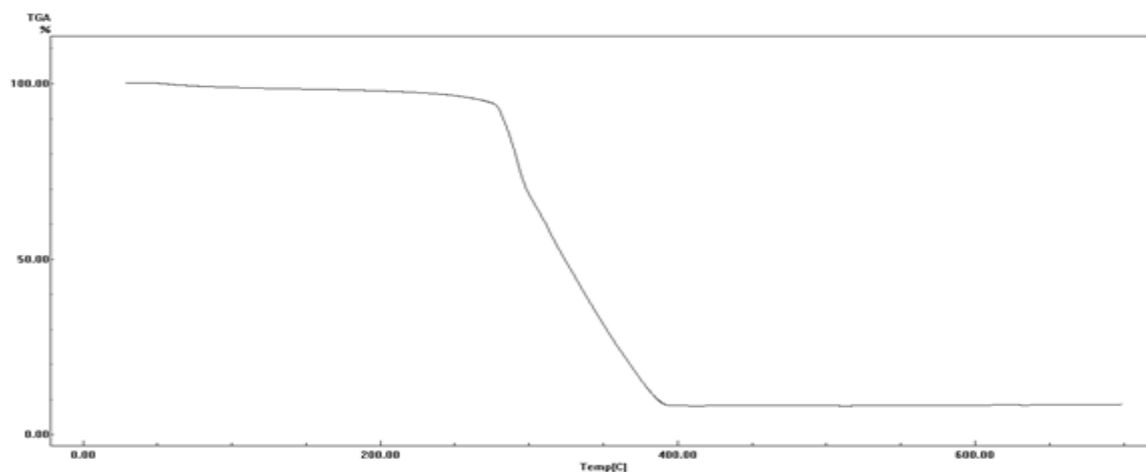


Figure 7: TGA of cobalt phthalocyanine

Synthesis and Characterization of Copper phthalocyanine
Copper phthalocyanine shown in Figure 8 was synthesized using 4-phthalonitrile and copper acetate in glycerol

solutions and the FT-IR results are presented in Table 2 and Figure 9.

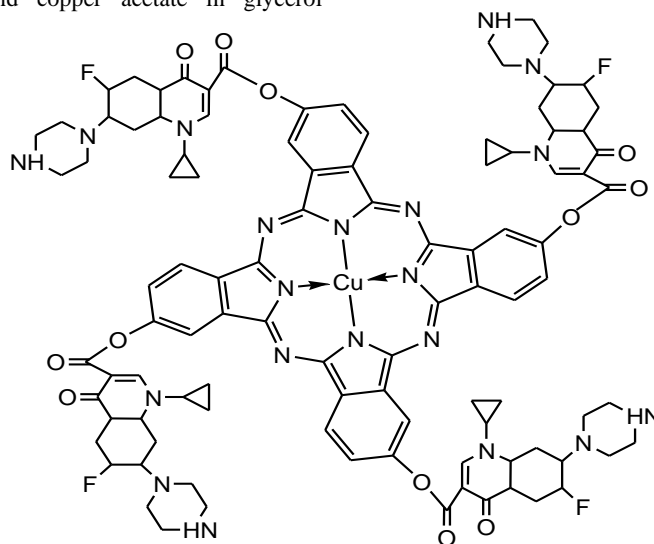


Figure 8: Copper phthalocyanine

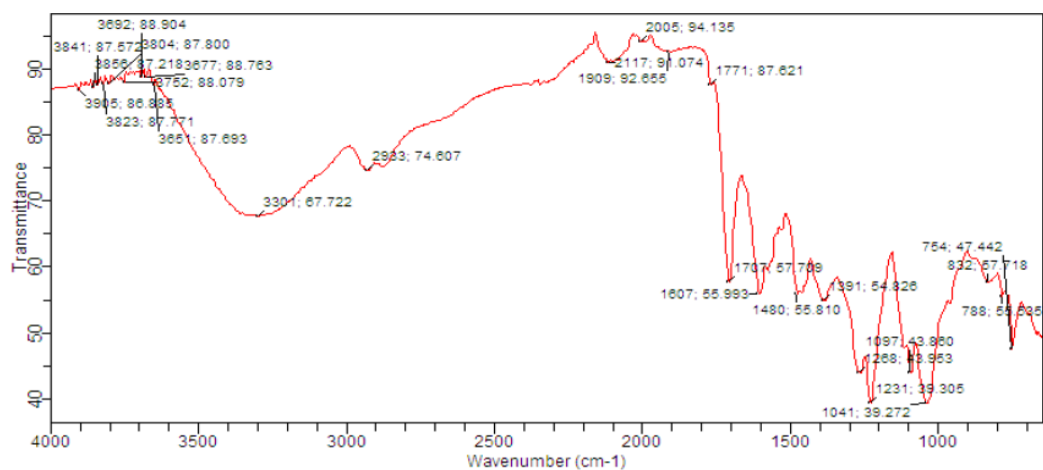


Figure 9: FT-IR of Copper phthalocyanine

Table 2. FT-IR results of copper (II) phthalocyanine

S/N	Frequency (cm ⁻¹)	Bond Vibration
1	2933	Ar-CH
2	1704	C=O
3	1603	C=C
4	1231	C-O

The synthesized CuPc compound showed an intense Q band at 690 nm, in the UV-VIS spectrum obtained in DMF solvent. This is attributed to $\pi-\pi^*$ transition from the highest occupied

molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 615 nm.

