




Heat gun-assisted rapid efficient synthesis of tetra-substituted Zinc(II) phthalocyanines functionalized with alkylthio or alkoxy chains

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Abstract: The most common method for metalated or metal-free phthalocyanines involves starting from phthalonitrile derivatives. These conventional reactions are generally carried out in high-boiling-point solvents (such as pentanol, DMF, DMSO, Quinoline, etc.) under reflux where they often have extended reaction times of up to 24 hours. New reaction methods with lower energy in short periods of time have been an issue to solve nowadays. Considering all, we aimed to synthesize substituted zinc phthalocyanine derivatives rapidly and with higher yields, without using any solvents. This study shows new synthesis methods for substituted phthalocyanine derivatives. ZnPc derivatives with different chain lengths functionalized with "O" and "S" donor atoms from the peripheral position have been synthesized in yields ranging from 52-75% in overall 3 minutes. Compared to conventional methods, which typically require extended reaction times and high energy consumption, this innovative approach reduces the reaction time from 18 hours to just 3 minutes and decreases energy consumption from 1.926 kWh to 0.063 kWh. The method achieves high reaction yields, highlighting its potential for sustainable chemical synthesis.

Keywords: Solid-state synthesis; heat-gun; high yield; green synthesis; alkyl substituted phthalocyanine.
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1. Introduction

Phthalocyanines (Pcs) have been an important research topic of chemistry and material science. Since the 1900s they have been synthesized in various areas and are widespread including electronics, sensors, solar cells, dye industry, optical films, photodynamic therapy etc.¹⁻³ Pcs are mostly famous for their remarkable color.

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Even though their various synthesis pathways, phthalocyanines have always faced significant challenges, especially extremely time consuming for obtaining a product with conventional methods. Moreover, the obtained yields through these procedures are disappointingly low. In addition to these limitations, the use of non-recyclable solvents, the need for organic basic catalysts, and the formation of by-products lead to adverse environmental conditions. Scientist's efforts to reduce solvent usage and minimize environmental impact have become a main point in this field. They have come up with new ideas, from microwave synthesis to ionic solvent synthesis and solid-state reactions with almost zero amount of solvents.^{4,5} These advancements represent significant strides toward achieving a sustainable and efficient synthesis of phthalocyanines.

2. Background

Phthalocyanine compounds can be started synthesized from phthalonitriles, phthalic anhydrides and phthalimides⁶, here in this work all Pcs compounds were synthesized from phthalonitriles. It is known that synthesis of Pc compounds requires a high amount of solvent which is environmentally harmful on the industrial field. Over recent years green chemistry has been a global concern all over the world.

Pcs have an 18 π -electron system due to its 4 aromatic rings coming together and these rings are making the molecule planar, and this increases its application areas.^{6,7} The phthalocyanine general structure and the substitution positions are given in Figure 1. Aromatic compounds have been a big study area for chemists due to their electrical, optical and stability. As stated above the significantly conjugated aromatic structure of phthalocyanines show very specific and characteristic Q band absorption that can be found between 650 to 700 nm of their UV-Vis absorption spectra. These bands are a result of π - π^* electronic transitions within the conjugated phthalocyanine macrocycle. The Q bands in phthalocyanines, whether metalated or metal-free, refer to the intense absorption bands in the visible region. These bands in phthalocyanines play a crucial role in defining their optical properties and applications. In metal-free phthalocyanines, these bands are split due to lower molecular symmetry (D_{2h}), while metalated derivatives exhibit a single, sharp Q band because of higher symmetry (D_{4h}).^{8,9}

