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The synthesis, photochemical and photophysical properties of zinc aryloxy- and alkyloxy azaphthalocyanines

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ABSTRACT

Octasubstituted zinc tetrapyrazinoporphyrazines bearing butyloxy, octyloxy, 2,6-diisopropylphenoxy and 4-(hydroxymethyl)phenoxy substituents were synthesized from the corresponding 5,6-disubstituted pyrazine-2,3-dicarbonitriles using $Zn(quinoline)_2Cl_2$ in yields varying from 14 to 44%. The reaction procedure proved to be efficient for the synthesis of both alkyloxy- and aryloxy- substituted zinc tetrapyrazinoporphyrazines and did not require strictly anhydrous conditions. Optimal cyclotetramerization conditions were identified for each derivative, in terms of reaction temperature, as overheating cleaved the ether bond leaving a vacant OH group on the macrocycle. The photochemical and photophysical properties of the synthesized compounds were investigated in pyridine. Singlet oxygen quantum yields (Φ_Δ) ranged from 0.49 to 0.61 and high fluorescence quantum yields (Φ_F) of ~0.30 were observed for non-aggregated compounds.

1. Introduction

Phthalocyanines (Pc) belong to a thoroughly investigated class of dye that enjoys widespread use in a variety of applications [1,2]. Azaphthalocyanines (AzaPc) are aza-analogs of Pc in which some of the carbon atoms in the Pc macrocycle are replaced by nitrogens. Tetrapyrazinoporphyrazines (TPyPz) belonging to the AzaPc subgroup have attracted attention of researchers owing to their promising photosensitizing [3], fluorescent [4], non-linear optical [5] and oxidative [6] properties. The photochemical and photophysical properties of TPyPz are known to be altered significantly by different peripheral substitutions. Whilst the singlet oxygen and fluorescence quantum yields have been investigated for alkylsulfanyl [7], alkylamino [8], aryl [9] or heteroaryl [10] substituted derivatives, this has not been the case for TPyPz with an oxygen linkage between the macrocycle and peripheral substituents. Despite the extensive investigation of aryloxy substituted Pc [11–19], studies of aryloxy as well as alkyloxy TPyPz are rare because of the lack of suitable synthetic procedures. Whilst the synthesis of aryloxy TPyPz was resolved by two research groups only recently [20,21] and the aggregation, crystal structure and UV–vis spectra of the compounds studied in detail [22–24], the photochemical and photophysical properties of the compounds has not attracted attention.

This paper concerns the synthesis of alkyloxy- and aryloxy-substituted zinc TPyPz (ZnTPyPz) and their singlet oxygen production and fluorescence. The peripheral substituents in the investigated compounds were chosen to cover both alkyloxy- and aryloxy- derivatives with the intention of presenting a synthetic procedure that is suitable for both types of substitution.

2. Experimental

All organic solvents were of analytical grade. Anhydrous octanol was stored over magnesium and distilled prior to use. TLC was performed on Merck aluminium sheets coated with silica gel 60 F254. Merck Kieselgel 60 (0.040–0.063 mm) was used for column chromatography. Infrared spectra were measured on an IR-Spectrometer Nicolet Impact 400 (in KBr pellets) or Nicolet 6700 (in ATR mode). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury – Vx BB 300 (299.95 MHz – ^1H and 75.43 MHz – ^{13}C); reported chemical shifts are relative to Me_4Si. Elemental analysis was carried out using an Automatic Microanalyser EA1110CE (Fisons Instruments S.p.A., Milano, Italy). UV–vis spectra were recorded on a UV-2401PC spectrophotometer (Shimadzu Europa, GmbH, Duisburg, Germany). Fluorescence spectra were obtained using an AMINCO-Bowman Series 2 luminescence spectrometer (SLM-Aminco, Urbana, IL, USA).

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The MALDI-TOF mass spectra were collected on a Voyager-DE STR mass spectrometer (Applied Biosystems, Framingham, MA, USA) calibrated externally with a five-point calibration procedure using Peptide Calibration Mix1 (LaserBio Labs, Sophia-Antipolis, France). A solution of TPyPz in DCM (approximate concentration 1×10^{-5} mol L^{-1}, 1.5×10^{-3} mL) was mixed with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile matrix in DCM (0.01 mL, 1 mg/0.5 mL) and spotted on the plate.

