Polyhedron 29 (2010) 1776-1783

Contents lists available at ScienceDirect

Polyhedron

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

Efficient green procedures for the preparation of novel tetraalkynyl-substituted phthalocyanines

Tamer Ezzat Youssef*

Applied Organic Chemistry Department, National Research Center, Dokki, Cairo 12311, Egypt

ARTICLE INFO

Article history: Received 28 December 2009 Accepted 15 February 2010 Available online 3 March 2010

Keywords: Alkynyl phthalocyanines Metal-free phthalocyanines Metallophthalocyanines UV-irradiation Microwave irradiation

ABSTRACT

This work provides a successful, easy and efficient process for the preparation of metal-free 2(3),9(10),16(17),23(24)-octamethoxyphthalocyanine, $[(OMe)_8PcH_2]$ (2), and its metal complexes $[(OMe)_8PcM]$ (3–11) (M = Zn, Cu, Ni, Mg, Co, Fe, Ru, TiCl and RhCl) by using green energy techniques such as exposure to UV-irradiation as well as microwave irradiation. Two different routes have been used, which involve modifications to that reported in the literature. The results suggest that these techniques drastically reduce the reaction time of metallophthalocyanine $[(OMe)_8PcM]$ (3–11) formation from 5–96 h to 5–11 min. The prepared octamethoxyphthalocyanines $[(OMe)_8PcM]$ (2–4) (M = H₂, Zn, Cu) are used as key materials to synthesize the corresponding novel tetraalkynyl-substituted phthalocyanines 15–17.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, phthalocyanines form an important group of aromatic macrocycles, dependant on a delocalized 18- π electron system that belongs to the most modern functional materials in scientific research [1-3]. They play an important role in many advanced applications and modern technologies, mostly by virtue of their characteristic optical absorption and high chemical stability. In addition, they can find commercial applications as photoconductors in xerographic machines [4–6], electrochromic displays [7], photovoltaic materials in solar cells [8–10], systems for fabrication of light emitting diodes (LED) [11,12], optical limiters [13,14], dyes for recording layers in recordable digital versatile discs (DVDs) [15], liquid crystalline materials [16], organic conductors [17,19], sensitizers for photodynamic cancer therapy (PDT) [18,20-22] and diverse catalytic systems [23,24]. Recently, metal-free phthalocyanines have been obtained by high temperature cyclotetramerization processes starting from diverse precursors, such as phthalonitrile, o-cyanobenzamide, phthalimide and 1,3-diiminoisoindoline, generally in high-boiling non-aqueous solvents at eletemperatures [25–28], or electrochemically vated from phthalonitriles [29-31], or at low temperature by UV-irradiation of the reaction system [32]. The use of microwave energy is one of the more efficient methods for selective heating in many processes. As well as being more environmentally friendly, requiring less energy than conventional processes, it is also a selective,

doi:10.1016/j.poly.2010.02.034

direct, rapid, internal and controllable method, leading to shorter reaction times, higher yields and easier work-up than classical thermal processing [33–35]. Moreover, by reducing the reaction time, the formation of side products is avoided and the reproduc-ibility of the reaction is improved [36].

The high-speed synthesis of metal-free phthalocyanine and metallophthalocyanines by using microwave irradiation had been reported previously by Shaabani [37–42], Villemin [43] and Davis [44] by using domestic oven and microwave assisted synthesis. In another study, the synthesis of metal-free and metallophthalocyanines bearing tetraaza macrocyclic moieties under microwave irradiation was investigated [45,46].

The author has prepared earlier novel symmetrical and asymmetrical metal-free and metallophthalocyanines carrying long chain alkoxy groups [47–49] or axial ligands [50] for potential use in applications. They were prepared by high temperature cyclotetramerization processes from the corresponding phthalonitriles.

In the present work, we describe for the first time the synthesis and characterization of 2,3,9,10,16,17,23,24-octamethoxyphthalocyanine [(OMe)₈PcH₂] (**2**) and its metallo-derivatives [(OMe)₈PcM] (**3–11**), (M = Zn, Cu, Ni, Mg, Co, Fe, Ru, TiCl and RhCl) by applying two different routes of preparation which are being developed in our group: (1) UV-irradiation of the reaction system for the synthesis of metal-free phthalocyanine **2** from phthalonitrile **1** [51] in alcohols. (2) Microwave assisted irradiation of the reaction system for the synthesis of metal-free and metallophthalocyanines in the presence of solvent, controlled temperature and smart conditions, either from phthalonitrile **1** (route A) or from the metal-free analogue **2** as a precursor (route B).





 ^{*} Present address: Institut für Organische Chemie, Universität Hannover, Schneiderberg 1B, D-30167, Hannover, Germany. Tel.: +49 15157291577.
E-mail address: tamezzat@yahoo.com

^{0277-5387/\$ -} see front matter © 2010 Elsevier Ltd. All rights reserved.

When alkynyl groups are attached to the phthalocyanine skeleton, they realize excellent chemical–physical properties of the Pcs, due to the coupling of the structural (*i.e.* rigidity and linearity) and electronic (*i.e.* the presence of π -electrons) features of the acetylene group. A variety of mono- [52,53] and octaalkynyl-substituted phthalocyanines [54,55] have been reported during the last decade. Torres and co-workers [56,57] reported a series of tetraethynyl-substituted phthalocyanines. Another series of peripherally alkynylated phthalocynanines have been prepared by Faust [58].

We are trying to contribute to this area of research by providing the prepared complexes **2–4** and using them as key materials to synthesize the corresponding novel tetraalkynyl-substituted phthalocyanines **15–17**. The structures of the novel compounds **15–17** were characterized by a combination of ¹H NMR, IR, UV– vis, elemental analysis and MS spectral data.

