Journal of Organometallic Chemistry 767 (2014) 101–107

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

The synthesis and structural characterization of new metallo phthalocyanines with 1,2,4-triazole fragments

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ARTICLE INFO

Article history:
Received 13 April 2014
Received in revised form
1 June 2014
Accepted 4 June 2014
Available online 12 June 2014

Keywords:
Phthalocyanine
Metallophthalocyanine
Triazole
Schiff base
Photophysic
Photochemistry

ABSTRACT

Novel Zn(II), Ni(II), Co(II) and Cu(II) phthaloyanine complexes that have [1,2,4]-triazole and Schiff's base moieties on peripheral positions have been synthesized. Key material, substituted phthalonitrile, was obtained in four-step reaction. Firstly hydrazone derivative has been obtained, then [1,2,4]-triazole moiety has been created, Schiff base fragment has been constituted and then phthalonitrile fragment has been added to the structure. The novel phthalocyanines are soluble in many organic solvents. The photophysical, photochemical and fluorescence quenching properties of zinc phthalocyanine derivative (**10**) have been studied in dimethylsulfoxide (DMSO) solution. These properties of the other metallophthalocyanine complexes (**11**, **12** and **13**) have not been appreciated because zinc phthalocyanine is the best compound for photocatalytic applications due to the d^{10} configuration of the Zn^{2+} ion in the phthalocyanine cavity.

Introduction

Modified porphyrins, porphyrazines and phthalocyanines (Pcs) is of much interest and many scientists have explored their gripping feature. Substituted metal free- (H_2Pc) and metallophthalocyanines (MPc) are a considerably unexplored class of compounds and in addition to classical fields -dyes and pigments-, they are used in areas such as electrophotography, chemical sensors, catalysis, electron transfer, laser technology and the photodynamic therapy (PDT) of tumors [1–5]. These wide applications of Pcs are results from their strongly delocalized $18-\pi$ electron systems. On the other hand, beside the advantages of these delocalization, aggregation phenomenon intermolecular interaction of the macrocycles because of electron clouds- is a disadvantage that should be considered. The aggregation decreases the solubility of Pcs and also utilization of them in mentioned areas. The aggregation can be prevented by substitution by bulky substituents on peripheral, non-peripheral or axial positions of Pcs [6].

Photodynamic therapy includes the use of light to destroy the different types of cells. The materials of this method are a photosensitizing agent, oxygen and light [7]. The name of the first-generation photosensitizer is Photofrin and it has been confirmed for tumor treatment in many countries. Pcs are the most promising second-generation photosensitizers for PDT applications. Pcs have favorable photophysical and photochemical properties and these properties are tunable by addition of different substituents. In the last decades, many scientists have been focused on the synthesis of new Pc derivatives that can be used in PDT [8,9].

There are many different drugs that contain 1,2,4-tiazole moiety and they are also used in many diverse biological activities in pharmaceutical and agrochemical fields [10]. Most of the 1,2,4-triazole derivatives have antibacterial [11,12], antifungal [11,13], antimicrobacterial [14,15], hypoglycemic [16], anti-inflammatory [17], antidepressant [18], antiviral [19], antitubercular [15], antihypertensive [20], antitumor [21], analgesic [22], anticonvulsant [23], enzyme inhibitor [24] activities. On the other hand, Schiff bases that can be obtained by the reaction between a substituted aldehyde or ketone and an amine in which the carbonyl group is replaced by the imine group are an important class of organic compounds that have wide applications in many biological aspects. Furthermore, many Schiff bases that have 1,2,4-triaole moiety show antibacterial, antifungal [25] and antitumor activities [21].

Recently, we described the synthesis, photochemical and photophysical properties of novel Pcs containing Schiff base [26], pyrazole [27] and 1,2,4-triazole [28]. However, there is no literature that presents the photochemical and photophysical properties of

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http://dx.doi.org/10.1016/j.jorganchem.2014.06.003
0022-328X/

Pcs that have 1,2,4-triazole and Schiff base moieties. So the objective of this research is to examine whether a novel peripherally substituted MPcs (**10**–**13**) containing triazole and Schiff base moiety have potential as photodynamic therapy. For this purpose, at the first stage substituted hydrazine (**3**) and triazole moieties (**5**) have been prepared. At the second part of the study, the Schiff base (**7**) and phthalonitrile (**9**) moieties have been synthesized. At the third step, peripherally tetra substituted MPc complexes (**10**–**13**) have been prepared successfully. At the final stage, the aggregation behavior, photochemical, photophysical and fluorescence quenching properties of the compound **10** have been investigated in DMSO solution.

Experimental

Materials

Reactions were realized under dry and oxygen-free nitrogen atmosphere by Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [29]. 4-nitrophthalonitrile (**8**) [30] was prepared according to the literature. Ethyl 2-(4-chlorophenyl)acetimidate hydrochloride (**1**), 4-chlorobenzohydrazide (**2**), hydrazine hydrate (**4**) and 4-hydroxybenzaldehyde (**6**) were purchased from their commercial suppliers.