2.1. Synthesis

5,6-Dichloropyrazine-2,3-dicarbonitrile (**1**) [25], 5,6-bis(butoxy) pyrazine-2,3-dicarbonitrile (**2**) [26] and Zn(quinoline)$_2$Cl$_2$ (ZnQ_2Cl_2) [27] were prepared according to published procedures.

2.1.1. 5,6-Bis(octyloxy)pyrazine-2,3-dicarbonitrile (**3**)

A solution of triethylamine (895 mg, 8.84 mmol) in anhydrous octanol (6 mL) was stirred for 45 min at room temperature and added dropwise to a suspension of **1** (800 mg, 4 mmol) in anhydrous octanol (25 mL). The suspension dissolved after approximately 15 min and stirring was continued for 60 min at room temperature. Octanol was then removed under reduced pressure and the crude product was purified by column chromatography on silica using toluene/hexane 2:1 as eluent, to provide a yellow oil (785 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.89$ (t, 6 H, $J = 6.6$ Hz, CH_3), 1.25–1.45 (m, 20 H, CH_2), 1.83 (p, 4 H, $J = 7.0$ Hz, OCH_2CH_2) and 4.45 (t, 4 H, $J = 6.7$ Hz, OCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.06, 22.61, 25.72, 28.16, 29.11 (4 carbons according to rough integration), 31.72, 69.49, 113.49, 122.57 and 151.95 ppm. IR (ATR): ν_{max} = 2953, 2924, 2855, 2236 (CN), 1549, 1495, 1458, 1379, 1344, 1299, 1239, 948 cm^{-1}.

2.1.2. 5,6-Bis(2,6-diisopropylphenoxy)pyrazine-2,3-dicarbonitrile (**4**)

2,6-Diisopropylphenol (446 mg, 2.5 mmol) was stirred for 15 min in an aqueous solution of sodium hydroxide ($c = 1$ mol dm^{-3}, 2.4 mL, 2.4 mmol,). Compound **1** (200 mg, 1 mmol) in THF (15 mL) was added dropwise and the mixture stirred for 30 min at room temperature. The crude product was concentrated to dryness and the brownish-yellow solid washed thoroughly with water (200 mL) and purified using column chromatography on silica with toluene/hexane 1:1, providing a white solid (404 mg, 83%, mp 208.5–209.5 °C (methanol), lit. [22] 253 °C (*n*-hexane)). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.39$–7.24 (m, 6H, aromH), 2.82 (sept, 4 H, $J = 7$ Hz, CH), 1.23 ppm (d, 24H, $J = 7$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 23.2$, 28.0, 112.6, 124.2, 124.6, 127.6, 139.8, 146.3, 151.1 ppm. IR (KBr): ν_{max} = 3068, 3032, 2967, 2930, 2871, 2360, 2344, 2237, 1545, 1460, 1441, 1403, 1385, 1357, 1331, 1258, 1233, 1142, 1112, 1089, 1062, 937, 849, 793 and 750 cm^{-1}. Elemental analysis calc. (%) for $C_{30}H_{34}N_4O_2$: C, 74.66, H, 7.10, N, 11.61; found: C, 74.40; H, 7.31; N, 11.99.

2.1.3. 5,6-Bis(4-(hydroxymethyl)phenoxy)pyrazine-2,3-dicarbonitrile (**5**)

Compound **1** (400 mg, 2 mmol) was dissolved in THF (10 mL) and then 4-(hydroxymethyl)phenol (1.24 g, 10.0 mmol) and pyridine (695 mg, 8.8 mmol) were added. After 24 h of stirring at room temperature the solvent was evaporated and the resulting yellow oil was dissolved in chloroform (150 mL) and extracted three times with brine (3 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica with ethylacetate/hexane 5:2 and recrystallized from EtOH/H_2O, yielding a white solid (486 mg, 65%, m.p. 150.1–152.5 °C). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 4.33$ (t, 2 H, $J = 5.8$ Hz, OH), 4.69 (d, 4H, $J = 5.8$ Hz, CH_2) 7.31 ppm (d, 4H, $J = 8.6$ Hz, aromH). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 64.0$, 114.3, 121.9, 124.5, 128.9, 142.1, 151.4, 153.3 ppm. IR (ATR): ν_{max} = 3303, 2936, 2873, 2233 (CN), 1729, 1701, 1598, 1544, 1501, 1441, 1400, 1374, 1350, 1237, 1194, 1153, 1105, 1039, 1011, 941, 924, 858, 847 and 809 cm^{-1}. Elemental analysis calc. (%) for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.77; N, 14.97; found: C, 62.45; H, 4.25; N, 14.37.