2. Experimental

2.1. General

All manipulations were performed under nitrogen using standard Schlenk techniques unless otherwise specified.

2.2. Materials

The precursor 4,5-dimethoxyphthalonitrile **1** was synthesized as described in another report [51]. 3,4-Diflurophenylacetylene (Aldrich) was commercially available and used as purchased. All other reagents, solvents and metal salts were of reagent-grade quality, obtained from commercial suppliers and used as received.

2.3. Instruments

UV Reactor Laboratory System: mercury medium pressure lamp, 150 W, combined immersion/cooling tube in quartz glass, reaction vessel of around 250 ml with a rotor to circulate the solution, power supply.

Microwave oven utilized for heating: Discover Lab Mate singlemode microwave cavity from CEM Corporation. The reactions were conducted in a 25 ml Schlenk tube, with a maximum operating temperature of 180 °C and a maximum operating pressure of 8 bar.

2.4. Physical measurements

¹H NMR spectra were measured on a Bruker ARX 250 (250.133 MHz) NMR spectrometer. FT-IR spectra were recorded on a Bruker IFS 48 spectrometer using KBr pellets. The UV–vis spectra were taken in *N*,*N*-dimethylformamide (DMF) using a Per-kin–Elmer Lambda 2 spectrometer. FD mass spectra measurements were carried out with a Varian MAT 711 A spectrometer and reported as mass/charge (m/z). Elementary analyses were performed on a Carlo Erba Elemental Analyzer 1104, 1106.

2.5. Procedures for the synthesis of metal-free 2,3,9,10,16,17,23,24-octamethoxyphthalocyanine [(OMe)₈PcH₂] (**2**)

2.5.1. UV-irradiation synthesis method

A mixture of 4,5-dimethoxyphthalodinitrile **1** (3.5 g, 18.5 mmol) and diazabicyclo[5.4.0]undec-7-ene (DBU, 0.5 ml) in deoxygenated 2-ethoxyethanol (50 ml) was placed in a quartz tube. The mixture was well stirred, then irradiated for 3.5 h in a photochemical reactor (mercury lamp of 150 W) at 70–75 °C under dry nitrogen. A green coloured solution was formed, cooled to room temperature then poured into MeOH/H₂O (3:1). The

suspended solution that formed was centrifuged. The precipitated solid was filtered off, washed with a methanol/water mixture (1/1, v/v) and dried under vacuum. The crude product (2.10 g) was purified with a Soxhlet extractor by extracting for 1 day with dichloromethane to give compound **2** as a green powder, yield: 60%. *Anal.* Calc. for C₄₀H₃₄N₈O₈: C, 63.65; H, 4.54; N, 13.85. Found: C, 62.01; H, 5.80; N, 13.90%. ¹H NMR (DMSO-*d*⁶) δ (ppm): -4.1 to -3.8 (br, 2H, NH), 3.94 (s, 24H, OMe), 7.25 (s, 8H, ArCH). IR (KBr) ν (cm⁻¹): 3229-3222 (br), 2956, 2926, 2855, 1653, 1540 (s), 1466 (s), 1434 (m), 1318 (m), 1228 (m), 1140 (s), 1126, 920 (s), 880 (m), 750 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 696(5.24), 661(5.17), 635(4.86), 602(4.78), 346(5.16). MS (FD): *m/z* 754.76 (M⁺).

2.5.2. Microwave irradiation synthesis method

A standard Schlenk tube was charged with a mixture of 4,5dimethoxyphthalodinitrile **1** (3.5 g, 18.5 mmol), deoxygenated *N*,*N*-dimethylaminoethanol (DMAE) (5 ml) and DBU (1 ml) under a nitrogen atmosphere and degassed several times. The mixture was well stirred, then irradiated in a microwave reactor at 350 W for 8 min. After cooling to room temperature, a green solution was formed, which was then poured into MeOH/H₂O (3:1). The suspended solution was centrifuged. The precipitated solid was filtered off, washed with a methanol/water mixture (1/1, v/v) and dried under vacuum. The crude product (2.34 g) was purified with a Soxhlet extractor, by extracting for 1 day with dichloromethane to give compound **2** as a green powder, yield: 68%.

2.6. General procedures for the synthesis of the metallo-2,3,9,10,16,17,23,24-octamethoxyphthalocyanine complexes [(OMe)₈PcM] (**3-11**)

2.6.1. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)zinc(II), [(OMe)₈PcZn] (**3**) [58]

2.6.1.1. Method A. A standard Schlenk tube was charged with a mixture of 4,5-dimethoxyphthalodinitrile 1 (3.5 g, 18.5 mmol), anhydrous zinc acetate (0.14 g, 0.77 mmol), deoxygenated DMAE (5 ml) and DBU (1 ml) under a nitrogen atmosphere, and degassed several times. The mixture was well stirred, then irradiated in a microwave reactor at 370 W for 10 min. After cooling to room temperature, a green solution was formed which was then poured into MeOH/H₂O (3:1). The suspended solution was centrifuged. The precipitated solid was filtered off, washed with a methanol/water mixture (1/1, v/v) and dried under vacuum. The crude product (2.6 g) was purified with a Soxhlet extractor by extracting for 2-3 days with acetone and dichloromethane to give compound **3** as a green powder, yield: 72%. Anal. Calc. for C40H32N8O8Zn: C, 58.72; H, 3.94; N, 13.70. Found: C, 59.01; H, 3.80; N, 13.94%. ¹H NMR (DMSO-*d*⁶) δ (ppm): 3.89 (s, 24H, OMe), 7.30 (s, 8H, ArCH). IR (KBr) v (cm⁻¹): 2959, 2865, 1657, 1548 (s), 1465 (s), 1444 (m), 1322 (m), 1221 (m), 1138 (s), 1125, 923 (s), 883 (m), 755 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log $\varepsilon dm^3 mol^{-1} cm^{-1})$]: 688(5.22), 622(4.85), 360(5.16). MS (FD): m/z 818.12 (M⁺).