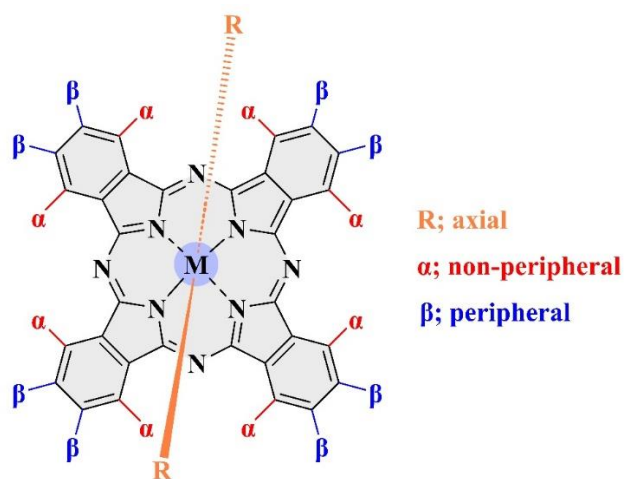


Figure 1. General structure of Phthalocyanine and showing functional groups positions

1. Experimental

3.1. Instruments and Chemicals

The Perkin Elmer Spectrum 100 FT-IR spectrophotometer was used to record the data between 4000 and 550 cm^{-1} with an attenuated total reflection (ATR) accessory. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was used to analyze

synthesized final products. ^1H NMR spectra were recorded on Bruker 500 MHz and Varian 600 MHz spectrometers using TMS as an internal reference. Absorption spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Chemical shifts (δ) are given in ppm, in CDCl_3 , UV-vis absorption spectra were recorded by Shimadzu UV 2600 spectrophotometer.

Chemicals used in this study were reagents of Sigma Aldrich, TCI chemicals including, 4-nitrophthalonitrile, 1-hexanol, 1-hexanethiol, 1-octanol, 1-octanethiol, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), potassium carbonate, zinc acetate dihydrate, *N,N*-dimethylformamide, ethanol, tetrahydrofuran, dichloromethane, methanol, acetonitrile, silica gel 60 F_{254} TLC plates, preparative thin-layer chromatography plates silica gel 60 F_{254} .

Heat guns, flameless handheld devices that emit a stream of highly heated air, are commonly utilized in research laboratories; an adjustable heat gun was used in solvent-free phthalocyanine syntheses.¹⁰ The heat gun model was the Steinel HL 2010 E, equipped with a microprocessor-controlled system, an LCD display, and a DuraTherm™ ceramic heating element. This device operates at a temperature of 49°C to 621°C, an output power of 1500 watts, and airflow rates of 3.6, 10.6, and 17.6 cfm. Additionally, the energy consumption was calculated using a Wellhise PM004+ wattmeter (max current 16A, power 3680W). The wattmeter was placed between the power out and the device to record the total energy consumption in kilowatt-hours (kWh) during the reaction.

3.2. Synthesis

The 4-(hexyloxy)phthalonitrile (1) was synthesized in this study, others; 4-(octyloxy)phthalonitrile (2)⁵, 4-(hexylthio)phthalonitrile (3)¹¹ 4-(octylthio)phthalonitrile (4)¹² was carried out following previously reported procedures. All phthalonitrile derivatives found in the literature were characterized using FT-IR, and mass spectrometry but, 4-(hexyloxy)phthalonitrile was characterized using FT-IR, NMR and mass spectrometry. As a conventional method, the synthesis of peripheral alkoxy- and alkylthio-substituted zinc phthalocyanine compounds was carried out under reaction conditions adapted from previous work.¹³ Details of the heat gun method for ZnPcs are provided in section 3.2.3. The reactions were completed within an average of 3 minutes, and their yields were determined using a method developed within the scope, based on UV-Vis spectroscopy.

3.2.1. Synthesis of Phthalonitriles

4-nitrophthalonitrile (500 mg, 1 eq), hexanol (354 mg, 1.2 eq), and 15 mL of dry DMF were placed in a proper reaction flask. The reaction mixture was stirred under an $\text{Ar}_{(\text{g})}$, and potassium carbonate (1.2 g, 3 eq) was gradually added in portions over 15 minutes. Subsequently, the reaction temperature was raised to 65 °C. After stirring overnight, the mixture was cooled to room temperature and extracted with the dichloromethane/water mixture. The organic phase was removed via evaporation, and then the precipitate was purified by column chromatography using dichloromethane. The other phthalonitrile derivatives are synthesized by using previous work. The characterization data are given in the Supporting Information, Figure S1-S10.

