Journal of Organometallic Chemistry 735 (2013) 65–71

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis, characterisation and aggregation properties of novel metal-free and metallophthalocyanines containing four 21-membered oxatetrathiadiaza macrocycles

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ARTICLE INFO

Article history:
Received 29 November 2012
Received in revised form
1 March 2013
Accepted 5 March 2013

Keywords:
2-Aminothiophenol
Mixed-donor Macrocycle
Metal-free phthalocyanine
Metallophthalocyanine
Aggregation
Transition metal

ABSTRACT

The synthesis of novel metal-free phthalocyanine **4** and metallophthalocyanines **5**, **6**, **7** (MPcs, M = Ni, Zn, Co) containing four 21-membered oxatetrathiadiaza macrocycles at the peripheral positions was achieved by cyclotetramerisation of a novel 6,16-dioxo-5,6,7,9,10,12,13,15,16,17-decahydrotribenzo [h,k,n] [1,4,10,13,19,7,16]oxatetrathiadiazacyclohenicosine-24,25-dicarbonitrile. The aggregation behaviours of phthalocyanines **4**, **5**, **6** and **7** were investigated at different concentrations in dimethylformamide. No aggregation behaviour was observed in dimethylformamide at concentrations between 10×10^{-6} and 1×10^{-6} mol dm$^{-3.}$ The aggregation properties of all phthalocyanines were also investigated in different solvents. All new compounds were characterised by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, IR, UV–Vis and MS spectral data.

1. Introduction

Phthalocyanines are an important class of compounds with many potential applications due to their high thermal and chemical stability [1]. Because of these properties, phthalocyanines have been extensively studied and are used in a wide variety of areas, for instance, in photodynamic therapy as photosensitisers [2]; as chemical sensors [3], green and blue pigments [4], corrosion inhibitors [5], and semiconductors; and in biomedicine, catalysis, electronics [6,7], and non-linear optics [8]. Because of their potential applications, tens of thousands of tons of phthalocyanines (Pc's) are produced per year worldwide [9].

The optical and electrochemical properties of phthalocyanines can be significantly altered by incorporating substituents at the peripheral and nonperipheral positions. The first introduction of crown ether into a phthalocyanine was reported in 1986 [10] and the ability of this molecule to bind alkali metal cations was investigated [11]. The design and synthesis of phthalocyanine-bearing macrocycles has found potential applications in biochemistry and materials science [12]. A goal of research on the chemistry of phthalocyanines is to achieve control over the structure of synthetic molecules and enhance their solubility in various solvents. Particularly, the attachment of a macrocycle containing nitrogen and sulphur donor atoms to phthalocyanines increases their selectivity towards alkaline-earth and soft transition metal cations. Complexation of phthalocyanines with metal ions has an influence on their photophysical properties [13,14]. To enhance the coordination properties of these macrocycles, different parameters have been modified such as the ring size, the nature of substituents, and the type of donor atoms present [15–19]. Macrocycles that contain sulphur and nitrogen atoms as donor atoms have high complexabilities with some transition metal ions [20]. A challenge in the synthesis of thiol-derivatised phthalocyanines is the time-consuming, tedious purification process and use of toxic chemicals. Therefore, phthalocyanines containing sulphur donors are the least reported class of phthalocyanines in literature [21].

We have previously described the synthesis of metal-free and metal-containing phthalocyanines that contain four 27-membered dioxadiazapentathia and diazaheptathia macrocycles [22,23]. The objective of this research is to describe a simple strategy for the synthesis of metal-free and metallophthalocyanines containing four 21-membered macrocycles with oxygen, nitrogen and sulphur donor atoms.

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http://dx.doi.org/10.1016/j.jorganchem.2013.03.019

2. Experimental

2.1. Materials and equipment

4,5-Bis(2′-aminophenylsulfanyl)-1,2-dicyanobenzene **1** was prepared according to the literature [24]. All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [25]. Melting points were determined with an electrothermal apparatus and are reported uncorrected. FTIR spectra were measured on a Perkin Elmer Spectrum 65 spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using $CDCl_3$ and DMSO-d_6 (99.9%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV–Vis region with a PG-T80 + spectrophotometer using 1 cm path length cuvettes at room temperature. Elemental analyses were obtained with a LECO Elemental Analyser (CHNS 0932) spectrophotometer. The homogeneity of the products was tested at each step using TLC.