2.6.1.2. Method B. A standard Schlenk tube was charged with a mixture of metal-free 2,3,9,10,16,17,23,24-octamethoxyphthalocyanine **2** (1.5 g, 2 mmol), anhydrous zinc acetate (0.07 g, 0.3 mmol), deoxygenated DMAE (3 ml) and DBU (1 ml) under a nitrogen atmosphere and degassed several times. The mixture was well stirred, then irradiated in a microwave oven at 300 W for 8 min. After cooling to room temperature, a green suspension was formed, which was then poured into MeOH/H₂O (3:1). The suspended solution was centrifuged. The precipitated solid was filtered off, washed with a methanol/water mixture (1/1, v/v) and dried under vacuum. The crude product (1.3 g) was purified with a Soxhlet extractor by extracting for 2–3 days with acetone and dichloromethane to yield (78%, 1.2 g) of compound **3** as a green powder.

2.6.2. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)copper(II), [(OMe)₈PcCu] (**4**) [58]

This product was obtained as a blue powder from CuCl₂ [P = 350 W, t = 8 min, method A]; yield: 62%, or [P = 330 W, t = 7 min, method B]; yield: 60%. *Anal.* Calc. for C₄₀H₃₂N₈O₈Cu: C, 58.72; H, 3.94; N, 13.70. Found: C, 59.01; H, 3.80; N, 13.94%. UV-vis (DMF), λ_{max} (nm) [(10^{-5} log ε dm³ mol⁻¹ cm⁻¹)]: 674(5.20), 606(4.76), 344(5.15). MS (FD): m/z 816.29 (M⁺).

2.6.3. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)nickel(II), [(OMe)₈PcNi] (**5**) [58]

This product was obtained as a green powder from NiCl₂ [P = 350 W, t = 8 min, method A]; yield: 83%, or [P = 300 W, t = 5 min, method B]; yield: 80%. *Anal.* Calc. for C₄₀H₃₂N₈O₈Ni: C, 59.21; H, 3.97; N, 13.81. Found: C, 60.71; H, 3.80; N, 14.94%. ¹H NMR (DMSO- d^6) δ (ppm): 3.77 (s, 24H, OMe), 7.33 (s, 8H, ArCH). IR (KBr) ν (cm⁻¹): 2950, 2924, 2850, 1651, 1548 (s), 1462 (s), 1438 (m), 1322 (m), 1227 (m), 1142 (s), 1125, 921 (s), 887 (m), 751 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 697(5.19), 671(4.88), 370(5.23), 315(5.17). MS (FD): *m/z* 811.43 (M⁺).

2.6.4. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)magnesium (II), (OMe)₈PcMg] (**6**)

This product was obtained as a green powder from MgCl₂ [P = 350 W, t = 7 min, method A]; yield: 89%, or [P = 350 W, t = 5 min, method B]; yield: 85%. *Anal* Calc. for C₄₀H₃₂N₈O₈Mg: C, 61.83; H, 4.15; N, 14.42. Found: C, 60.71; H, 3.80; N, 14.94%. ¹H NMR (DMSO- d^6) δ (ppm): 3.65 (s, 24H, OMe), 7.23 (s, 8H, ArCH). IR (KBr) ν (cm⁻¹): 2950, 2929, 2848, 1651, 1543 (s), 1469 (s), 1439 (m), 1317 (m), 1225 (m), 1141 (s), 1127, 922 (s), 879 (m), 756 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 680(5.22), 610(4.90), 353(5.19). MS (FD): m/z 777.05 (M⁺).

2.6.5. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)cobalt(II), [(OMe)₈PcCo] (**7**) [50]

This product was obtained as a violet powder from CoCl₂·6H₂O [*P* = 360 W, *t* = 10 min, method A]; yield: 58%. UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 668(5.26), 602(4.83), 346(5.20). MS (FD): *m/z* 811.68 (M⁺).

2.6.6. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)iron(II), [(OMe)₈PcFe] (**8**) [50]

This product was obtained as a black blue powder from $(NH_4)_2Fe(SO_4)_2$ [*P* = 360 W, *t* = 12 min, method A]; yield: 52%. UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 652(5.24), 594(4.81), 383(5.21). MS (FD): *m/z* 808.59 (M⁺).

2.6.7. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)ruthenium (II), [(OMe)₈PcRu] (**9**)

This product was obtained as a blue-green solid from RuCl₃·3H₂O [*P* = 370 W, *t* = 11 min, method A]; yield: 45%. *Anal.* Calc. for C₄₀H₃₂N₈O₈Ru: C, 56.27; H, 3.88; N, 13.72. Found: C, 55.27; H, 4.10; N, 13.98%. ¹H NMR (DMSO-*d*⁶) δ (ppm): 3.95 (s, 24H, OMe), 7.39 (s, 8H, ArCH). IR (KBr) ν (cm⁻¹): 2952, 2923, 2845, 1658, 1542 (s), 1465 (s), 1433 (m), 1313 (m), 1222 (m), 1145 (s), 1128, 919 (s), 879 (m), 745 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 624(5.15), 568(4.79), 382(5.20). MS (FD): *m/z* 853.81 (M⁺).

