

Microwave-assisted synthesis and characterization of the monomeric phthalocyanines containing naphthalene-amide group moieties and the polymeric phthalocyanines containing oxa-aza bridge

Musa Özil^a, Erbil Açar^{b,*}, Selami Şaşmaz^a, Bahittin Kahveci^a, Nesuhi Akdemir^b, İsmail Erdem Gümrukçüoğlu^b

^a Department of Chemistry, Rize Faculty of Arts and Sciences, Karadeniz Technical University, 53050 Rize, Turkey

^b Department of Chemistry, Ondokuz Mayıs University, 55139 Samsun, Turkey

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Abstract

New naphthalene-amide substituted phthalocyanines and oxa-aza bridge polymeric phthalocyanines were prepared by conventional and microwave methods. The chlorides of Cu(I), Ni(II) and Co(II) were employed in order to synthesize the corresponding metal phthalocyanines and Zn(CH₃COO)₂ was used for the preparation of the zinc phthalocyanines. For the preparation of the Co-containing phthalocyanines, ammonium molybdate had to be added as catalyst. In the microwave-assisted synthesis, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or DMAE (dimethylaminoethanol) was used as a solvent. The solubility of the phthalocyanines containing naphthalene-amide group (**1a–e**, **3a–e**) is low in ethanol, ethyl acetate, chloroform, DMF and DMSO. Polymeric phthalocyanines (**2a–e**) are not soluble in common organic solvents such as chloroform, DMF and DMSO but are soluble in dilute H₂SO₄.

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1. Introduction

High-speed synthesis with microwave irradiation has attracted a considerable amount of attention in recent years [1]. Microwave irradiation is an electromagnetic irradiation in the frequency range of 0.3–300 GHz. The energy of the microwave photon in this frequency region (0.0016 eV) is too low to break chemical bonds and is also lower than the energy of Brownian motion. It is therefore clear that microwave cannot induce chemical reactions [2–4].

Phthalocyanines have been intensively investigated since their first synthesis in 1907, and intensively used as blue and green dyestuffs due to their unique properties of being very

stable against thermal or chemical decomposition and very intense optical absorption in the visible region [5–7].

Our previous contributions describing a series of phthalocyanines with aza, [8–10] oxa-thia [11–14] and triazol-5-on [15] macrocycles reported enhanced solubility of the product with bulky macrocycles on the periphery.