The used equipments, photophysical and photochemical parameters were supplied as Supplementary information.

Synthesis

*(Z)-ethyl N′-4-chlorobenzoyl-2-(4-chlorophenyl)acetohydrazonate (**3**)*

In an ice-bath, compound **2** (1.70 g, 0.01 mol) was added to the solution of compound **1** (2.34 g, 0.01 mol) in absolute ethanol (75 mL) and the reaction content was mixed at this temperature (0–5 °C) for 6 h and then was mixed for 2 h at room temperature. At the end of the reaction, the mixture was poured into ice-water (200 mL) and the white precipitate was filtered and washed with cold water. The crude product was dried purified by crystallization in petroleum ether and ethanol, respectively. Yield: 2.73 g, (77.8%), mp: 134–136 °C. Anal. Calc. for $C_{17}H_{16}Cl_2N_2O_2$: C, 58.13; H, 4.59; N, 7.98. Found: C, 58.19; H, 4.52; N, 8.04. IR (KBr tablet) υ_{max}/cm^{-1}: 3205 (–NH), 3049 υ(Ar–CH), 2930 υ(Aliph. C–H), 1647 υ(C=O), 1614–1569 (C=N), 1538, 1491, 1372, 1315, 1092, 1017, 884. ^{1}H NMR (DMSO, d_6), (δ: ppm): 10.73 (s, 1H, NH), 7.82–7.78 (d, 2H, Ar–H), 7.56–7.52 (d, 2H, Ar–H), 7.37–7.33 (d, 2H, Ar–H) 7.23–7.19 (d, 2H, Ar–H), 4.16–4.12 (q, 2H, OCH_2), 3.69 (s, 2H, CH_2), 1.23–1.16 (t, 3H, CH_3). ^{13}C NMR (DMSO, d_6), (δ: ppm): 167.10 (C=O), 161.17 (C=N), 150.12 140.04, 134.15, 132.52, 130.59, 129.15, 128.33, 128.24, 62.37 ($-OCH_2$), 34.10 (CH_2), 13.92 (CH_3). MS (ESI), (*m*/*z*): Calculated: 350.06; Found: 351.06 $[M + H]^+$ (100%), 373.02 $[M + Na]^+$ (20%).

*3-(4-chlorobenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-4-amine (**5**)*

In round bottomed flask (500 mL), hydrazine hydrate (**4**) (2.50 g, 0.05 mol) was added to the solution of compound **3** (8.75 g, 0.025 mol) in n-propanol (150 mL) and the mixture was heated under reflux for 24 h. After the completion of the reaction, the solvent was evaporated under vacuum and cream-colored product crystallized in ethanol–water (6:4) solvent system. Yield: 5.90 g, (73.9%), mp: 227–229 °C. Anal. Calc. for $C_{15}H_{12}Cl_2N_4$: C, 56.44; H, 3.79; N, 17.55. Found: C, 56.57; H, 3.71; N, 17.64. IR (KBr tablet) υ_{max}/cm^{-1}: 3243–3120 υ($-NH_2$), 3075 υ(Ar. CH), 2998–2923 υ(Aliph. CH), 1518 υ(C=N), 1480, 1403, 1094, 1015, 991, 833. ^{1}H NMR (DMSO, d_6), (δ: ppm): 8.05–8.0 (dd, 1H, Ar–H), 7.58–7.54 (dd, 1H, Ar–H), 7.36–7.25 (m, 6H, Ar–H), 6.11 (s, 2H, NH_2), 4.15 (s, 2H, CH_2). ^{13}C NMR (DMSO, d_6), (δ: ppm): 156.02 (C=N), 154.17 (C=N), 132.60, 131.88, 131.52, 131.43, 130.32, 129.26, 128.99, 126.67, 29.59 (CH_2). MS (ESI), (*m*/*z*): Calculated: 318.04; Found: 319.00 $[M + H]^+$.

*(E)-4-((3-(4-chlorobenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-4-ylimino) methyl)phenol (**7**)*