2.6.8. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)titanium chloride(III), [(OMe)₈PcTiCl] (**10**)

This product was obtained as a green solid from TiCl₃ [P = 360 W, t = 10 min, method A]; yield: 40%. *Anal.* Calc. for C₄₀H₃₂N₈O₈TiCl: C, 57.46; H, 3.96; N, 13.40. Found: C, 56.01; H, 4.30; N, 12.94%. ¹H NMR (DMSO- d^6) δ (ppm): 3.85 (s, 24H, OMe), 7.29 (s, 8H, ArCH). IR (KBr) v (cm⁻¹): 2949, 2921, 2850, 1651, 1544 (s), 1462 (s), 1438 (m), 1313 (m), 1222 (m), 1139 (s), 1124, 922 (s), 881 (m), 754 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 689(5.22), 622(4.83), 442(5.21), 420(5.19). MS (FD): m/z 836.08 (M⁺).

2.6.9. (2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato)rhodium chloride(III), [(OMe)₈PcRhCl] (**11**)

This product was obtained as a blue-green solid from RhCl₃·3H₂O [*P* = 360 W, *t* = 11 min, method A]; yield: 52%. *Anal.* Calc. for C₄₀H₃₂N₈O₈RhCl: C, 54.92; H, 3.92; N, 12.57. Found: C, 56.01; H, 4.30; N, 12.94%. ¹H NMR (DMSO-*d*⁶) δ (ppm): 3.88 (s, 24H, OMe), 7.34 (s, 8H, ArCH). IR (KBr) ν (cm⁻¹): 2952, 2924, 2850, 1658, 1542 (s), 1468 (s), 1437 (m), 1318 (m), 1227 (m), 1142 (s), 1126, 920 (s), 880 (m), 750 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 658(5.13), 597(4.86), 366(5.14). MS (FD): *m/z* 891.10 (M⁺).

2.7. General procedure for the synthesis of 2,3,9,10,16,17,23,24 octahydroxyphthalocyanines [(OH)₈PcM] (**12–14**) [58], $M = H_2$, Zn, Cu

The Pcs **2–4** were suspended in dichloromethane (100 mL) and BBr₃ (24 mL, 254 mmol) was added under N₂. The mixtures were stirred for 3 days at room temperature, then methanol was added slowly and dark green suspensions were formed. The suspended solutions were centrifuged. The precipitated solids were filtered off, washed with methanol and dried under vacuum, to yield 78–85% of Pcs **12–14**, respectively, as black green powders.

2.7.1. [(OH)₈PcH₂] (**12**)

IR (KBr) ν (cm⁻¹): 3228–3220 (br), 3310 (br), 2953, 2926, 2853, 1650, 1542 (s), 1468 (s), 1439 (m), 1320 (m), 1270 (m), 1145 (s), 1128, 921 (s), 880 (m), 753 (m). UV–vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 697(5.22), 662(5.18), 633(4.19), 601(4.85), 345(5.24). MS (FD): *m/z* 642.54 (M⁺).

2.7.2. [(OH)8PcZn] (13)

IR (KBr) ν (cm⁻¹): 3310 (br), 2955, 2923, 2850, 1658, 1541 (s), 1467 (s), 1439 (m), 1320 (m), 1270 (m), 1141 (s), 1129, 922 (s), 881 (m), 751 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 687(5.19), 620(4.88), 357(5.16). MS (FD): m/z 705.91 (M⁺).

2.7.3. [(OH)₈PcCu] (14)

IR (KBr) ν (cm⁻¹): 3310 (br), 2955, 2923, 2850, 1658, 1541 (s), 1467 (s), 1439 (m), 1320 (m), 1270 (m), 1141 (s), 1129, 922 (s), 881 (m), 751 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 679(5.22), 610(4.87), 353(5.19). MS (FD): *m/z* 704.07 (M⁺).

2.8. General procedure for the synthesis of tetraethynyl-substituted phthalocyanines

Pcs **12–14**, 3,4-diflurophenylacetylene (0.6 g, 4 mmol) and a small quantity of potassium carbonate (0.12 g, 0.855 mmol) were heated at 60 °C in DMF (70 mL) for 24 h under N₂. The mixtures were cooled, then methanol was added slowly and green suspensions were formed. The suspended solutions were centrifuged. The precipitated solids were filtered off, washed with methanol and dried under vacuum. The crude products were purified by a

Soxhlet extractor, extracting for 2 days with acetone and dichloromethane to yield 70–77% of the corresponding tetraethynyl-substituted phthalocyanines **15–17** as green powders.

2.8.1. Tetraethynyl-substituted phthalocyanine (15)

Anal. Calc. for $C_{64}H_{26}N_8O_8$: C, 73.27; H, 3.53; N, 10.83. Found: C, 73.01; H, 3.80; N, 9.94%. ¹H NMR (DMSO- d^6) δ (ppm): -3.9 to -3.7 (br, 2H, NH), 3.6 (s, 1H, 4x CH=CH), 7.54 (s, 8H, ArCH), 8.2 (s, 4H, ArCH), 8.7 (d, 8H, ArCH). IR (KBr) ν (cm⁻¹): 3415 (CH=CH), 3239-3248 (br), 2955, 2922, 2850, 1650, 1543 (s), 1468 (s), 1435 (m), 1318 (m), 1230 (m), 1141 (s), 1125, 922 (s), 880 (m), 751 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 697(5.26), 662(5.16), 634(4.23), 600(4.88), 342(5.19). MS (FD): m/z 1034.96 (M⁺).

