



Microwave-assisted synthesis, electrochemistry and spectroelectrochemistry of phthalocyanines bearing tetra terminal-alkynyl functionalities and click approach



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ABSTRACT

This work provides a successful, easy and efficient process for the preparation of both symmetrically tetra nonperipheral and peripheral terminal alkynyl substituted zinc and cobalt phthalocyanines (Pcs) and click approach. Two different routes, conventional and microwave-assisted synthesis, have been used by direct cyclotramerization reactions. While novel cobalt Pcs were synthesized by using only conventional method, a very fast, efficient and novel method of preparation using microwaves has been also described for the synthesis of ZnPc complexes. In order to develop a novel phthalimide conjugated zinc phthalocyanine, [2,9(10),16(17),23(24)-tetrakis((1-(2-(1,3-dioxoisindoline-2-yl)ethyl)-1H-1,2,3-triazol-4-yl)ethoxy)phthalocyaninato]zinc(II), was also synthesized via the click reaction. The precursors and the target complexes were characterized comprehensively with ¹H NMR, ¹³C NMR, FT-IR, UV-Vis spectra together with elemental and mass analyses. Electrochemical properties of peripheral and nonperipheral complexes were examined to determine effect of the position of the substituents. While nonperipheral substitution of the complexes shifted the redox processes toward the negative potentials, peripherally substituted complexes gave more reversible processes. On the other hand, while ZnPc complexes gave Pc ring-based electron transfer reactions and metal-based reduction and oxidation reactions were also recorded with CoPc complex. Moreover phthalimide–triazole substituent on the periphery was also found to affect the electrochemical properties of ZnPc complex.

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1. Introduction

Phthalocyanines (Pcs) are highly conjugated synthetic porphyrin analogs that have been the subject of study due to their intense absorbance in the visible region, electron mobility, thermal, and photo stabilities [1,2]. The functions of Pcs are almost all based on their electron transfer reactions because of π electron conjugated ring system. These macrocyclic compounds used alone or in combination with other electro- and photoactive moieties have been ideal building blocks for the construction of molecular materials. The properties of Pcs can be tuned by introducing substituents on the peripheral or nonperipheral position of the ligand. They have been used in a wide range of different applications: organic light-emitting diodes (OLEDs) [3], organic solar cell [4], dye-sensitized solar cells [5–7], photodynamic therapy (PDT) [8],

in vitro photodynamic activity [9], electrochromic materials [10], liquid crystal displays [11], chemical sensors [12], oxidation or reduction catalysts [13], and nonlinear optical properties [14].

The acetylenic derivatives of phthalonitriles have gained a great deal of importance when compared with other phthalonitriles due to their usage in click reactions providing that many technological and biological applications in a new way [15–18]. The terminal alkynyl moiety of Pc macrocycles can be easily attached to molecules bearing azide functional groups by “click” chemistry. This method has been recently applied in a wide variety of research areas, including material science, polymer chemistry, and pharmaceutical sciences because of the simplicity of this reaction and the easy workup procedure for the resulting products [15,16]. Amphiphilic dendrimers [19], near-infrared imaging evaluation of glucose conjugated [20], near infrared fluorescence imaging probe for liver cancer targeting [21], polystyrene or poly(*tert*-butylacrylate) star polymerization [22], electrode modification [14,15], binding to the surface of silica nanoparticles [23] and producing immobilized layers on electrodes or solid materials were introduced [24] to

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alkynyl Pcs via click reactions. Thus these types of Pc complexes have been rarely reported for terminal alkynyl-Pcs [21,25,26].

The usage of microwave synthesis as well as being more environmentally friendly is selective, direct, rapid, higher yields and easier work-up procedures; the formation of side products is avoided [27]. Although it is an effective method and requires less power than conventional processes, to the best of our knowledge, there is no study on microwave-assisted synthesis of terminal alkynyl substituted phthalocyanines, there is only one sample applied click chemistry to Pc core not to synthesis of the alkynyl Pc in literature [28]. In line with aforementioned statements, the preparation of terminal alkynyl-phthalocyanines with green procedure has taken great attention for further “click” reactions. With this purpose, metal phthalocyanines (MPcs) (M = Zn and Co) which were peripherally substituted with four 4-propargyloxy and non-peripherally substituted with four 3-propargyloxy phthalonitrile units were synthesized with conventional methods. Rapid and effectively microwave-assisted synthesis and characterization of both kinds of zinc phthalocyanines were also reported. New phthalimide-triazole decorated zinc phthalocyanine was synthesized after click reaction as a new method instead of the traditional synthesis method.