4-(hexyloxy)phthalonitrile (**1a**): IR ATR (cm^{-1}): 3082, 2952, 2917, 2852, 2228. MS (ESI): m/z calculated for [M^*]: 228.30, found: 229.12. ^1H NMR (δ , ppm, 600 MHz, CDCl_3): 7.93 (d, J = 8.8 Hz, 1 H), 7.25 (d, J = 2.6 Hz, 1 H), 7.17 (dd, J = 8.8, 2.6 Hz, 1 H), 4.04 (t, J = 6.5, 2H), 1.85 – 1.79 (m, 2H), 1.49 – 1.43 (m, 2H), 1.35 (m, 4H), 0.94 – 0.90 (t, 3H). ^{13}C NMR (δ , ppm, 150 MHz, CDCl_3): 162.38, 136.24, 124.00, 123.68, 118.85, 114.65, 114.27, 69.48, 31.54, 28.86, 25.63, 22.67, 14.13.

4-(octyloxy)phthalonitrile (**2a**): IR ATR (cm^{-1}): 3082, 2952, 2917, 2852, 2229. MS (ESI): m/z calculated for [M^*]: 256.35, found: 255.13.

4-(Hexylthia)phthalonitrile (**3a**): IR ATR (cm^{-1}): 3100, 2955, 2927, 2858, 2232. MS (ESI): m/z calculated for [M^*]: 244.36, found: 244.12.

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4-(*Octylthia*)phthalonitrile (**4a**): IR ATR (cm^{-1}): 3092, 2958, 2927, 2853, 2228. MS (ESI): m/z calculated for $[\text{M}^*]$: 272.41, found: 271.22.

3.2.2. Conventional Synthesis of Alkyl-Functionalized Zinc Phthalocyanines

Functionalized phthalonitrile (50 mg, 4 eq), dry zinc acetate (~18 mg, 2 eq), DBU (20 μL , 0.075 eq), and 1 mL $\text{DMF}_{(\text{dry})}$ were placed in a proper reaction flask. After stirring under reflux conditions in an $\text{Ar}_{(\text{g})}$ atmosphere for 18 hours, it was brought to room conditions. Each final product was purified using preparative TLC plates with a 100:1 DCM: EtOH mobile phase. The target bands were scraped, and extracted with DCM: EtOH mixture, and the solvents were removed to obtain the purified products. Since MPcs except **1b** are known in the literature, the characterization of the purified products was performed using FT-IR and MALDI-TOF MS spectra. The characterization data are given in the supporting information, Figure S11-S18.

Tetrakis(hexyloxy)zinc(II)phthalocyanine (**1b**): IR ATR (cm^{-1}): 3073, 2923, 2854. MALDI-TOF (matrix: DIT) calcd: m/z : 978.68, found: m/z : 978.32 $[\text{M}^+]$.

Tetrakis(octyloxy)zinc(II)phthalocyanine (**2b**): IR ATR (cm^{-1}): 3073, 2923, 2854. MALDI-TOF (matrix: DIT) calcd: m/z : 1090.78, found: m/z : 1090.01 $[\text{M}^+]$.

Tetrakis(hexylthia)zinc(II)phthalocyanine (**3b**): IR ATR (cm^{-1}): 3011, 2924, 2860. MALDI-TOF (matrix: DIT) calcd: m/z : 1042.80, found: m/z : 1042.0 $[\text{M}^+]$