2.8.2. Tetraethynyl-substituted phthalocyanine (16)

Anal. Calc. for $C_{64}H_{24}N_8O_8Zn$: C, 69.99; H, 3.20; N, 10.20. Found: C, 69.01; H, 3.70; N, 9.94%. ¹H NMR (DMSO- d^6) δ (ppm): 3.4 (s, 1H, 4x CH=CH), 7.3 (s, 8H, ArCH), 8.4 (s, 4H, ArCH), 8.6 (d, 8H, ArCH). IR (KBr) ν (cm⁻¹): 3390 (CH=CH), 2956, 2929, 2856, 1653, 1541 (s), 1466 (s), 1433 (m), 1320 (m), 1229 (m), 1140 (s), 1126, 920 (s), 881 (m), 750 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ϵ dm³ mol⁻¹ cm⁻¹)]: 687(5.23), 620(4.83), 357(5.21). MS (FD): m/z 1098.32 (M⁺).

2.8.3. Tetraethynyl-substituted phthalocyanine (17)

Anal. Calc. for $C_{64}H_{24}N_8O_8Cu$: C, 69.91; H, 2.44; N, 9.70. Found: C, 70.11; H, 2.21; N, 10.22%. ¹H NMR (DMSO- d^6) δ (ppm): 3.4 (s, 1H, 4x CH=CH), 7.3 (s, 8H, ArCH), 8.4 (s, 4H, ArCH), 8.6 (d, 8H, ArCH). IR (KBr) v (cm⁻¹): 3392(CH=CH), 2957, 2930, 2857, 1655, 1542 (s), 1466 (s), 1436 (m), 1319 (m), 1228 (m), 1138 (s), 1123, 918 (s), 883 (m), 749 (m). UV-vis (DMF), λ_{max} (nm) [(10⁻⁵ log ε dm³ mol⁻¹ cm⁻¹)]: 675(5.19), 605(4.80), 345(5.16). MS (FD): m/z 1096.49 (M⁺).

3. Results and discussion

Our synthetic routes start from the commercially obtained 1,2-dimethoxybenzene, which was brominated to 1,2-dibromo-4,5-dimethoxybenzene using molecular bromine according to a procedure reported earlier [51]. Replacing the bromine atom with a cyano group was carried out by the Rosenmund–Von Braun reaction, yielding the corresponding 4,5-dimethoxyphthalonitrile **1**.

The author has chosen 4,5-dimethoxyphthalonitrile **1** as a precursor to prepare the metal-free octamethoxyphthalocyanine **2** or metallo-octamethoxyphthalocyanines $[(OMe)_8PCM]$ (**3–11**), (M = Zn, Cu, Ni, Mg, Co, Fe, Ru, TiCl and RhCl) because of their lower yields in preparation by conventional thermal treatment under strictly similar sets of conditions as described in the literature



i: DMF, DBU, 150 °C [58] ii: hv, 150 W, 3.5 hrs, 2-ethoxyethanol, 75 °C iii: Microwave, 350 W, 8 min, DMAE iv: Microwave, 300-370 W, 5-11 min, DMAE v: Microwave, 350-370 W, 7-10 min, DMAE

Scheme 1. The synthesis of metal-free and metallo-octamethoxyphthalocyanines 2-11.

previously [51,59,60], for example the yields in case of M = Co and Fe were 41.1% and 37%, respectively [51]. The general aspects of the synthetic route are shown in Scheme 1.

For ultraviolet and microwave irradiation of phthalonitriles to MPcs, various conditions have been examined in a trial to study the parameters that influence the formation and yields of metalfree and metallophthalocyanines, such as starting materials, reaction temperature, solvent, additives and use of the conventional chemicals.

3.1. UV irradiation effect on Pc formation

The author suggested very mild conditions for preparing phthalocyanines at room temperature with the use of a series of primary alcohols, DBU as a base and metals that had different natural activity but were not chemically activated.

We started our UV-irradiation experiments for the preparation of metal-free octamethoxyphthalocyanine **2** by using ethanol and methanol as solvents in the presence of DBU as a catalyst. 4,5-Dimethoxyphthalodinitrile **1** was put in a quartz tube. The mixture was well stirred, and then irradiated for 3.5 h in a photochemical reactor (mercury lamp of 150 W) at 70–75 °C under dry nitrogen, and low quantitative yields were obtained of 40% and 44%. In a parallel experiment, octamethoxyphthalocyanine **2** was formed in 52% yield by using DMAE as the solvent. We observed that by using 2-ethoxyethanol as the solvent and in the presence of DBU as a catalyst at 70 °C, the yield increased to 60%, which indicated that 2ethoxyethanol appeared to be a good solvent for Pc formation by UV-irradiation.

In a trial to prepare the corresponding metallophthalocyanines **3–11** with UV-irradiation under the same conditions as above, all attempts were failed. Unfortunately, as was mentioned in earlier work describing the synthesis of metallophthalocyanines with UV-irradiation [61], our results indicate that it is difficult to prepare and separate them.

3.2. Microwave irradiation effect on Pc formation

The preparation of the metal-free octamethoxyphthalocyanine **2** by microwave-assisted cyclization of 4,5-octamethoxyphthalonitrile **1** under various conditions has been examined. The most frequently used base is DBU in DMAE, and using 350 W irradiation power the reaction went to completion in 8 min.

In the case of MPcs **3–11**, we started the preparation with a lower power of 200–300 W for 15–20 min in the presence of DBU in DMAE, but no Pcs were formed. To solve this problem, we controlled the temperature during the syntheses under M_w conditions. Thus, 300–370 W power of M_w -irradiation was applied to precursor **1** in DMAE and DBU as a base, in the presence of anhydrous metal chlorides as metal sources, for 5–12 min. MPcs **3–11** were formed and isolated in 40–89% yields after purification.

Table 1
Comparison between method A and method B in yields and times.

