# EFFICIENT SYNTHESIS AND DETAILED THERMAL STUDIES OF ZINC PHTHALOCYANINE

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## Abstract

A facile and efficient, one step synthesis of macrocyclic molecule zinc phthalocyanine (ZnPc), was proposed. Dark violet crystals of ZnPc dye were obtained in high boiling point solvent of dimethylformamide (DMF) in the presence of 2,2,6,6-tetramethylpiperidine (TMP) as a catalyst. Detailed thermogravimetric and kinetic analysis revealed high thermal stability of the investigated compound.

## Introduction

In today's world, it's hard to find scientist who hasn't worked or be in touch with organic dyes. As a result, complex structures of metallophthalocyanines (MPs) with near-infrared incidence continue to pique the study community's curiosity. Phthalocyanines (Pcs) are aromatic heterocycles consisting of a planar conjugated system with 18 π-electrons and 4 isoindole subunits bridged by meso positioned nitrogen atoms. They feature a distinctive UV-Vis absorption spectrum with two primary bands, the weak Soret band at 300-400 nm and the Q-band located at around 600-800 nm. A compelling MPcs chemistry experienced its greatest growth in last two decades, revealing molecules that meet the high demands of photodynamic therapy (PDT), chemical sensor technology, non-linear optics (NLO) and dye-sensitized solar cells (DSSC). Furthermore, they have been used as electrocatalysts in fuel-cell reactors for dioxygen reduction. Notably, the nature of the coordinated central metal ion has a big impact on their photochemical characteristics. Thus, singlet oxygen production is poor in MPcs with paramagnetic metal centers. Closed shell and diamagnetic ions, such as $Zn^{2+}$, $Ga^{3+}$, and $Si^{4+}$, play a vital role in MPc complexes and contribute great features such as high singlet oxygen production, which is critical for photosensitizer PDT efficiency [1, 2].

The synthetic process for creating MPcs is constantly improving over the years based on the available research data [1, 3]. MPcs are frequently produced via cyclotetramerization of phthalonitrile or phthalic acid analogues, in the presence of a metal or metal salt, at high temperatures and reaction durations of several hours [2, 4]. Numerous investigations have been conducted to improve the synthesis approach of unsubstituted ZnPc, which is one of the most spectroscopically studied phthalocyanines [5]. On the contrary to the potential utility of these approaches, reaction condditions necessary for these reactions are very long reaction time and high temperature, resulting in a low obtained macromolecule yield.

In order to obtain a new and efficient catalysts for the ZnPc synthesis, adequate for organic solvents, we have examined the catalytic activity of 2,2,6,6-tetramethylpiperidine (TMP) in reaction of cyclotetramerization of phthalonitrile in dimethylformamide (DMF). Investigation toward extension of this procedure to other derivatives is in progress.
In addition, comprehensive thermal stability research of ZnPc crystals provides a realistic assessment for their real application.

## Experimental

Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and methanol were purchased from Merck. Zinc acetate dihydrate, 1,2-dicyanobenzene (phthalonitrile) and 2,2,6,6-tetramethylpiperidine (TMP) were purchased from Sigma Aldrich.

The ultraviolet–visible (UV/Vis) absorption spectra were recorded on a Shimadzu UV–Visible UV-2600 (Japan) spectrophotometer in the range 200–800 nm. FTIR spectroscopy measurements were performed on Nicolet TM 380 FT-IR spectrometer with Smart Orbit ATR accessory (Thermo Electron Corporation, Madison, U.S.A).

Thermogravimetric analysis of the ZnPc was tested on a TGA/DTA instrument (Setaram Setsys 1750 Evolution (France)). The sample was heated from 30 to 1000 °C in an atmosphere of pure argon ($\varphi$=20 $cm^3$/min), with heating rates $\beta$ = 5, 10 and 15°C/min. The average weight of the sample was 3 mg.

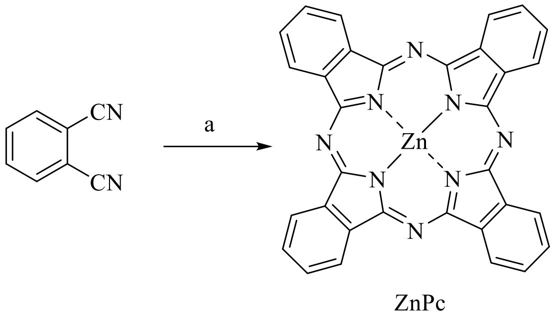
Synthesis

In a round bottom flask equipped with a reflux condenser and a magnetic stirrer, 2.5 mmol of phthalonitrile and 0.625 mmol of zinc acetate dihydrate were dissolved in 1 mL of DMF after which TMP was added. The reaction mixture was heated for 6 h at 153°C. After cooling to room temperature, the reaction mixture was precipitated by the addition of methanol. The precipitate was filtered off and washed with 2 mL of 3% HCl, water (20 mL) and methanol (15 mL). The resulting deep purple cristals remain after processing of reaction mixture.