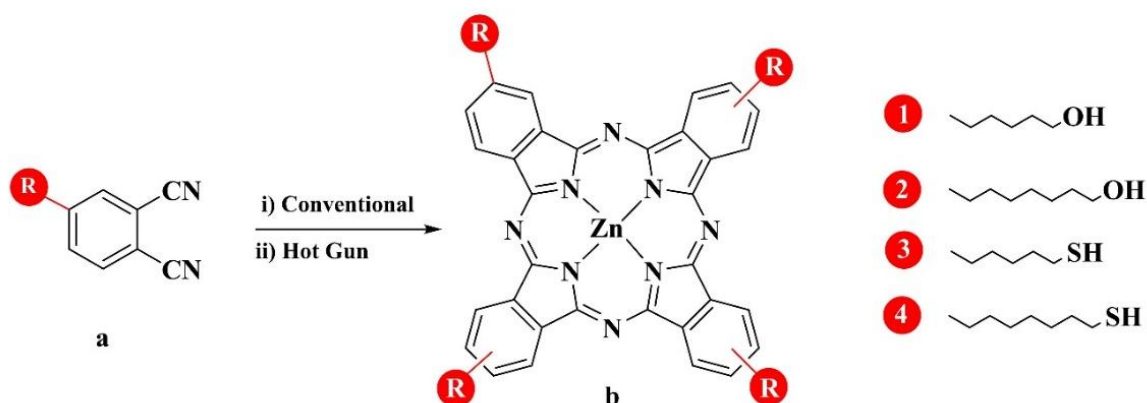
Tetrakis(octylthia)zinc(II)phthalocyanine (**4b**): IR ATR (cm^{-1}): 3065, 2955, 2853. MALDI-TOF (matrix: DIT) calcd: m/z : 1155.02, found: m/z : 1115.03 $[\text{M}^+]$

3.2.3. Heat Gun Synthesis of Alkyl-Functionalized Zinc Phthalocyanines

Functionalized phthalonitrile (50 mg, 4 eq), dry zinc acetate (~18 mg, 2 eq), and DBU (20 μL , 0.075 eq) were placed in a 5 mL pressure-resistant screw-cap tube and mixed using an appropriate magnetic stirrer. The reaction mixture was subjected to heating using a hot gun preheated to 300 $^{\circ}\text{C}$. A nozzle was attached to the heat gun (57 mm x 33 mm x 35 mm (L x W x H)), and the distance between the reaction tube and the heat gun output was set to 20 mm for each experiment. Performed for each compound five times under these conditions. During reactions, the internal temperature was measured with the help of an electronic thermometer. The average internal temperature value was determined as 172.4 ± 4.7 $^{\circ}\text{C}$. Samples were collected at 1-minute intervals, and the reaction yields were monitored using UV-Vis spectroscopy. This procedure was repeated for four different phthalonitrile derivatives to synthesize their corresponding zinc phthalocyanines.

2. Present Study

In this paper, four different ZnPcs, containing alkylthio and alkoxy groups with different chain lengths, were synthesized using two different methods. In the conventional method, the syntheses were completed in DMF under reflux conditions over 18 hours. On the other hand, by the heat gun method, the syntheses were successfully performed in an average of 3 minutes without the use of any solvents. All synthesized ZnPc compounds are shown in Scheme 1. To compare the energy consumption of the two synthesis methods, the amount of electrical energy consumed during the reaction times was measured in kWh using a wattmeter.



Scheme 1. Synthesis of alkyl substituted ZnPcs.

Initially, the reaction yields and energy consumption values for ZnPcs synthesized using conventional methods were determined. To observe the absorbance properties of the ZnPcs, UV-Vis spectra were recorded in the range of 500-800 nm at concentrations varying from 0.5 ppm to 12 ppm. The absolute areas under the curves were calculated, and these values were plotted against specific concentrations to generate standard calibration graphs for each compound. The graph for compound 1a is shown in Figure 2, while the standard graphs for the other compounds are given in the supporting information, Figures S19 to S21.

