Zinc-Coordination Oligomers of Phenanthrolylporphyrins

Kathryn Phillips-McNaughton and John T. Groves*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Supplementary Information

Experimental

I. INSTRUMENTS AND MATERIALS

^1H NMR spectra were obtained on a JEOL GSX-500 or 270 MHz instrument. FAB mass spectrometry (FAB MS) was performed in house on a Kratos MS50RFTC mass spectrometer with a 3-nitrobenzyl alcohol matrix, or performed by Joseph Lech at the Rutgers's Food Sciences laboratory. Laser Desorption mass spectrometry was performed by Kratos on a sinapinic acid matrix. Absorption spectra were measured on a Hewlett Packard 8452A Diode Array Spectrophotometer.

Column chromatography was performed on silica gel (60-200 mesh, Baker). Thin layer chromatography (TLC) was performed on analytical (0.25 mm thick, Analtech, G or GF), preparatory (1 mm thick, Analtech, G) or tapered (Analtech, G) glass silica gel plates. Compounds accessible from commercial sources were used without further purification unless otherwise noted. THF was distilled over sodium metal with benzophenone as an indicator. Water used in the preparations of phenanthroline-substituted porphyrins was purified by Millipore (Millipore, Milli Q). Metal-ion salts were obtained from Aldrich and were of 99.99% or higher purity. Fresh bottles of spectrophotometric grade methylene chloride from Baker were used to prepare solutions of phenanthrolylporphyrins.

Phenanthrolineporphyrins were treated with acid before use to remove all metal-ion impurities and to solubilize the porphyrin residue, especially with BPPc, in methylene chloride. MPPc solutions were prepared by first dissolving the porphyrin in methylene chloride and then rinsing with an aqueous solution of 10% HCl. The porphyrin was then neutralized by rinsing several times with water until the organic phase turned from dark green to a bright red color. The porphyrin solution was then diluted to the desired concentration which was determined spectrophotometrically ($C=A/\epsilon b$ where $b=1$ and $\epsilon=134,000$). BPPc solutions were prepared by dissolving the solid in TFA and then adding methylene chloride. The solution was washed many times with water to remove all traces of acid until the color changed from dark green to bright red. The porphyrin solution was then diluted to the desired concentration which was determined spectrophotometrically ($C=A/\epsilon b$ where $b=1$ and $\epsilon=148,000$).

II. KINETIC EXPERIMENTS

All experiments were run at room temperature in a glass cuvette of 1 cm path length and 4 cm³ volume. Two milliliters of a methylene chloride solution of porphyrin (MPPc or BPPc, 4-10 μ M) was loaded into the cuvette and 2 ml of an aqueous metal-ion solution (10 μ M to 0.1 M) was layered on top of the organic phase. Fast stirring of the organic solution was accomplished without much perturbation of the aqueous phase with a (5x2 mm) microstirrer. The reaction was monitored by measuring the decrease in intensity of the porphyrin Soret band absorption at either 412 nm (MPPc) or 416 nm (BPPc).

III. SYNTHESSES

2-1,10-phenanthroline aldehyde and 9-formyl-1,10-phenanthroline-2-carboxylic acid (3)

These compounds were previously prepared in this laboratory and the procedure reported elsewhere.¹

Ethyl 4-ethyl-3,5-dimethyl pyrrole-2-carboxylate.

This compound was prepared following the general procedure of A.W. Johnson *et. al.*² in 49% yield (lit. 45.5%).

Bis[5-(ethoxycarbonyl)-4-methyl-3-propyl-2-pyrryl] methane and Bis(3-ethyl-4-methyl-2-pyrryl) methane (2).

These compounds were prepared from Ethyl 4-ethyl-3,5-dimethyl pyrrole-2-carboxylate following the general procedure reported by Sessler, Hugdahl and Johnson.³

Condensation of (2) with phenanthroline aldehydes to form mono and bis-substituted phenanthroline porphyrins.

These compounds were synthesized following the general procedure reported by Gunter and Mander for preparing 5,15-bis(*o*-nitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrins.⁴ The following paragraphs describe the exact procedures used for preparing the 5,15-*meso*-substituted phenanthroline porphyrins, since there were several modifications of the reported method.

