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Synthesis, characterization, electrochemical and spectroelectrochemical properties of novel peripherally tetra-1,2,4-triazole substituted phthalocyanines

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ABSTRACT

The synthesis and characterization of novel 1,2,4-triazole derivative (**3**), nitrile compound (**5**) and peripherally tetra 1,2,4-triazole substituted metal-free (**6**), zinc(II) (**7**), nickel(II) (**8**), cobalt(II) (**7**), lead(II) (**9**) and copper(II) (**10**) phthalocyanines were accomplished for the first time. Electrochemical characterization of the complexes were carried out in solution with voltammetric and in situ spectroelectrochemical measurements in different electrolytic systems. Phthalocyanines having redox inactive centers (H^+, Zn^{+2}, Cu^{+2}, and Ni^{+2}) illustrated similar phthalocyanine based electron transfer processes. Redox peaks of these complexes shift slightly due to the different effective nuclear charge of the ions in the core of phthalocyanine ring. The easiest reducible one is the metal free phthalocyanine due to the highest effective nuclear charge of H^+. Although big size of ion in the core of lead(II) phthalocyanine disturbed the square planar structure of the complex, this phenomena did not considerably influence the redox processes of lead(II) phthalocyanine.

1. Introduction

Thanks to their special properties such as strong delocalized 18 π-electronic structure, good thermal stability and visible area optical properties, phthalocyanines have many potential applications in many areas like as chemical sensors [1–3], electrochromic displaying systems [4], non-linear optics [5], solar cells [6], photovoltaic optics, molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10], laser dyes [11], catalyst [12] and photo dynamic therapeutic agents (PDT) [13].

[1,2,4]-triazole derivatives have well known pharmacological and biological properties [14]. They used as anti-inflammatory [15], antiviral/anti-HIV and anti-tuberculosis [16], antibacterial agents [17] in medicine. In addition, triazoles are used as corrosion inhibitors in some electrochemical studies [18–20] and their electrosorption and polymerization properties have been discussed [21–23].

There are only a few studies about the synthesis of [1,2,4]-triazole substituted phthalocyanines. Electrochemical and spectroelectrochemical properties of phthalocynanine ring has widely known but the investigation of electrochemical properties have been made for only a few of [1,2,4]-triazole bearing phthalocynanine [24].

In our previous works we successfully synthesized different phthalocyanine molecules [25,26] and investigated electrochemical and spectroelectrochemical properties of them [27,28]. In this study, we aimed to prepare tetra substituted [1,2,4]-triazole containing phthalocyanine and its Zn(II), Ni(II), Pb(II) and Cu(II) metal complexes and perform their electrochemical characterization to support the proposed structure and insight the possible usage of the complexes in various electrochemical technologies, such as electrocatalytic, electrosensing and electrochromic fields.

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2. Experimental

2.1. Materials and equipment

All reactions were carried out under inert N_2 atmosphere using schlenk system. DMF (dimethylformamide) was dried and purified as described by Perrin and Armarego [29]. Ethyl 2-(ethoxy(*p*-tolyl) methylene) hydrazine-1-carboxylate **(1)** [30], 2-(4-methoxy phenyl) ethanamine **(2)** [31] and 4-nitrophthalonitrile **(4)** [32] were prepared as described in the literature. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrometer in $CDCl_3$ and DMSO-d_6 and chemical shifts were reported (δ) relative to Me_4Si (tetramethylsilane) as internal standard. IR spectra were recorded on a Perkin-Elmer One FT-IR spectrometer with ATR technique. The MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. Methanol and chloroform were used as solvents in mass analysis and all analysis were conducted in positive ion mode. UV–vis spectra were recorded by Perkin Elmer Lambda 25 spectrometer, using 1 cm path length cuvettes at room temperature. Melting points were measured by an electrothermal apparatus.