During the M_w -assisted transformation of **1**, when the reaction time or the temperature was increased, coloration of the mixture and formation of some Pcs were detected by TLC in several cases. Obviously, the excess of DBU acted as a sufficiently strong base to promote the tetramerization, whilst without DBU no Pcs were formed under these conditions.

It was found that the molar ratios of the reagents (i.e., phthalonitrile (1) to the inorganic salt) influenced the conversion as well as



Fig. 1. UV-vis spectra of Pcs 2-6 in DMF.



Fig. 2. UV-vis spectra of Pcs 7-11 in DMF.

_		•				
	Complex	Metal	Microwave method	Power (Watt)	Time (min)	Yield (%)
	3	Zn	A/B	300/370	8/10	72/78
	4	Cu	A/B	330/350	7/8	60/62
	5	Ni	A/B	300/350	5/8	80/83
	6	Mg	A/B	350	5/7	85/89
	7	Co	Α	360	10	58
	8	Fe	Α	360	12	52
	9	Ru	Α	370	11	45
	10	TiCl	Α	360	10	40
	11	RhCl	Α	360	11	52

the yields, and the best results were obtained when **1** was used in an excess in comparison to the metal salts.

Table 1 shows the difference in the yields of the formation of Pcs **3–11** under microwave irradiation with method A or with method B, in which the best results were obtained in both cases. The yields of products under conventional conditions were much lower and the purity of the products were unacceptable.

3.3. Characterization of octasubstituted phthalocyanines 2-14

The IR spectra of metal-free **2** and metallophthalocyanines **3–11** are very similar. The only difference is the presence of a NH stretching band at $3229-3222 \text{ cm}^{-1}$ due to the inner core. This band was absent in the spectra of the metallophthalocyanines **3–11**. In the IR spectra of octahydroxyphthalocyanines [(OH)₈PcM] (**12–14**) the appearance of OH stretches at $v = 3228-3210 \text{ cm}^{-1}$ were observed.

All the spectral investigations of the newly synthesized phthalocyanines were in accordance with the proposed structures. The ¹H NMR spectra of **2** and **12** in DMSO-*d*⁶ showed the inner core – NH protons of the metal-free phthalocyanines at δ = –4.1 to –3.8 ppm. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and the phthalocyanine skeleton gave significant absorbances characteristic of the proposed structure. The aromatic protons appeared as a multiplet at δ = 7.30–7.39 ppm and aliphatic CH₃ protons as a singlet at δ = 3.80–3.95 ppm.

The electronic spectra are especially fruitful in establishing the structure of the phthalocyanines. The phthalocyanines exhibit typical electronic spectra with two strong absorption regions, one of them is in the UV region at about 300-350 nm (B-band) and the other one is in the visible region at 600-700 nm (Q-band). The UV-vis spectrum of the metal-free octamethoxyphthalocyanine 2 in DMF showed a doublet Q-band at λ_{max} 696 and 661 nm as a result of its D₂h symmetry, while the B-band remained at λ_{max} 346 nm (Fig. 1). The UV-vis absorption spectra of the octamethoxyphthalocyanine complexes [(OMe)₈PcM] (3-11) in DMF are given in Figs. 1 and 2. These compounds show the expected absorptions in the main peaks of the Q and B bands (see Section 2). The UV-vis spectra of 12-14 are quite similar in shape in comparison with the starting materials, the octamethoxyphthalocyanine complexes $[(OMe)_8PcM]$ (**2–4**), (M = H₂, Zn, Cu). Only a small red shift of the O-bands of between 1 and 5 nm was observed for 12-14 in comparison with 2-4.

In the mass spectrum of all the prepared compounds **2–14**, the observed molecular ion peaks confirmed the proposed structure.

3.4. Synthesis and characterization of tetraalkynyl-substituted phthalocyanines **15–17**

According to the literature [54–58], alkynyl-containing Pcsystems have been synthesized mainly by following two different synthetic strategies: (i) the cyclotetramerization of alkynyl-substi-



Scheme 2. The synthesis of tetraalkynyl-substituted phthalocyanines 15-17.

tuted phthalonitriles and (ii) the incorporation of alkynyl-containing moieties onto a preformed Pc macrocycle *via* some metal catalyzed coupling reactions.

In our work, the preparation was carried through the demethylation of octamethoxyphthalocyanines [(OM*e*)₈PcM] (**2**–**4**) (M = H₂, Zn, Cu), by stirring in BBr₃ for 3 days, affording the octahydroxyphthalocyanines [(OH)₈PcM] (**12–14**) [59] (M = H₂, Zn, Cu).

The addition of 3,4-diflurophenylacetylene to Pcs **12–14** in the presence of a small quantity of potassium carbonate converted them into the tetraalkynyl-substituted phthalocyanines **15–17** as shown in Scheme 2. The green tetraethynyl-substituted phthalocyanines **15–17** were obtained as a mixture of isomers, as expected. This presence of isomers could be verified by the slight broadening encountered in the UV-vis absorption bands and broadening in the ¹H NMR spectra as compared with the spectra of α -tetra-substituted Pcs composed of a single isomer [56]. The structures and purities of Pcs **15–17** were confirmed by ¹H NMR spectroscopy, elemental analysis and UV-vis absorption spectroscopy.