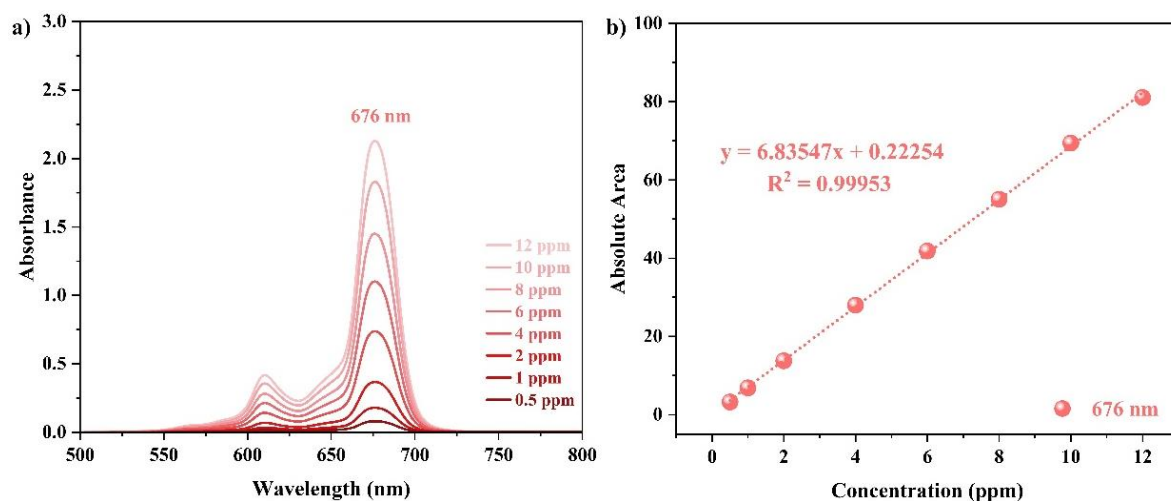


Figure 2. a) UV-Vis graph in the range of 500-800 nm obtained at different concentrations of compound 1b, b) A graph of concentration versus area prepared for use as a standard for 1b.

Samples were taken from the reaction at 1-minute intervals, and stock solutions were prepared in 20 ppm THF. UV-Vis measurements were made in the 500-800 nm range for these prepared stock solutions. Reaction% yields were calculated from standard graphs using the areas under the UV-Vis graphs. The average yields calculated from five replicates are presented in Table 1, compared with the conventional method.

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Table 1. The reaction yields for synthesized by conventional and heat gun methods

Compound	Time (min)	Solid-State Yield %	Conventional Yield %
1b	1	10.2 ± 2.1	49
	2	51.5 ± 3.7	
	3	75.4 ± 2.4	
	4	74.7 ± 1.8	
	5	67.6 ± 2.4	
2b	1	9.9 ± 1.6	44
	2	35.2 ± 1.7	
	3	53.3 ± 2.5	
	4	52.1 ± 2.1	
	5	46.9 ± 2.8	
3b	1	9.3 ± 1.8	46
	2	34.6 ± 2.1	
	3	53.6 ± 1.8	
	4	52.1 ± 2.7	
	5	47.9 ± 3.2	
4b	1	22.9 ± 2.3	42
	2	42.5 ± 3.4	
	3	52.1 ± 2.1	
	4	51.2 ± 2.7	
	5	47.6 ± 2.3	

The results show that ZnPcs were formed in the reaction medium with maximum efficiency in the 3-minute reaction time. The decrease of yield when the time is extended indicates that degradation products have started to form. In addition, a wattmeter was used to determine the total energy consumption differences between the two methods. In the conventional method consumed a total of 1.926 kWh for 18 hours, on the other side the heat-gun consumed a total of 0.038 kWh during the 3-minute reaction time. To treat the reactions identically, the heat gun was pre-heated to 300 °C for approximately 1 minute and consumed 0.025 kWh of energy. Including the energy cost for heating, only 0.063 kWh of energy consumption was realized in this proposed method.

3. Conclusion

In this study, MPcs syntheses were carried out using both conventional and solvent-free heat-gun methods. An innovative and environmentally friendly method was proposed for ZnPcs functionalized with alkoxy and alkylthio groups. This method reduced the reaction time from 18 hours to only 3 minutes moreover it was observed that the synthesis of ZnPcs using the heat gun method provides approximately 30 times lower energy consumption, eliminates the need for solvents, and achieves higher yields. Also enabling higher reaction yields. The heat-gun-assisted method offers an affordable and highly sustainable approach that advances green chemical synthesis. In addition, a UV-Vis-based method was established that enables easy and rapid monitoring of the reaction. In our future perspective, we aim to build on the principles of the heat-gun method to design a specialized reactor capable of large-scale production. Our work will not only allow us to scale up the process but also further explore the potential of this environmentally friendly and energy-efficient method for industrial applications.

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Supporting Information

Supporting information accompanies this paper on <http://www.acgpubs.org/journal/organic-communications>

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