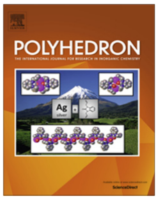
Polyhedron 72 (2014) 147–156

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Concise synthesis, electrochemistry and spectroelectrochemistry of phthalocyanines having triazole functionality

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ARTICLE INFO

Article history:
Received 7 December 2013
Accepted 27 January 2014
Available online 13 February 2014

Keywords:
Phthalocyanine
Huisgen 1,3-dipolar cycloaddition
Click chemistry
Soluble Pc
1,2,3-Triazole peripheral unit
Electrochemistry
Spectroelectrochemistry

ABSTRACT

The synthesis of novel metallophthalocyanines (M = Zn, Ni) bearing substituted benzyl protected 1,2,3-triazole moieties at peripheral positions is described for the first time via direct cyclotetramerization. These complexes have been characterized by a combination of FT-IR, ^{1}H NMR, HRMS and UV–Vis spectroscopy techniques and all the new compounds are highly soluble in most common organic solvents. In addition, the electrochemical and electrochromic behaviors of the complexes are investigated. Cyclic voltammetry and differential pulse voltammetry measurements demonstrate ligand base oxidations and reductions for both the Zn(II) and Ni(II) phthalocyanines by the transfer of one electron in each electrochemical step. The redox couples are identified *in situ* by monitoring the electronic absorption spectral changes during the electrolysis.

1. Introduction

In recent years, functional phthalocyanines (Pcs) have gained special attention due to their large areas of applications, including diagnostic imaging agents [1], organic photovoltaic devices [2–6], organic field-effect transistors [7] and emerging therapeutics in photodynamic therapy (PDT) [8–13]. In addition, they are similar to the porphyrins seen in biological systems [14]. In spite of their enormous potential, the synthesis of smart Pcs bearing functional groups remains a challenge. Thus, there are many reports on the peripheral modification of Pcs.

The 1,2,3-triazole moiety, having a variety of biological activities, is found in a large number of molecules [15]. The Cu catalyzed 1,3-dipolar cycloaddition reaction between azides and alkynes, named as the “click” reaction [16,17], has recently been demonstrated by a straightforward method for obtaining functionalized Pcs with 1,2,3-triazole groups [18–24]. So far, all attempts at examining Pcs bearing 1,2,3-triazole groups have been for a phthalocyanine post modification approach. The Pcs' cores are obtained first and then post modifications are applied. However, in some cases, extra protection/deprotection steps are required. Moreover, the solubility problem of Pcs with propynyloxy moieties accelerating aggregation behavior does not allow triazole formation because of their linear geometry [23]. In order to overcome these problems, a direct approach for Pcs bearing 1,2,3-triazole groups has been examined. We present herein a detailed synthetic, spectroscopic and electrochemical study of metallo (Zn, Ni) derivatives of Pcs, where the bulky and basic character of 1,2,3-triazole type peripheral substitutions on the Pcs core enhances the solubility in organic media and controls the aggregation behaviour [11,12]. To the best of our knowledge, a direct approach has not been previously used for the construction of phthalocyanines bearing 1,2,3-triazole before cyclotetramerization.

2. Experimental

2.1. General

All experiments were carried out in pre-dried glassware (1 h, 150 °C) under an inert atmosphere of argon. The following reaction solvents were distilled from the indicated drying agents: DMAE (CaH_2), DMF (CaH_2). All other chemicals were purchased from commercial suppliers and used without further purification.

Flash column chromatography was performed by using thick-walled glass columns with flash grade silica (Merck Silica Gel 60). The reactions were monitored by thin layer chromatography using precoated silica gel plates (Merck Silica Gel PF-254),

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http://dx.doi.org/10.1016/j.poly.2014.01.037
0277-5387/

visualized by UV-light and polymolybdenum phosphoric acid in ethanol as appropriate. All extracts were dried over anhydrous magnesium sulfate and solutions were concentrated under vacuum by using a rotary evaporator.

2.2. Spectroscopy

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 spectrometer. The chemical shifts were expressed in ppm relative to $CDCl_3$ (δ 7.26 and 77.0 for ^{1}H and ^{13}C NMR, respectively) as the internal standards. Infrared spectra were recorded on a Thermo Nicolet IS10 ATR-FT-IR spectrometer. HRMS spectra were detected on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS at the national nanotechnology research center of Bilkent University (UNAM). UV–Vis spectra were recorded on a VARIAN CARY 100 Bio spectrophotometer.

Voltammetric studies were performed with a Gamry PCI4/3007 Potentiostat–Galvanostat. In this system a platinum bead and a platinum plate electrode (0.5 cm^2) were employed as the working and counter electrodes, respectively and an Ag/AgCl electrode was used as a reference electrode. These electrodes were positioned as close as possible to minimize the IR drop. Voltammograms of 0.001 M complex solutions were recorded in DMF containing 0.10 M tetrabutylammonium tetrafluoroborate (TBABF) as the supporting electrolyte under an argon atmosphere, at room temperature. The voltage scan rate during the measurements was kept at100 mV/s.

Constant potential electrolyses, which were followed *in situ* using a UV–Vis HP 8453 A spectrophotometer, were carried out at the peak potentials with an Ag-wire reference electrode, after making the necessary correction between Ag/AgCl and the Ag-wire (about 0.10 V for Ag/AgCl). A platinum gauze (2 cm^2) served as the working electrodeand Pt-wire as the counter electrode during the electrolyses.

Color measurement experiments were performed with a Specord S-600 spectrophotometer every 20 min. during the electrolysis in DMF at room temperature.

