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Derivatization and in situ metallation of phthalocyanines using click chemistry

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ABSTRACT

Dialkyl (3,4-dicyanophenyl)propargylmalonates were prepared by the reaction of propargyl bromide and the potassium salt of dialkyl-3,4-dicyanophenylmalonates. A cyclotetramerization reaction was achieved in pentanol in the presence of DBU without protective/deprotective chemistry, affording the peripherally tetrasubstituted alkynyl phthalocyanines. Subsequently, in situ metallation and 'clicking' were employed for the first time as an efficient and quantitative route to tetratriazole-functionalized phthalocyanines.

1. Introduction

Phthalocyanines (Pc) and their metal complexes (MPc) have attracted considerable interest and have been found to be highly promising candidates for a variety of uses, such as liquid crystals [1], gas sensors [2], catalysts [3,4], photosensitizers [5] and dye-sensitized solar cells [6,7]. Tailoring of the properties of these compounds either by addition of various groups on the periphery or by insertion of different metal ions gives rise to outstanding architectural flexibility. Ester functionalities have often been added on the periphery of phthalocyanines to improve their solubility in a number of solvents and to obtain phthalocyanines containing carboxylic acid moieties [8–15]. We reported on the synthesis and spectroscopic studies of MPc's substituted with tricarbethoxyethyl and dicarboxyethyl groups designed to control intermolecular dimerization of the MPc's in solution [16]. The introduction of a fluorescent group together with ester moieties on the phthalocyanine core has been also accomplished [17,18]. On the other hand, alkynyl-substituted phthalocyanines have been found to be particularly interesting in that each alkynyl group causes a red shift of 4–6 nm in the Q band region of the spectrum, and can hence be applied in "fine tuning" a Pcs absorption spectrum. Alkynyl phthalocyanines are also convenient starting materials for the preparation of Pc-based dyads and triads [19–21].

Recently, 1,3-dipolar cycloadditions, from the reactions between azides and alkynes known as "click reactions", have been recognized as a useful synthetic methodology due to their being fast, quantitative, reproducible, resistant to side reactions and highly tolerant to reaction conditions. The Cu^{I}-catalyzed click reaction has been utilized for the functionalization and preparation of novel materials, such as macromonomers [22], dendrimers [23], bioconjugates [24] and shell cross-linked nanoparticles [25], among many others. Although numerous applications of click chemistry for the preparation of novel macromolecules have been frequently reported, only four examples are available for phthalocyanine derivatives [26–29]. In the present work, novel phthalocyanine derivatives carrying a terminal alkyne unit on each benzo group together with ester functionalities have been synthesized for the first time without protective/deprotective chemistry. Derivatization and in situ metallation of the alkynyl-substituted free-base Pcs has been also accomplished using click chemistry. To the best of our knowledge, this in situ metallation of a metal-free macrocycle under the click reaction conditions is the first example in the literature.

2. Experimental

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, and electronic spectra on a Unicam UV2 UV–Vis spectrophotometer. Elemental analyses were performed on a Thermo Flash EA 1112. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer using TMS as an internal reference. Mass spectra were measured on a Bruker Microflex LT MALDI-TOF MS and VG Zabspec GC–MS. Melting points were determined on an Electrothermal Gallenkamp apparatus. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC (SiO_2). Dialkyl-3,4-dicyanophenylmalonates and their potassium salts were synthesized according to the published procedure [30]. Dimethyl-3,4-(dicyanophenyl)propargylmalonate (**2**)