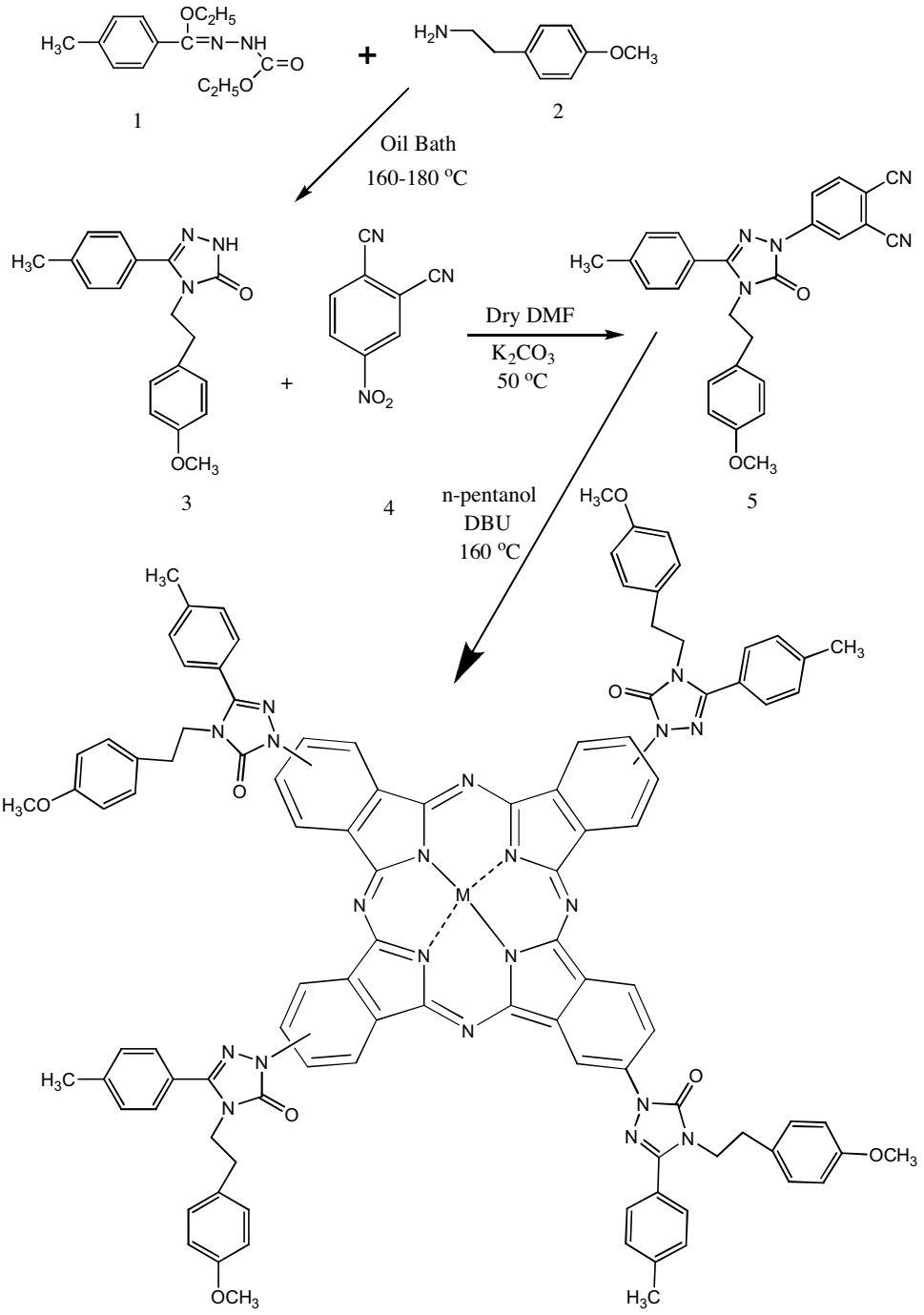

Fig. 1. Synthetic route of novel phthalocyanine compounds.