Yield: 0.249 g (69%, $C_{32}H_{16}ZnN_8$). UV/Vis (DMSO): $\lambda$ (nm) 670, 640, 603, 343. FT-IR, $\nu$ ($cm^{-1}$): 753, 775, 882, 1060, 1085, 1120, 1167, 1282, 1334, 1445.

## Results and discussion

The synthesis of ZnPc was realized by a one step procedure starting from 1,2-dicyanobenzene in the presence of zinc acetate dihydrate and DMF as a solvent (Scheme 1.). After 6 hours of heating, deep purple ZnPc crystals were obtained in a high yield of 69% in the presence of an organic base, TMP, which acted as an excellent catalyst for the cyclotetramerization process.



Scheme 1. General synthetic scheme for the synthesis of zinc phthalocyanine (ZnPc) with precursors (a) $Zn(CH_3COO)_2{\cdot}2H_2O$, TMP, DMF

The resulting purple crystals of metallophthalocyanine were characterised using the spectroscopic methods including UV-Vis and FT-IR. The UV-Vis absorption spectrum of macrocyclic compound ZnPc was shown in Figure 1. As can be seen from the spectrum there are two groups of absorption bands at 550–700 nm and 300–450 nm, respectively. The band from 550 to 700 nm were characteristic Q-band absorption of ZnPc. In this band group, the two well resolved absorption peaks at 670 and 603 nm should be assigned to the $\pi$–$\pi$* transition of monomer from the HOMO to the LUMO of the $Pc^{-2}$ ring [6]. Notably, between the two peaks of Q bands, there appeared a weak peak at 640 nm, which might be assigned to the vibronic band due to the dimers and multimers while the band of 300–450 nm should belong to the typical B-band absorption of ZnPc arising from the deeper π levels-LUMO transition [7].

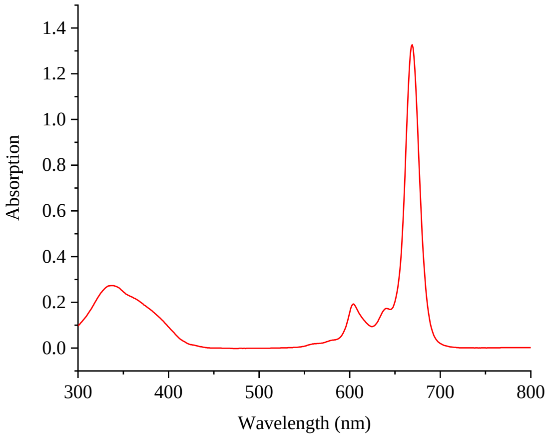


Figure 1. UV-Vis absorption spectra of ZnPc in DMSO at room temperature

The FT-IR spectral measurement is carried out to ascertain the functional group structures for ZnPc. The absorption peaks at 1334 cm$^{-1}$, 1167 cm$^{-1}$, 1120 cm$^{-1}$, 1085 cm$^{-1}$, 882 cm$^{-1}$, 753 cm$^{-1}$ were assigned to Pc skeletal vibration. Absorption peaks observed around 1445 cm$^{-1}$ and 1282 cm$^{-1}$ were assigned to aromatic phenyl ring and C–N=strech vibrations. The peaks at 1060 cm$^{-1}$ and 775 cm$^{-1}$ are assigned the C–H in-plane bending vibrations and C–H out-of-plane bending vibrations, respectively. In the IR absorption spectra, the formation of Pc was confirmed by disappearance of phthalonitrile C≡N band at 2226 cm$^{-1}$.

Thermal stability of ZnPc was analyzed using TGA-DTG and DTA techniques. The thermal stability of the sample is represented by the temperature at which its decomposition begins. TG curve (Figure 2a.) of compound shows that thermal degradation occurs in two steps. The first temperature loss at 50 °C is caused by evaporation of free adsorbed water which also can be seen on DTA curve (Figure 2b.) as an endothermic peak at around 50 °C.