5,15-Bis(1,10-phenanthroline-2)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (BPPdc)

A solution of bis(3-ethyl-4-methyl-2-pyrryl) methane (39.1 mg, 0.17 mmol), 2-(1,10-phenanthroline) aldehyde (35.4 mg, 0.17 mmol), and *p*-toluene sulfonic acid (15 mg, 0.09 mmol) in methanol (5 mL) was allowed to stand at room temperature for 13 hours. The mixture was treated with *p*-chloranil (65 mg) which had been dissolved in THF (2 mL). The resulting solution was stirred for one hour. After evaporation of the solvent, the residue was chromatographed on silica gel preparatory plates. The sample

was eluted first with 15% MeOH/CHCl₃ and then again with 7%MeOH/CHCl₃. The α,α and α,β -atropisomers eluted together. The porphyrin sample was recrystallized first with CHCl₃/CH₃CN and then with CHCl₃/hexanes to yield BPPdc (20 mg, 28%). ¹H NMR (270 MHz, 20% CD₃COOD in CDCl₃), some peaks * are split due to the presence of two conformers. δ 10.30 (s, 2H, *meso* -H)*, 9.23 (dd, J=4.29, J=1.65, 2H, 9-phen), 8.98 (d, J=8.25, 2H, phen), 8.81 (d, J=8.25, 2H, phen)*, 8.43 (d, J=7.26, 2H, 7-phen), 8.20 (d, J=8.91, 2H, phen), 8.07 (d, J=8.91, 2H, phen), 7.74 (dd, J=7.92, J=4.29, 2H, 8-phen), 3.75 (m, 8H, methylene of ethyl), 2.14 (s, 6H, methyl of β -pyrrole)*, 1.50 (m, 12H, methyl of ethyl)* ppm; FAB MS *m/z* 835 (M+H⁺); λ_{max} (CH₂Cl₂) 414, 508, 542, 576, 628 nm.

5,15-Bis(9-methoxycarbonyl-1,10-phenanthroline -2)-2,8,12,18-tetraethyl, 3,7,13,17-tetramethylporphyrin (BPPE, 4)

A solution of bis(3-ethyl-4-methyl-2-pyrrolyl)methane (**2**) (78 mg, 0.34 mmol), 9-Formyl-1,10-phenanthroline-2-carboxylic acid (**3**) (85.6 mg, 0.34 mmol), and *p*-toluene sulfonic acid (30 mg, 0.17 mmol) in DMF (10 mL) was allowed to stand at room temperature for 13 hours. The mixture was then treated with *p*-chloranil (135 mg) which had been dissolved in THF (2 mL). The resulting solution was stirred for one hour. After evaporation of the solvent, the sample was dissolved in MeOH (20 mL), to which concentrated HCl (15 drops) was added. The mixture refluxed for 87 h. After evaporation of the methanol, the sample was dissolved in CHCl₃. The CHCl₃ solution was washed several times with H₂O to remove the acid still present in the sample. The sample was concentrated and the residue chromatographed 3 times on silica gel preparatory plates. The eluant was a 80:15:5:1 mixture of CHCl₃:CH₃CN:MeOH:TFA. The α,α and α,β -atropisomers eluted together. The protonated porphyrin was neutralized by dissolving it in CHCl₃ and washing the CHCl₃ solution several times with H₂O. After evaporation of the solvent, the porphyrin sample was recrystallized first with

CHCl₃ /CH₃CN and then with CHCl₃ /hexanes to give **4** (49 mg, 30%). ¹H NMR (270 MHz, 1% CD₃COOD in CDCl₃) δ 10.29 (s, 2H, *meso*-H), 8.93 (d, J=8.25, 2H, phen), 8.81 (d, J= 8.25, 2H, phen), 8.54 (d, J=8.25, 2H, phen), 8.45 (d, J=8.57, 2H, phen), 8.27 (d, J=9.24, 2H, phen), 8.12 (d, J=8.91, 2H, phen), 3.76 (s, 6H, methyl of ester), 3.75 (m, 8H, methylene of ethyl), 2.15 (s, 12H, methyl of β-pyrrole), 1.53 (t, 12H, methyl of ethyl) ppm; FAB MS *m/z* 951 (M+H⁺).

5,15-Bis(9-carboxy-1,10-phenanthroline-2)-2,8,12,18-tetraethyl- 3,7,13,17-tetramethylporphyrin (BPPc, **1**).