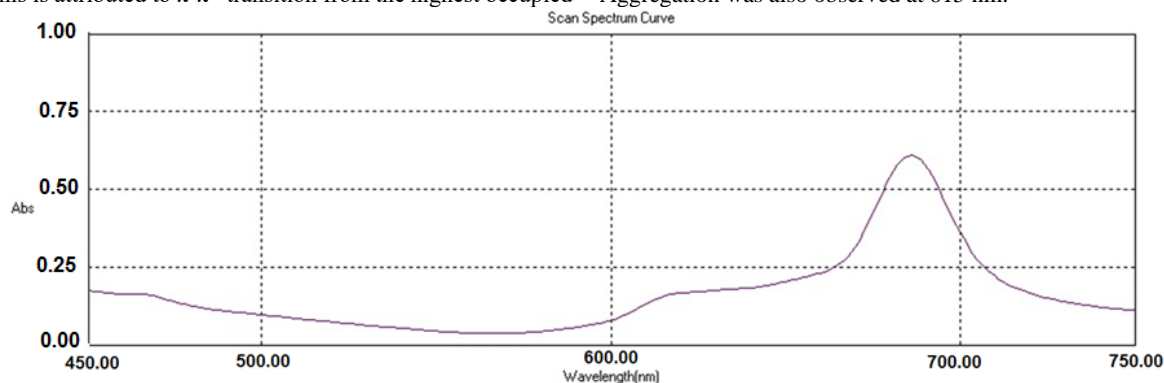


Figure 10: UV spectrum of Copper phthalocyanine

The thermographic analysis result of the synthesized copper phthalocyanine compound showed that the synthesized compound began to exhibit weight loss at a temperature of

309 °C which indicates a suitably high thermal stability for the newly synthesized compound.

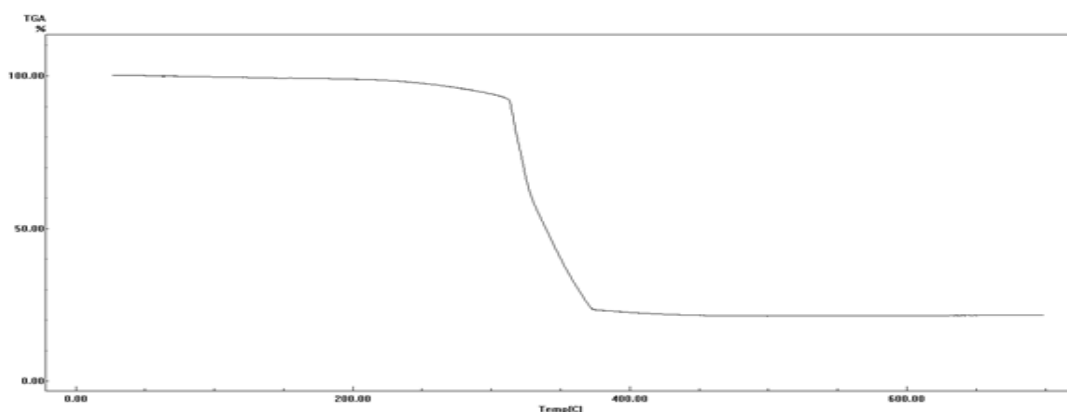


Figure 11: TGA of copper phthalocyanine

CONCLUSION

Synthesis of Cobalt and copper phthalocyanine metals complex were achieved by using phthalonitrile derivative as precursor, the structures of the synthesized compounds were characterized by FT-IR, UV-VIS and TGA, the disappearance of the $\text{-C}\equiv\text{N}$ vibrations at 2230 cm^{-1} in the IR spectra of the substituted metal phthalocyanine confirmed the cyclotetramerization of nitrile groups forming the phthalocyanine complex. Solubility of the compounds was confirmed in some common laboratory solvent (acetone, methanol and DMF). This report has therefore shown that the availability of this compound as a general synthetic reagent to phthalocyanine based materials will make alteration of physical properties through steric hindrance effects achievable. Variation of phthalocyanine electronic structure will also be possible by introducing substituents at electronically influential sites.

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