There are growing interests in studying possible applications in various electrochemical fields, electrochemical characterizations of the alkynyl Pcs complexes during the past decades [29]. In order to estimate the full potential of these materials, a better understanding of the electrochemical properties of these compounds is crucial. For these reasons, another purpose of this work is to identify the effects of the peripheral and non-peripheral positions of terminal-alkynyl substituents to the redox activity of the ZnPc and CoPc complexes with different voltammetric and in situ spectroelectrochemical techniques in different electrolytic systems. The phthalimide-triazole substituents effect to the redox behaviors of ZnPc complex was also established by CV and SWV methods. Electrochemical results of the complexes may be used to identify the suitability of these functional materials in various electrochemical technologies.

2. Experimental

2.1. Reagents and instruments

All reagents and solvents were of reagent grade quality obtained from Merck, Fluka and Aldrich. Chemicals employed were of the highest grade available. The solvents were stored over molecular sieves. The homogeneity of the products was tested in each step by TLC (SiO₂) and visualized with UV light (254/366 nm) using a Camag UV Lamp (Switzerland). Column chromatography was performed on silica gel 60 (70–230 mesh). The FT-IR spectra were recorded in the 4000–400 cm⁻¹ range on a Perkin Elmer Spectrum One (ATR sampling accessory) spectrophotometers. The electronic spectra and absorbance measurements were recorded on an Agilent 8453 UV-Vis spectrophotometer. Proton NMR spectra were recorded on a Bruker 250 MHz and a Bruker Avance III 500 MHz spectrometers using TMS as internal reference. The mass spectra were acquired on a Bruker Daltonics (Bremen, Germany) MALDI-TOF and MicroTOF mass spectrometer equipped with an electron spray ionization (ESI) source. The instrument was operated in positive ion mode using an *m/z* range of 50–3000. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 1 bar and drying gas flow 8 mL/min. Melting points were obtained with a Gallenkamp CAP MPD-350 apparatus in open capillaries. Microwave-assisted syntheses were carried out using modified a Beko MD microwave oven. Phthalonitriles **1**

[25,30] and **4** [31,32], *N*-2-(azidoethyl)phthalimide (**7**) [33] and ZnPc complexes **2** [26], **5** [31] and were synthesized prepared by modification of the published procedure and characterized by comparing their spectral data to those reported earlier.

2.2. General method of synthesis for phthalonitriles

4-Nitrophthalonitrile or 3-nitrophthalonitrile and 2-propyn-1-ol were dissolved in 10.0 mL dry DMSO and stirred at room temperature under nitrogen for 15 min. Then anhydrous potassium carbonate (9.83 mmol, 0.679 g) was added. Dry ground potassium carbonate (2.85 mmol, 0.399 g) was further added after 3 h and again after 24 h. After 25 h, water (100 mL) was added to the reaction mixture. The brownish raw product was extracted with CHCl₃, washed with pure water, dried with Na₂SO₄, and finally the solvent was removed under vacuum. Subsequently the crude product was purified by the column chromatography on silica gel using eluent CHCl₃:MeOH (10:1).