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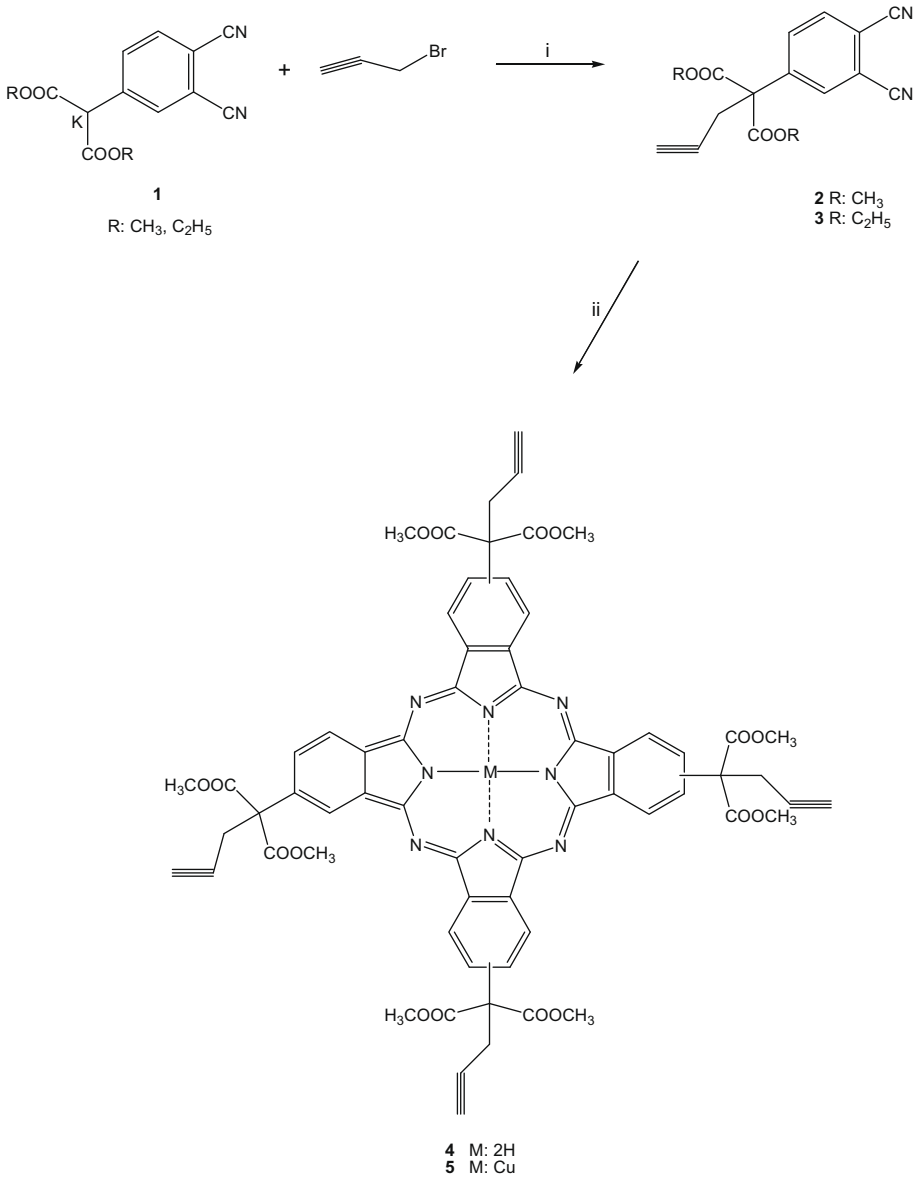

Scheme 1. Reagents and conditions: (i) acetone/acetonitrile, reflux; (ii) *n*-pentanol, DBU, reflux, $CuCl_2$ for **5**.

was also synthesized according to the literature procedure, with some minor modifications [31].

2.1. General procedures for the preparation of dialkyl (3,4-dicyanophenyl)propargylmalonates (**2**, **3**)

To the potassium salt of dialkyl-3,4-dicyanophenylmalonate (3.0 mmol, 0.9 g dimethyl-3,4-dicyanophenylmalonate, 0.97 g diethyl-3,4-dicyanophenylmalonate) in 2:1 acetone/acetonitrile (150 mL) was added propargyl bromide (3.6 mmol, 80% in toluene, 0.54 g). The mixture was boiled for 20 h under Ar and then filtered. The solvent was evaporated under reduced pressure to give an oily residue, which was washed with water until the product was free of KBr and finally crystallized from dichloromethane. These compounds were soluble in acetone, chloroform and THF. **2**. Yield: 0.75 g, 84%. Mp: 90–91 °C. FT-IR ν (cm^{-1}): 3288 (H–C≡C–), 3103–3049 (CH, aromatic), 2957 (CH, aliphatic), 2237 (C≡N), 1753, 1731 (C=O). **3**. Yield: 0.79 g, 81%. Mp: 47 °C. FT-IR ν (cm^{-1}): 3278 (H–C≡C–), 3085 (CH, aromatic), 2979–2940 (CH, aliphatic), 2241 (C≡N), 1753, 1724 (C=O); ^{1}H NMR (DMSO-d_6) δ: 8.19–8.16 (aromatic H), 7.96–7.94 (aromatic H), 4.25–4.19 (OCH_2), 3.26 (CH_2), 2.95–2.94 (H–C≡), 1.19–1.16 (CH_3); ^{13}C NMR ($CDCl_3$) δ: 168.1, 142.2, 134.8, 134.4, 134.3, 116.3, 116.2, 115.1, 114.9, 79.4, 75.7, 63.2, 62.2, 25.5, 14.3; GC–MS *m/z*: 324 $[M]^+$, 252 $[M-COOC_2H_5]^+$, 223 $[M-(C_2H_5+COOC_2H_5)]^+$, 205 $[M-(OC_2H_5+COOC_2H_5)]^+$, 179 $[M-2(COOC_2H_5)]^+$, 152 $[M-(2(COOC_2H_5)+HCN)]^+$, 125 $[M-(2(COOC_2H_5)+2(HCN))]^+$.

2.2. 2,9,17,23-(1,1-(Dimethoxycarbonyl)-2-(ethynyl)ethyl)phthalocyanine (**4**)

A mixture of dinitrile **2** (0.1 g, 0.33 mmol) and a catalytic amount of DBU in *n*-pentanol (1 mL) was heated at 140 °C with stirring for 20 h. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, chloroform/methanol 100:1). Yield: 0.075 g, 20%. FT-IR ν (cm^{-1}): 3311 (N–H), 3291 (H–C≡C–), 2956–2856 (CH, aliphatic), 2114 (–C≡C–), 1726 (C=O); UV–Vis λ_{max} (nm) in chloroform: 698, 661, 342; MALDI-TOF MS (2,5-dihydroxybenzoic acid or sinapic acid) *m/z*: 1179.6