2.2. Synthesis

2.2.1. *N,N′-(2,2′-(4,5-Dicyano-1,2-phenylene)bis(sulfanediyl) bis(2,1-phenylene))bis(2-chloroacet-amide) (**2**, Fig. 1)*

Chloroacetic anhydride (4.176 g, 36.97 mmol) in CH_2Cl_2 (65 ml) was added dropwise through a dropping funnel to a stirred solution of 4,5-bis(2′-aminophenylsulfanyl)-1,2-dicyanobenzene **1** (4.61 g, 12.32 mmol) in CH_2Cl_2 (260 ml) at 0–5 °C over a 1.5 h period. The reaction was monitored by thin layer chromatography using ethyl acetate–hexane (4:6) as the solvent system. The mixture was stirred overnight under a nitrogen atmosphere at room temperature. At the end of this period, saturated aqueous $NaHCO_3$ was added to neutralise the reaction mixture. The organic layer was separated and washed twice with a 100 ml portion of saturated aqueous $NaHCO_3$ and then twice with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to give the crude product. The crude product was crystallised from acetonitrile to give 5.65 g (87%). Mp 221–222 °C. Anal. calcd. for $C_{24}H_{16}Cl_2N_4O_2S_2$: C, 54.65; H, 3.06; N, 10.62%. Found: C, 53.89; H, 2.99; N, 10.55%. IR (KBr disc) ν_{max}/cm^{-1}: 3336 (NH), 3080 (CH_{Ar}), 2230 (C≡N), 1697 (C=O), 1584, 1565, 1525, 1437, 1348, 1304, 1219, 1161, 1105, 1035, 918, 757, 632, 528, 501. ^{1}H NMR ($CDCl_3$) δ: 9.27 (s, 2H, NH), 8.65 (d, J = 8.31 Hz, 2H, ArH), 7.70 (t, J = 8.31 Hz, 2H, ArH), 7.66 (d, J = 7.82 Hz, 2H, ArH), 7.38 (t, J = 7.82 Hz, 2H, ArH), 6.92 (s, 2H, ArH), 4.21 (s, 4H, O=CCH_2Cl). ^{13}C NMR ($CDCl_3$) δ: 163.80 (C=O), 141.75, 139.38, 137.21, 133.36, 129.48, 126.46, 121.61, 116.14 (ArC), 114.79 (C≡N), 113.16, 43.26 (O=CCH_2Cl). MS (LC-MS/MS) m/z: 527 $[M + H]^+$, 549 $[M + Na]^+$.

2.2.2. *6,16-Dioxo-5,6,7,9,10,12,13,15,16,17-decahydrotribenzo[h,k,n] [1,4,10,13,19,7,16]oxatetrathiadiazacyclohenicosine-24,25-dicarbonitrile (**3**, Fig. 1)*

A two-necked round-bottom flask containing a solution of 2-mercaptoethylether (1.05 g, 7.59 mmol) and anhydrous sodium carbonate (3.22 g, 30.36 mmol) in dry dimethylformamide (400 ml) was placed under a nitrogen atmosphere in an ice bath and cooled to 0–5 °C. A solution of **2** (4 g, 7.59 mmol) in dry dimethylformamide (300 ml) was added to the above solution using a dropping funnel with stirring and under dry inert gas over 1.5 h at 0–5 °C. After addition was complete, the reaction mixture was stirred for another 16 h at 0–5 °C. The reaction was monitored by thin layer chromatography [hexane–ethyl acetate (6:4)]. When the reaction was complete, the mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The yellowish oil was dissolved in CH_2Cl_2. The organic layer was washed twice with 100 ml portions of a 5% Na_2CO_3 solution and then twice with water. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to give a crude product that was purified by silica gel chromatography. The elution was carried out with hexane–ethyl acetate (6:4). The product was obtained as white solid. The yield was 2.7 g (60%). Mp 213–215 °C. Anal. calcd. for $C_{28}H_{24}N_4O_3S_4$: C, 56.73; H, 4.08; N, 9.45%. Found: C, 56.42; H, 4.13; N, 9.40. IR (KBr disc) ν_{max}/cm^{-1}: 3251 (NH), 3067 (CH_{Ar}), 2919, 2860 (CH_3), 2227 (C≡N), 1691 (C=O), 1577, 1455, 1435, 1346, 1295, 1103, 1033, 917, 763, 667, 529. ^{1}H NMR ($CDCl_3$) δ: 9.68 (s, 2H, NH), 8.73 (d, J = 8.31 Hz, 2H, ArH), 7.69 (t, J = 7.82 Hz, 2H, ArH), 7.61 (d, J = 7.58 Hz, 2H, ArH), 7.33 (t, J = 7.58 Hz, 2H, ArH), 6.87 (s, 2H, ArH), 3.80 (t, J = 5.13 Hz, 4H, OCH_2), 3,52 (s, 4H, O=CCH_2Cl), 2.80 (t, J = 5.13 Hz, 4H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 167.22 (C=O), 142.16, 140.60, 137.14, 133.39, 128.99, 126.06, 121.58 (ArC), 115.31 (C≡N), 114.89, 112.79 (ArC), 71.19 (OCH_2), 38.15 (O=CCH_2S), 33.10 (SCH_2). MS (LC-MS/MS) m/z: 593 $[M + H]^+$, 615 $[M + Na]^+$.