A mixture of compound **5** (3.19 g, 0.01 mol) and 4-hydroxybenzaldehyde (**6**) (1.22 g, 0.01 mol) in glacial acetic acid (50 mL) was refluxed for 5 h. Then the mixture was added to ice-water (500 mL) and cream-colored precipitate was filtrated and purified by crystallization in ethanol. Yield: 3.47 g, (82.0%), mp: 247–249 °C. Anal. Calc. for $C_{22}H_{16}Cl_2N_4O$: C, 62.42; H, 3.81; N, 13.24. Found: C, 62.51; H, 3.75; N, 13.31. IR (KBr tablet) υ_{max}/cm^{-1}: 3373 υ(–OH), 3076 υ(Ar–CH), 2974 υ(Aliph. CH), 1595 υ(CH=N), 1571 υ(C=N), 1509, 1492, 1470, 1432, 1294, 1247, 1210, 1164, 1093, 1067, 832. ^{1}H NMR (DMSO, d_6), (δ: ppm): 10.33 (bs, 1H, OH), 8.55 (s, 1H, CH=N), 7.80–7,76 (d, 2H, Ar–H), 7.67–7.62 (d, 2H, Ar–H), 7.55–7.51 (d, 2H, Ar–H), 7.34–7.30 (d, 2H, Ar–H), 7.23–7.18 (d, 2H, Ar–H), 6.91–6.87 (d, 2H, Ar–H), 4.22 (s, 2H, CH_2). ^{13}C NMR (DMSO, d_6), (δ: ppm): 169.48 (C=N), 162.38 (C=N), 150.30 (CH=N), 148.82 (C–O), 134.82, 134.44, 131.47, 130.63, 129.49, 128.90, 128.43, 125.49, 122.42, 116.12, 29.73 (CH_2). MS (ESI), (*m*/*z*): Calculated: 422.07; Found: 423.09 $[M + H]^+$.

*(E)-4-(4-((3-(4-chlorobenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-4-ylimino) methyl)phenoxy)phthalonitrile (**9**)*

Compound **7** (4.23 g, 0.01 mol) and 4-nitrophthalonitrile (**8**) (1.73 g, 0.01 mol) was dissolved in dry *N*,*N*-dimethylformamide (DMF) (50 mL) and dry K_2CO_3 (1.38 g, 0.01 mol) was added to the media in 2 h. After the addition of K_2CO_3, the mixture was stirred efficiently for 5 days at 55–60 °C. Then the mixture was poured into ice-water (500 mL) and precipitate was filtrated and fawn colored product was obtained after crystallization in ethanol. Yield: 3.78 g, (68.9%), mp: 213–214 °C. Anal. Calc. for $C_{30}H_{18}Cl_2N_6O$: C, 65.58; H, 3.30; N, 15.30. Found: C, 65.68; H, 3.39; N, 15.24. IR (KBr tablet) υ_{max}/cm^{-1}: 3060 υ(Ar. CH), 2920 υ(Aliph. CH), 2231 (C≡N), 1591 υ(CH=N), 1492, 1487, 1249, 1215, 1170, 1096, 1014, 950, 839. ^{1}H NMR (DMSO, d_6), (δ: ppm): 8.19–8.14 (d, 1H, CH=N), 7.97–7.93 (d, 5H, Ar–H), 7.59–7.48 (m, 3H, Ar–H), 7.36–7.34 (m, 7H, Ar–H), 4.10 (s, 2H, CH_2). ^{13}C NMR (DMSO, d_6), (δ: ppm): 163.60 (C=N), 159.85 (C=N), 158.68 (CH=N), 153.38 (C–O), 149.69, 137.01, 135.69, 134.23, 132.18, 131.18, 130.15, 129.21, 126.77, 124.40, 122.40, 121.17, 119.16, 117.48, 115.95, 113.76, 110.32, 108.28, 106.27, 29.80 (CH_2). MS (ESI), (*m*/*z*): Calculated: 548.09; Found: 549.90 $[M + H]^+$.

*General method for the preparation of the phthalocyanines (**10**–**13**)*

MPcs (**10**–**13**): Substituted phthalonitrile (**9**) (0.2 g, 0.36 mmol) and corresponding metal salts were dissolved in *N*-dimethylaminoethanol (DMAE) (3 mL) and 1,8-diazabycyclo[5,5,0]undec-7-ene (DBU) (3 drops) was added to the media. The temperature of the system was raised to 160 °C and stirred for 24 h. Then the contents of the reactions were precipitated by the addition of methanol (30 mL) and filtrated and washed with methanol, ethanol and diethyl ether, respectively. The green-colored pure products were obtained by silica-gel column chromatography.

*Zinc(II) phthalocyanine (**10**).* The used solvent system during column chromatography: Chloroform:Methanol (7:1). Yield: 0.053 g, (26%), mp:>300 °C (decomposition). Anal. Calc. for $C_{120}H_{72}Cl_8N_{24}O_4Zn$: C, 63.69; H, 3.21; N, 14.85. Found: C, 63.85; H, 3.09; N, 14.68. IR (KBr tablet) υ_{max}/cm^{-1}: 3049 υ(Ar. CH), 2920 υ(Aliph. CH), 1604 υ(CH=N), 1484, 1469, 1406, 1330, 1283, 1217, 1163, 1087, 1066, 947, 886. ^{1}H NMR (DMSO, d_6), (δ: ppm): 7.88 (bs, 20H, CH=N + Ar–H), 7.45–7.23 (m, 44H, ArH), 4.09 (s, 8H, CH_2