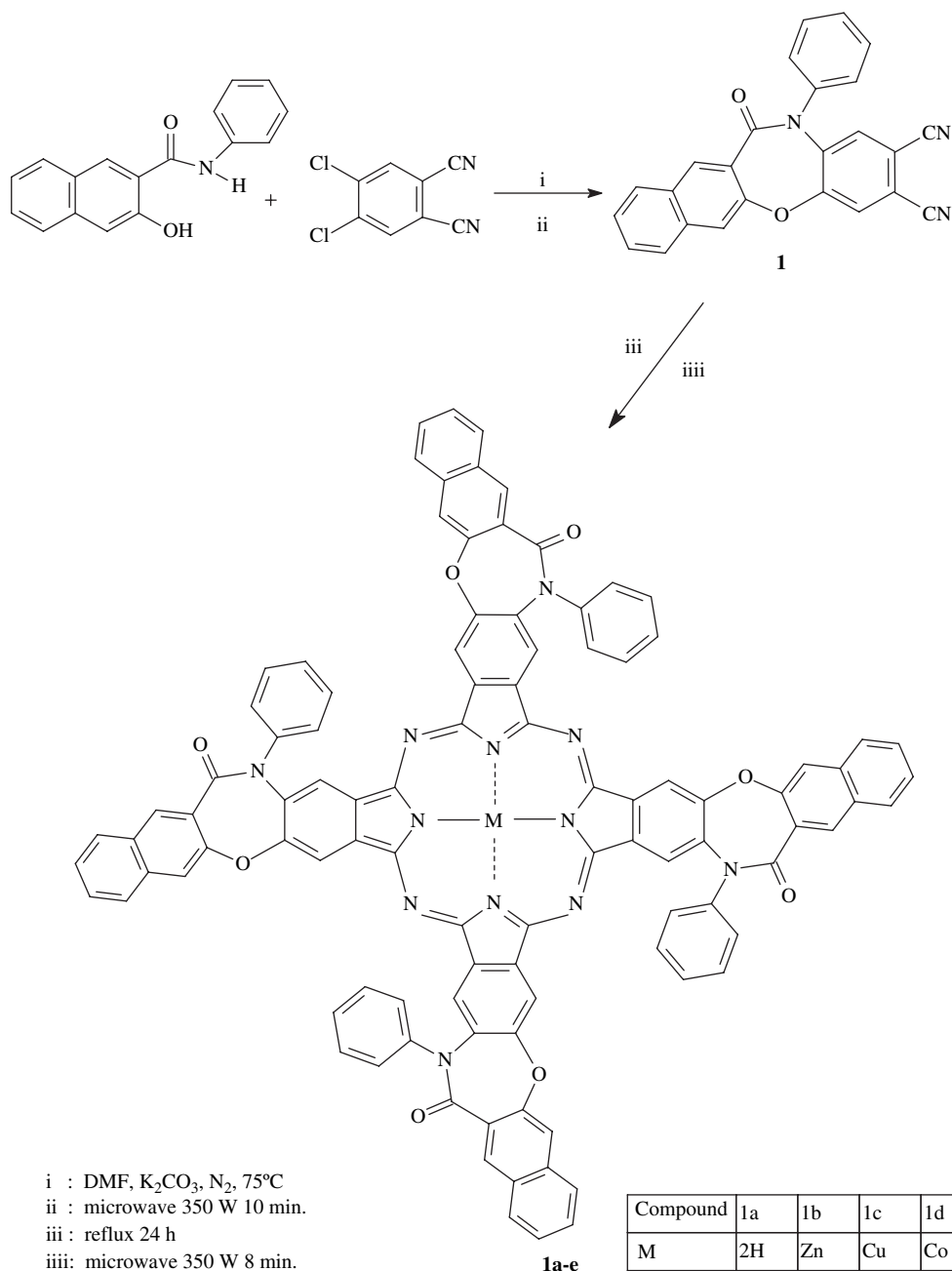
In this study, the monomeric phthalocyanines with four naphthalene-amide substituents and oxa-aza bridge polymeric phthalocyanines were prepared by conventional and microwave methods.

2. Results and discussion

The first step in the synthetic procedure was to obtain phthalonitrile derivatives containing naphthalene-amide group. The general route for the synthesis of the new phthalocyanines is shown in Scheme 1. This was accomplished by a base

* Corresponding author. Fax: +90 464 223 53 76.

E-mail address: musaozil@hotmail.com (E. Açar).



Scheme 1. Synthesis of ligands and complexes.

catalyzed nucleophilic aromatic dichloro displacement of 4,5-dichlorophthalonitrile with 3-hydroxy-2-naphthoic acid anilide [16]. This reaction was carried out at 75 °C in DMF with K₂CO₃ as the base and the yield (**1**) was moderate. In addition to this, the reaction was also carried out by using microwave method in DMAE at 350 W for 10 min. In this method the yield was more than the conventional method and also the reaction time was reduced from 48 h to 10 min.

The metal-free derivative (H₂Pc) (**1a**) was obtained directly by the reaction of phthalonitrile (**1**) with amyl alcohol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

Cyclotramerization of phthalonitrile in the presence of metal salts by two different methods gave the metal phthalocyanines

(**1b–e**). The solvents used for conventional method were quinoline for Zn(II) (**1b**), *N,N*-dimethylethanolamine (DMAE) for Cu(I) (**1c**), ethyleneglycol for Co(II) (**1d**) and quinoline for Ni(II) (**1e**). In these reactions we used different solvents which were more useful for obtaining more yields in shorter times. In the microwave-assisted method, the reactions of **1a–e** were accomplished in DMAE at 350 W for 8 min. The solubility of the phthalocyanines was low in common organic solvents such as ethyl acetate, chloroform, DMSO and DMF.

For this reason, the ¹³C NMR spectra of these phthalocyanines could not be obtained in DMSO-*d*₆ or CDCl₃.

The second step of the synthetic procedure was to obtain the oxa-aza bridge polymeric phthalocyanines (**2a–e**) and other

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