2.2.3. *Metal-free phthalocyanine (**4**, Fig. 1)*

A mixture of **3** (0.4 g, 0.674 mmol) and a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry *n*-pentanol (1.5 ml) were placed under a nitrogen atmosphere in a standard Schlenk tube. The reaction mixture was heated and stirred under nitrogen at 145 °C for 24 h. After cooling to room temperature, the mixture was diluted with ethanol (10 ml) until the product precipitated. The precipitated crude product was filtered. The crude product was refluxed with ethanol (25 ml) in a Soxhlet extractor for 4 h. The product was then filtered and washed with ethanol, diethyl ether, CH_2Cl_2 and dried under vacuum. Finally, pure metal-free phthalocyanine was obtained by silica gel column chromatography using dichloromethane:-methanol as the solvent system. This product was soluble in DMF, DMSO and THF. The yield was 0.085 g (21%). Mp >300 °C. Anal. calcd. for $C_{112}H_{98}N_{16}O_{12}S_{16}$: C, 56.68; H, 4.16; N, 9.44%. Found: C, 56.42; H, 4.21; N, 8.92. IR (KBr disc) ν_{max}/cm^{-1}: 3386 (NH), 3290(NH), 3051 (CH_{Ar}), 2918 (CH_3), 1658 (C=O), 1607, 1576, 1508, 1473, 1439, 1379, 1304, 1262, 1107, 1025, 877, 740, 677. ^{1}H NMR (DMSO-d_6) δ: 9.92 (s, 8H, NH), 9.07 (m, 8H, ArH), 7.39–6.85 (m, 32H, ArH), 3.54 (br, 16H, OCH_2), 3.45 (s, 16H, O=C–CH_2), 2.89–2.74 (m, 16H, SCH_2), −3.28 (br, s, 2H, NH). UV–Vis (DMF): λ_{max}, nm (log ε): 324 (5.23), 364 (5.21), 743 (5.06). MS (MALDI-TOF) m/z: 2371 $[M + H]^+$.

2.2.4. *Nickel(II) phthalocyanine (**5**, Fig. 2)*

A mixture of **3** (0.3 g, 0.506 mmol), anhydrous $NiCl_2$ (0.020 g, 0.153 mmol) and quinoline (2 ml) was heated and stirred at 190 °C for 7 h in a Schlenk tube under nitrogen. After cooling to room temperature, the product was precipitated by adding ethanol (10 ml) and filtered off. The crude product was refluxed with ethanol (25 ml) in a Soxhlet extractor for 4 h. The green product was then filtered and washed with ethyl acetate, acetone, and diethyl ether. Finally, pure nickel(II) phthalocyanine was obtained by silica gel column chromatography using dichloromethane:methanol as the solvent system. The product was dried under vacuum over P_2O_5. The yield was 0.100 g (33%). Mp >300 °C. Anal. calcd. for $C_{112}H_{96}N_{16}O_{12}S_{16}Ni$: C, 55.36; H, 3.98; N, 9.22%. Found: C, 54.78; H, 4.36; N, 9.31. IR (KBr disc) ν_{max}/cm^{-1}: 3275 (NH), 3058 (CH_{Ar}), 2914 (CH_3), 2856, 1686 (C=O), 1578, 1513, 1434, 1410, 1380, 1296, 1116, 961, 754. ^{1}H NMR (DMSO-d_6): δ 10.02 (s, 8H, NH), 8.59 (m, 8H, ArH), 8.02-6.99 (m, 32H, ArH), 3.58 (br, 16H, OCH_2), 3.48 (s, 16H, O=C–CH_2), 2.77 (m, 16H, SCH_2). UV–Vis (DMF): λ_{max}, nm (log ε): 322 (4.97), 416 (4.47), 634 (4.49), 707 (5.17). MS (MALDI-TOF) m/z: 2427 $[M + H]^+$.

2.2.5. *Zinc(II) phthalocyanine (**6**, Fig. 2)*

A mixture of **3** (0.3 g, 0.506 mmol), anhydrous $Zn(CH_3CO_2)_2$ (0.028 g, 0.153 mmol) and quinoline (2 ml) was heated and stirred at