2.3. Synthesis

2.3.1. Synthesis of 4-(prop-2-ynyloxy)phthalonitrile, 3

Propargyl alcohol (0.26 mL, 4.33 mmol) was added into a stirred mixture of 4-nitrophthalonitrile (0.50 g, 2.89 mmol) and anhydrous potassium carbonate (3.19 g, 23.1 mmol) in DMSO (6 cm^3) under an argon atmosphere at room temperature. The mixture was stirred at room temperature for three and a half hour under an argon atmosphere, and then distilled to remove DMSO under reduced pressure. Water (100 cm^3) was added to the dried mixture, which was then extracted with DCM. The organic layer was dried over $MgSO_4$, and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane to afford **3** as a solid (0.49 g, 85% chemical yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.57 (t, *J* = 2.4 Hz, 1H), 4.75 (d, *J* = 2.4 Hz, 2H), 7.25 (dd, *J* = 8.8, *J* = 2.6 Hz, 1H), 7.31 (d, *J* = 2.6 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.6, 76.2, 77.8, 108.2, 115.2, 115.5, 117.4, 119.9, 120.2, 135.2, 160.5. *Anal.* Calc. for C, 72.52; H, 3.32; N, 15.38. Found: C, 71.94; H, 3.42; N, 15.48%.

2.3.2. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy)phthalonitrile, 4

3 (0.848 g, 4.65 mmol) was dissolved in DMSO (15 cm^3), then sodium ascorbate (0.9218 g, 0.465 mmol) and $CuSO_4 \cdot 5H_2O$ (1.1618 g, 0.465 mmol) were added under an argon atmosphere. After stirring for a half hour, benzyl azide was added to the reaction mixture and it was stirred for a further 12 h. Water (250 cm^3) was added to the reaction mixture, which was then extracted with DCM. The organic layer was dried over $MgSO_4$, and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane to afford **4** as a white solid (0.61 g, 42% chemical yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.21 (s, 2H), 5.47 (s, 2H), 7.18–7.24 (m, 2H), 7.26–7.36 (m, 5H), 7.48 (s, 1H), 7.63 (dd, *J* = 7.6, *J* = 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 53.4, 61.5, 106.9, 113.9, 114.3, 116.5, 118.4, 119.3, 122.0, 127.1, 128.0, 128.2, 133.0, 134.2, 141.2, 160.1. *Anal.* Calc. for C, 68.56; H, 4.16; N, 22.21. Found: C, 68.12; H, 4.28; N, 22.34%.

2.3.3. General procedure for the synthesis of phthalocyanines 5a–b and 6a–b

Phthalonitriles, **3** and **4**, were dissolved in a mixture of DMEA/DMF (1:2). After adding the metal salts ($Zn(OAc)_2$ and $NiCl_2$), stirring was continued at 150 °C for 7 h for the metallophthalocyanines **5a** and **5b** and for 48 h for the metallophthalocyanines **6a** and **6b**. After TLC monitoring, the reaction was stopped by adding a water–methanol (1:1) mixture (100 cm^3). The precipitate formed was washed with ether, then extracted with DCM. The organic layer was dried over $MgSO_4$, and then the solvent was evaporated under reduced pressure [24]. The residue was purified by column chromatography on silica gel eluting with DCM:CH_3OH (95:5 for **6a** and 90:10 for **6b**) to afford the phthalocyanines.

2.3.4. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy substituted Zn phthalocyanine, 6a

Compound **4** (0.39 g, 1.23 mmol) was reacted with $Zn(OAc)_2$ (0.067 g, 0.31 mmol) and gave **6a** (0.344 g, 20.3% chemical yield). FT-IR (ATR System, cm^{-1}): 2960, 2920, 2850, 1714, 1604, 1485, 1454, 1388, 1334, 1259, 1217, 1182, 1087, 1045, 1024, 1010, 943, 850, 796, 761, 744, 711, 694, 659. ^{1}H NMR (400 MHz, DMSO) δ: 5.65–5.90 (m, 16H), 7.35–7.85 (m, 24H), 8.34–9.21 (m, 12H). MS(TOF-ESI): *m/z* $[M+Na]^+$ calcd. for $C_{72}H_{52}N_{20}NaO_4Zn$: 1349.6847; found $[M+Na]^+$:1349.3831.

2.3.5. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy substituted Ni phthalocyanine, 6b

Compound **4** (0.564 g, 1.79 mmol) was reacted with $NiCl_2$ (0.077 g, 0.595 mmol) and gave **6b** (0.173 g, 20.7% chemical yield). FT-IR (ATR System, cm^{-1}): 2960, 2924, 2852, 1714, 1608, 1531, 1479, 1454, 1415, 1336, 1259, 1226, 1116, 1091, 1047, 1010, 956, 864, 796, 748, 731, 711, 694. ^{1}H NMR (400 MHz, DMSO) δ: 4.68–6.05 (m, 16 H), 6.75–8.66 (m, 36H). MS(TOF-ESI): *m/z* $[M+K]^+$ calcd. for $C_{72}H_{52}KN_{20}O_4Ni$: 1359.1066; found $[M+K]^+$:1359.3773.

3. Results and discussion

3.1. Synthesis

The Huisgen 1,3-dipolar cycloaddition of azides to alkynes has been proven to be versatile for the functionalization of macromolecules, in addition to other applications. The derivatization of metallo Pcs via the click approach will not only pave the way to the rapid and effective synthesis of highly diverse Pcs, but also towards the integration of Pc cores into functional supramolecular systems for harvesting of energy at a molecular level [25–28]. However, as we mentioned above, there are some drawbacks for derivatization. To synthesize the target Pcs **5a**, our first attempt started with the S_NAr type substitution reaction between **2** and 4-nitrophthalonitrile **1** (Scheme 1), resulting in compound **3** in 85% yield. After characterization, completed by NMR spectroscopy, compound **3** was subjected to the appropriate conditions using