The ¹H NMR spectrum of **15** in DMSO-*d*⁶ showed the inner core -NH protons of the metal-free phthalocyanine at $\delta = -3.9$ to -3.7 ppm. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave significant absorbance characteristics of the proposed structure for the Pcs 15-17. The aromatic protons appeared as a singlet at δ = 7.3–8.40 ppm. The confirmation of the presence of CH=CH groups in the derived Pcs 15-17 has been clearly shown by the ¹H NMR spectra with a peak at δ = 3.2–3.4 ppm, appearing as a singlet. The IR spectra of the metal-free 15 and metallophthalocyanines 16 and 17 are very similar. The only difference is the presence of the NH stretching band at 3239-3248 cm⁻¹ in the metal-free Pc 15 due to the inner core. This band was absent in the spectra of the metal complexes 16 and 17. The IR spectra of 15-17 showed the disappearance of OH stretches, along with the appearance of new band at v 3390–3425 cm⁻¹ arising from CH=CH groups. The NH proton of the metal-free tetraalkynylsubstituted phthalocyanine **15** was also identified in the ¹H NMR spectrum with a broad peak at δ –3.9 to –3.7 ppm, which becomes absent on deuterium exchange.

The UV-vis spectrum of the metal-free tetraalkynyl-substituted phthalocyanine **15** showed a doublet Q-band at λ_{max} = 697 and 662 nm, as a result of the D₂h symmetry, while the B-band remained at λ_{max} = 342 nm. The attachment of alkynyl groups at the periphery of the given Pcs **15–17** cannot change the absorptions bathochromically or hyperchromically in comparison with



Fig. 3. UV-vis spectra of Pc 13 in DMF (---) and 16 (-).



Fig. 4. UV-vis spectra of Pc 14 in DMF (- - -) and 17 (-).

the UV–vis spectra of the starting materials octamethoxyphthalocyanine complexes [(OH)₈PcM] (**12–14**) (M = H₂, Zn, Cu, respectively), as is shown in the UV–vis spectra of **15–17** (see Figs. 3 and 4). The tetraalkynyl zinc(II) Pc derivative **16** exhibits an intense Q-band around $\lambda_{max} = 687$ nm and the Q-band of the tetraalkynyl copper(II) Pc derivative **17** appears at $\lambda_{max} = 675$ nm.

In the mass spectra of all the prepared compounds **15–17**, the observed molecular ion peaks confirmed the proposed structures.

The solubilities of the alkynyl substituents can be easily finetuned to comply with the requirements of a given medium for a specific application.

4. Conclusions

Here, we were able to prepare metal-free $[(OMe)_8PcH_2]$ (2), under UV or microwave irradiation methods. Both methods enable us to greatly shorten the reaction time and avoid laboratory pollution by using an oil bath as in the case of the conventional thermal method. Therefore it is very attractive from the viewpoint of green chemistry. Also, the metallophthalocyanines $[(OMe)_8PcM]$ (3–11) (M = Zn, Cu, Ni, Mg, Co, Fe, Ru, TiCl and RhCl) have been prepared under microwave irradiation.

The efficient microwave syntheses were performed easily within a reduced timescale using phthalonitrile **1**, leading by far to the best results to date, i.e. higher yield, clean reaction product and to easy-to-perform procedures with considerable improvements over classical methods.

The demethylation of the octamethoxyphthalocyanines $[(OMe)_8PcM]$ (**2–4**) has been used to prepare the precursors octahydroxyphthalocyanines $[(OH)_8PcM]$ (**12–14**). The addition of 3,4-diflurophenylacetylene to the ring oxygens of $[(OH)_8PcM]$ (**12–14**) has been used to prepare the functionalized tetraethynyl-substituted phthalocyanines **15–17**.

It was thought that our work is a further example of the commercial application of microwaves for organic synthesis.

References

- C.C. Leznoff, A.B.P. Lever, C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 1, VCH, Weinheim, 1990.
- [2] T. Torres, The Porphyrin Handbook, vol. 15, Academic Press, 2003.
- [3] N.B. McKeown, Phthalocyanine Materials: Synthesis, Structure and Function, Cambridge University Press, Cambridge, 1998.
- [4] R.S. Gairns, The Chemistry and Technology of Printing and Imaging Systems, Blackie, London, 1996.
- [5] Xerox Corporation, US patent 3.816 118 1974.
- [6] Y. Oda, T. Homma, Y. Fujimaki, Denshi Shashin Gakkaishi 29 (1990) 250.

- [7] M.M. Nicholson, C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 3, VCH, Weinheim, 1993, p. 71.
- [8] T.D. Anthopoulos, T.S. Shafai, Appl. Phys. Lett. 82 (2003) 1628.
- [9] D. Wöhrle, A. Boguta, Molecular Low Dimensional and Nanostructured Materials for Advanced Applications, NATO Sciences Series Volume, Kluwer Academic Publishers, New York, 2002.
- [10] C. Pannemann, V. Dyakonov, J. Parisi, O. Hil, D. Wohrle, Synth. Met. 121 (2001) 1585.
- [11] M. Ishii, Y. Taga, Appl. Phys. Lett. 80 (2002) 3430.
- [12] S.H. Jung, S.M. Choi, J.H. Yang, W.J. Cho, C.S. Ha, Mater. Sci. Eng. B 85 (2001) 160.
- [13] H.S. Nalwa, J.S. Shirk, C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 4, VCH, Weinheim, 1996, p. 79.
- [14] D. Dini, M. Barthel, M. Hanack, Eur. J. Org. Chem. (2001) 3759.
- [15] R. Hurditch, Adv. Colour Sci. Technol. 4 (2001) 33.
- [16] J. Sleven, C. Gorller-Walrand, K. Binnemans, Mater. Sci. Eng. C 18 (2001) 229.
- [17] I. Thurzo, G. Pham, D.R.T. Zahn, Chem. Phys. 287 (2003) 43.
- [18] B. Simic-Glavaski, C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 3, VCH, Weinheim, 1993, p. 119.
- [19] M. Hanack, M. Lang, Adv. Mater. 6 (1994) 819.
- [20] J. Blochwitz, T. Fritz, M. Pfeiffe, K. Leo, D.M. Alloway, P.A. Lee, N.R. Armstrong, Org. Electron. 2 (2001) 97.
- [21] I. Rosanthal, J. Photochem. Photobiol. 53 (1991) 859.
- [22] S. Muller, V. Mantareva, N. Stoichkova, H. Kliesch, A. Sobki, D. Wöhrle, M. Shopova, J. Photochem. Photobiol. B: Biol. 35 (1996) 167.
- [23] D. Schlettwein, N.I. Jaeger, T. Oekermann, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 16, Elsevier Science, Amsterdam, 2003, p. 247.
- [24] K. Ishii, N. Kobayashi, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 16, Elsevier Science, Amsterdam, 2003, p. 1.
- [25] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vol. 4, VCH, Weinheim, 1996.
- [26] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vol. 3, VCH, Weinheim, 1993.
- [27] A.L. Thomas, Phthalocyanines: Research and Application, CRC Press, Boca Raton, 1990.
- [28] P.F. Thoma, W.M. Habermann, J.L. Kranz, US Patent 4 145 264 1979.
- [29] F.H. Moser, A.L. Thomas, Phthalocyanines Properties, vol. 1, CRC Press, Boca Raton, 1983.
- [30] C.H. Yang, S.F. Lin, H.L. Chen, C.T. Chang, Inorg. Chem. 19 (1980) 3541.
- [31] M.A. Petit, V. Plichon, H. Belkacemi, New J. Chem. 13 (1989) 459.
- [32] H. Tomoda, E. Hibiya, T. Nakamura, H. Ito, S. Saito, Chem. Lett. (1976) 1003.