2.2.1. Synthesis of 4-(prop-2-ynyl)-phthalonitrile (**1**)

4-Nitrophthalonitrile (5.78 mmol, 1.07 g) and 2-propyn-1-ol (6.94 mmol, 0.38 g) was used to get **1** as a pale-green solid. Yield: 0.921 g (88%); m.p. 152–158 °C. FT-IR (ATR), ν_{\max} /(cm⁻¹): 3286 (—C≡C—H), 3120, 3077 (C—H_{arom}), 2997 (C—H_{alip}), 2230 (C≡N), 2135 (C≡C), 1594, 1492 (C=C_{arom}), 1256, 1086 (C—O—C). ¹H NMR 250 MHz (CDCl₃) δ : 7.77 (dd, 1H, H_{arom}), 7.38 (t, 1H, H_{arom}), 7.30 (dd, 1H, H_{arom}), 4.82 (d, 2H, —CH₂), 2.63 (t, 1H, —C≡CH). ¹³C NMR (CDCl₃) δ : 160.41, 135.20, 120.10, 119.90, 117.51, 115.48, 115.12, 108.31, 77.80, 76.14, 56.57. Anal. Calc. for C₁₁H₆N₂O: C, 72.52; H, 3.32; N, 15.38. Found: C, 72.45; H, 3.25; N, 15.29%. EI-MS (70 eV): *m/z* Calc.: 182.05; Found: 181.07 [M—H]⁺.

2.2.2. Synthesis of 3-(prop-2-ynyl)-phthalonitrile (**4**)

3-Nitrophthalonitrile (5.81 mmol, 1.02 g) and 2-propyn-1-ol (6.96 mmol, 0.39 g) was used to get **2** as a pale-green solid. Yield: 0.934 g (88%); m.p. 160–166 °C. FT-IR (ATR), ν_{\max} /(cm⁻¹): 3295 (—C≡C—H), 3120, 3077 (C—H_{arom}), 2997 (C—H_{alip}), 2230 (C≡N), 2137 (C≡C), 1580, 1471 (C=C_{arom}), 1298, 1048 (C—O—C). ¹H NMR 500 MHz (CDCl₃) δ : 7.71–7.67 (t, 1H, H_{arom}), 7.45–7.41 (t, dd, 2H, H_{arom}), 4.91 (d, 2H, —CH₂), 2.63 (t, 1H, —C≡CH). ¹³C NMR (CDCl₃) δ : 159.72, 134.41, 125.96, 117.50, 117.25, 115.18, 112.75, 105.55, 78.00, 76.12, 57.12. Anal. Calc. for C₁₁H₆N₂O: C, 72.52; H, 3.32; N, 15.38. Found: C, 72.63; H, 3.29; N, 15.32%. EI-MS (70 eV): *m/z* Calc.: 182.05; Found: 182.07 [M]⁺.

2.3. 2(3),9(10),16(17),23(24)-Tetrakis-[(prop-2-ynyl)-phthalocyaninato]zinc(II) (**2**)

2.3.1. Method A (conventional synthesis for **2**)

A mixture of 4-(prop-2-ynyl)-phthalonitrile **1** (0.105 g, 0.55 mmol), anhydrous Zn(CH₃COO)₂ (0.025 g, 0.14 mmol) and 0.18 mL of DBU in dry *n*-pentanol was heated to 160 °C with stirring for 6 h under N₂ in a sealed tube. The dark green mixture was cooled to the room temperature and then was precipitated in hexane. The precipitate was filtered off and adequately washed with hexane and methanol. The crude product was purified with the column chromatography on silica gel using eluent THF to afford zinc phthalocyanine **2** as a green solid. Yield: 0.346 g (79%); m.p. >300 °C. FT-IR (ATR), ν_{\max} /(cm⁻¹): 3280 (—C≡C—H), 3077, 3052 (C—H_{arom}), 2919 (C—H_{alip}), 2122 (C≡C), 1605, 1477 (—C=C_{arom}), 1279 and 1089 (C—O—C). ¹H NMR (CDCl₃ 500 MHz) (δ , ppm): 7.26–6.98 (m, 12H, H_{arom}), 5.01 (t, 8H, —OCH₂—), 2.27 (m, 4H, —C≡C—H). UV-Vis (THF) λ_{\max} nm (log ϵ): 675 (4.39), 349 (5.09). Anal. Calc. for C₄₄H₂₄N₈O₄Zn: C, 66.55; H, 3.05; N, 14.11. Found: C, 66.22; H, 2.98; N, 14.06%. ESI-MS: *m/z* Calc.: 794.12; Found: 795.54 [M+H]⁺.

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