2.1.4. Alternative preparation of 5,6-bis(4-(hydroxymethyl) phenoxy)pyrazine-2,3-dicarbonitrile (**5**)

NaOH (100 mg, 2.5 mmol) was dissolved in water (20 mL) and 4-(hydroxymethyl)phenol (311 mg, 2.5 mmol) was added. The suspension was sonicated and stirred for 20 min at room temperature and ethanol (10 mL) was added to expedite solubilisation. Thereafter, compound **1** (200 mg, 1.0 mmol) in tetrahydrofuran (10 mL) was added dropwise and the ensuing solution was stirred for 10 min at room temperature. Ethanol and tetrahydrofuran were evaporated and the mixture was diluted with water (70 mL) and extracted three times with ethylacetate (3 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to dryness. The mixture was purified by column chromatography on silica with chloroform/acetone 10:1. The two important fractions were isolated, one corresponding to **5** ($R_f = 0.15$, white solid, 86 mg, 23%) and the second was 5,6-bis (ethoxy)pyrazine-2,3-dicarbonitrile ($R_f = 0.79$, a pale yellow solid, 89 mg, 41%; m.p. 112.2–113.0 °C, lit.[28] 117–118 °C). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 1.43$ (t, 6 H, $J = 7.1$ Hz, CH_3), 4.54 ppm (q, 4 H, $J = 7.1$ Hz, OCH_2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 14.15$, 65.82, 114.81, 123.34 and 153.16 ppm.

2.1.5. 2,3,9,10,16,17,23,24-Octakis(butoxy)-1,4,8,11,15,18,22,25-(octaaza)phthalocyanine zinc (II) (**6**)

Precursor **2** (80 mg, 0.29 mmol) and ZnQ_2Cl_2 (115 mg, 0.29 mmol) were mixed in a round bottom flask and heated at 190 °C for 60 min. The crude product was dissolved in chloroform (100 mL), filtered and the solvent removed under reduced pressure. The solid was then washed with water/methanol 1:1 (300 mL), adsorbed on silica and thoroughly washed with methanol (300 mL) on a glass frit. Afterwards, the product was purified by column chromatography on silica using chloroform as eluent to give a blue solid (12 mg, 14%). NMR, IR, UV–vis spectra showed the same characteristics as described in the literature for this compound prepared using different approach [26]. MS (MALDI-TOF) *m*/*z* 1160 $[M]^+$, 1183 $[M + Na]^+$, 1199 $[M + K]^+$, 2321 $[2M]^+$, 2344 $[2M + Na]^+$, 2360 $[2M + K]^+$.

2.1.6. 2,3,9,10,16,17,23,24-Octakis(octyloxy)-1,4,8,11,15,18,22,25-(octaaza)phthalocyanine zinc (II) (**7**)

ZnQ_2Cl_2 (153 mg, 0.39 mmol) was transferred to a round bottom flask, **3** (150 mg, 0.39 mmol) was added and the mixture heated at 190 °C for 60 min. The crude product was dissolved in chloroform (100 mL), filtered and the solvent removed under reduced pressure. The solid was then washed with water/methanol 1:1 (300 mL), adsorbed on silica and thoroughly washed with methanol (300 mL) on a glass frit. The product was purified using column chromatography on silica with chloroform as eluent. The pure product was dissolved in chloroform (1 mL), added dropwise to methanol (50 mL) and the precipitate collected, giving a blue-green solid (31 mg, 20%). ^{1}H NMR (300 MHz, $CDCl_3/C_5D_5N$, 25 °C): $\delta = 0.50$–0.58 (m, 24 H, CH_3), 0.68–1.21 (m, 64 H, CH_2), 1.22–1.45 (m, 16H, CH_2), 1.59–1.91 (m, 16H, CH_2), 4.28–4.85 ppm (m, 16 H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3/C_5D_5N$, 25 °C): δ = 13.20, 21.79, 25.53, 28.21, 28.54, 28.80, 31.03, 67.49, 139.48, 147.31 and 151.45 ppm. IR (ATR): ν_{max} = 2954, 2921, 2853, 1638, 1541, 1444, 1377, 1303, 1252, 1121, 1062, 960 cm^{-1}. UV/Vis (pyridine): λ_{max} (ε) = 624 (199 700), 599 sh (31 500), 568 (28 400), 369 nm (134 300 dm^3 mol^{-1} cm^{-1}). MS (MALDI-TOF): *m*/*z* 1609 $[M]^+$,