- [33] H.M. Kingston, S.J. Haswell, Microwave-Enhanced Chemistry: Fundamentals, Sample Preparation and Applications, American Chemical Society, Washington, DC, 1997.
- [34] W.H. Sutton, Am. Ceram. Soc. Bull. 68 (1989) 376.
- [35] S.S. Park, E.H. Wang, B.C. Kim, H.C. Park, J. Am. Ceram. Soc. 83 (2000) 1341.
- [36] C.O. Kappe, Angew. Chem. Int. Ed. 43 (2004) 6250.
- [37] A. Shaabani, J. Chem. Res. (1998) 672.
- [38] A. Shaabani, F. Bahadoran, N. Safani, Indian J. Chem. (2001) 195.
- [39] C. Kantar, N. Akdemir, E. Agar, N. Ocak, S. Sxas xmaz, Dyes Pigments 76 (2008) 7.
- [40] N. Safari, P.R. Jamaat, M. Pirouzmand, A.J. Shaabani, J. Porphyrins Phthalocyanines 8 (2004) 1209.
- [41] A. Shaabani, F. Bahadoran, A. Bazgir, N. Safani, Iran J. Chem. 18 (1999) 104.
- [42] M.O. Liu, C.H. Tai, W.Y. Wang, J.R. Chen, A.T. Hu, T.H. Wei, J. Organomet. Chem. (2004) 1078.
- [43] D. Villemin, M. Hammadi, M. Hachemi, N. Bar, Molecules 6 (2001) 831.
- [44] D.A. Davies, C. Schnik, J. Silver, J.L. Sosa-Sanchez, P.G. Riby, J. Porphyrins Phthalocyanines 5 (2001) 376.
- [45] A. Shaabani, R. Maleki-Moghaddam, A. Maleki, A.H. Rezayan, Dyes Pigments 74 (2007) 279.
- [46] A. Burczyk, A. Loupy, D. Bogdal, A. Petit, Tetrahedron 61 (2005) 179.
- [47] T.E. Youssef, M. Hanack, J. Porphyrins Phthalocyanines 6 (2002) 571.
- [48] T.E. Youssef, O.F. Sean, W. Blau, M. Hanack, Eur. J. Org. Chem. 1 (2004) 101.
- [49] T.E. Youssef, M. Hanack, J. Porphyrins Phthalocyanines 9 (2005) 28.
- [50] A.M. Abdel Ghaffar, T.E. Youssef, Polym. Compos. 28 (2007) 631.
- [51] J. Metz, O. Schneider, M. Hanack, Inorg. Chem. 23 (1984) 1065.
- [52] S. Vigh, H. Lam, P. Janda, A.B.P. Lever, C.C. Leznoff, R.L. Cerny, Can. J. Chem. 69 (1991) 1457.
- [53] E.M. Maya, P. Vazquez, T. Torres, J. Eur. Chem. 5 (1999) 2004.
- [54] D.S. Terekhov, K.J.M. Nolan, C.R. McArthur, C.C. Leznoff, J. Org. Chem. 61 (1996) 3034.
- [55] C.C. Leznoff, Z.Li.H. Isago, A.M. Ascanio, D.S. Terekhov, J. Porphyrins Phthalocyanines 3 (1999) 406.
- [56] E.M. Maya, P. Haisch, P. Vázquez, T. Torres, Tetrahedron 54 (1998) 4397.
- [57] B. Giovanni, Díaz D. David, T. Torres, J. Porphyrins Phthalocyanines 10 (2006) 1083.
- [58] F. Mitzel, S. FitzGerald, R. Faust, Chem. Eur. J. 5 (2003) 1233.
- [59] J.F. Van der Pol, E. Neeleman, J.C. Miltenburg, J.W. Ywikker, R.J.M. Nolte, W. Drenth, Macromolecules 23 (1990) 155.
- [60] M. Ruf, A.M. Lawrence, B.C. Noll, C.G. Pierpont, Inorg. Chem. 37 (1999) 1992.
- [61] B.I. Kharisov, U. Ortiz Mendez, J.L. Almaraz Garza, J.R. Almaguer Rodriguez, New J. Chem. 29 (1987) 686.