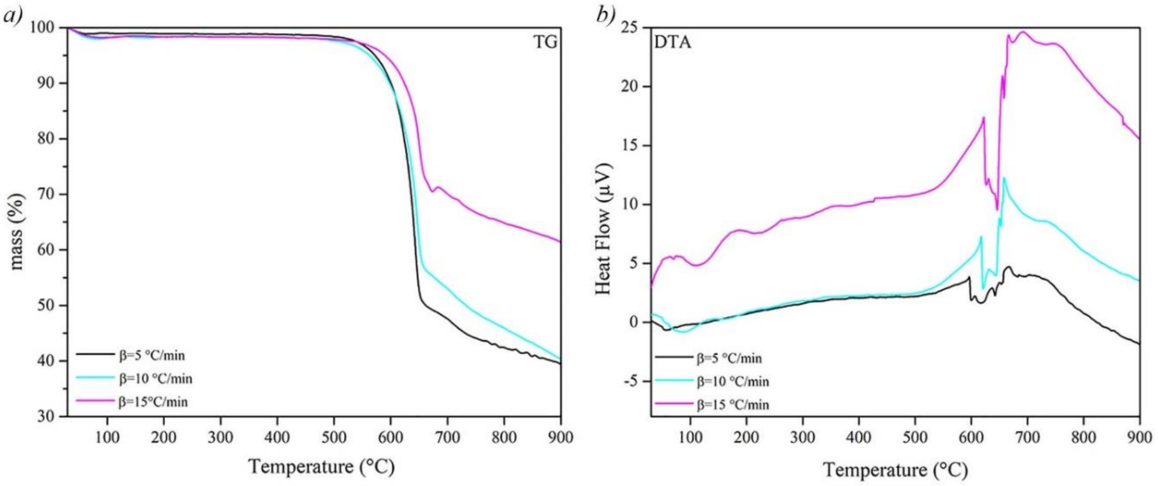


Figure 2. TG (a) and DTA (b) curves for ZnPc at three different heating rates (5, 10 and 15 °C/min)

The second temperature loss, between 500-700 °C, is due to the decomposition of Pc skeleton. These mass losses are observed as two peaks in DTG feature (Figure 3.) at 50 and 639 °C (for heating rate 5 °C/min) [8].

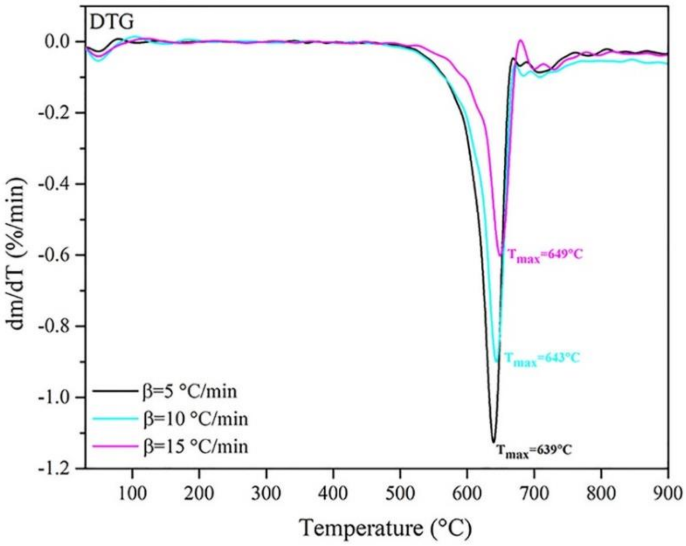


Figure 3. DTG curves for ZnPc at three different heating rates (5, 10 and 15 °C/min)

The kinetic parameters, pre-exponential factor (A) and apparent activation energy ($E_a$) for ZnPc molecular structure degradation process that occurred at the second steps are obtained by Kissinger (Eq. 1) [9] and Ozawa (Eq. 2) methods. These two methods are based on shift of the peak temperature $T_{max}$, with heating rate (β) changes:

$$\log\frac{\beta}{T_{max}^2} = \log\frac{AR}{E_a} - \frac{E_a}{2.303\cdot RT_{max}} \qquad (1)$$

$$\log\beta = \log\frac{AE_a}{R} - 2.315 - 0.4567\left(\frac{E_a}{RT_{max}}\right) \qquad (2)$$

A is determined from the intercept, while the $E_a$ is determined from the slope of linear dependence log $(\beta/T_{max}^2)$–$1/T_{max}$ for Kissinger and log β–$1/T_{max}$ for Ozawa method.

A high value of activation energy, over 700 kJ/mol, indicates exceptional thermal stability of the investigated compound. The value of the pre-exponential factor greater than $10^{16}$ $min^{-1}$ means that a large number of collisions of molecules as well as high values of $E_a$ are required for the degradation of the compound.

Table 1 *The value of A and Ea using Kissinger and Ozawa method for ZnPc*

| Sample | Kissinger method | | Ozawa method | |
|---|---|---|---|---|
| | $E_a$, kJ/mol | A, $min^{-1}$ | $E_a$, kJ/mol | A, $min^{-1}$ |
| ZnPc | 730.67 | $4.00\times10^{41}$ | 709.20 | $6.85\times10^{40}$ |

## Conclusion

In conclusion, we have developed a convenient procedure for the high-yield synthesis of ZnPc employing TMP as an efficient catalyst. Refluxing phthalonitrile and zinc acetate in DMF and TMP, gave deep purple crystals of macrocyclic ZnPc compound. Noteworthily, this approach is currently being investigated to see whether it can be extended to other MPcs. The investigated compound's exceptional thermal stability was revealed by detailed thermogravimetric and kinetic analysis.

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