The ester groups of **4** were hydrolyzed by refluxing in a 2% NaOH/MeOH solution. After the mixture had refluxed for 24 h, the solvent was evaporated to leave a slurry of porphyrin, MeOH and NaOH. The slurry was dissolved in CH₂Cl₂ and H₂O. The porphyrin was extracted into the CH₂Cl₂ layer. To remove residual Na⁺ or other extraneous metal ions, TFA was added to the CH₂Cl₂ solution. The solution was then neutralized by washing several times with H₂O and **1** obtained in quantitative yield after removal of the solvent on a rotary evaporator. After the solution was concentrated, **1** could only be redissolved with a strong acid. Therefore to make a CHCl₃ solution of **1**, it was first dissolved in TFA and then diluted with chloroform. The TFA was then removed from the organic solution by washing several times with water until the green (protonated porphyrin) color became a deep red (neutral porphyrin). FAB MS *m/z* 923 (M+H⁺, 100), 834 (M-2CO₂, 45); λ_{max} (CH₂Cl₂) 416, 510, 542, 578, 628 nm.

5-(1,10-phenanthroline-2),15-(*p*-tolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (MPPdc).

A solution of bis(3-ethyl-4-methyl-2-pyrrolyl)methane (78.2 mg, 0.34 mmol), 2-(1,10-phenanthroline) aldehyde (35.4 mg, 0.17 mmol), *p*-toluene aldehyde (20 mL, 0.17 mmol) and *p*-toluene sulfonic acid (25 mg, 0.15 mmol) in MeOH (10 mL) was allowed to

stand at room temperature for 15 h. The mixture was then treated with *p*-chloranil (135 mg) which had been dissolved in THF (2 mL). The resulting solution was stirred for one hour. After evaporation of the solvent, the residue was purified chromatographically on silica with CHCl₃. The 5,15-bis(*p*-tolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin was eluted first and was followed by MPPdc. The compound was further purified on silica gel preparatory plates with 3% MeOH/CHCl₃ and was isolated in 13% yield. ¹H NMR (270MHz, CDCl₃) δ 10.20 (s, 2H, *meso*-H), 9.17 (dd, J=4.29, J=1.98, 1H, 9-phen), 8.53 (d, J=7.92, 1H, phen), 8.38 (dd, J=8.25, J=1.65, 1H, 7-phen), 8.34 (d, J=8.25, 1H, phen), 8.13 (d, J=8.57, 1H, phen), 8.04 (d, J=8.91, 1H, phen), 7.93 (m, 2H, tolyl), 7.66 (dd, J=8.25, J=4.29, 1H, 8-phen), 7.53 (m, 2H, tolyl), 3.97 (m, 8H, methylene of ethyl), 2.71 (s, 3H, tolyl methyl), 2.50 (s, 6H, methyl of β-pyrrole), 2.28 (s, 6H, methyl of β-pyrrole), 1.73 (m, 12H, methyl of ethyl) ppm; FAB MS *m/z* 747 (M+H⁺, 100), 657 (18); λ_{max} (CH₂Cl₂) 410, 506, 540, 574, 626 nm.

5-(9-carboxy-1,10-phenanthroline-2),15-(*p*-tolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (MPPc, **5**).

A solution of bis(3-ethyl-4-methyl-2-pyrrolyl)methane (82.1 mg, 0.36 mmol), 9-Formyl-(1,10-phenanthroline)-2-carboxylic acid (45 mg, 0.18 mmol), *p*-toluene aldehyde (21 mL, 0.18 mmol) and *p*-toluene sulfonic acid (18.1 mg, 0.095 mmol) in DMF (10 mL) was allowed to stand at room temperature for 15 h. The mixture was treated with *p*-chloranil (135 mg) which had been dissolved in THF (2 mL). The resulting solution was stirred for one hour. After evaporation of the solvent, the residue was chromatographed on silica gel preparatory plates in 10% MeOH /CHCl₃. The 5,15-bis(*p*-tolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin eluted first and was followed by **5**. Compound **5** was further purified on silica gel preparatory plates with 8% MeOH /CHCl₃. The porphyrin was dissolved in CHCl₃ and a few drops of TFA was added to remove any extraneous metals from the phenanthroline appendage. The protonated porphyrin was

neutralized by washing the CHCl_3 solution several times with H_2O . The solvent was evaporated to yield **5** (25.3 mg, 17%). ^1H NMR (500MHz, CDCl_3 + 1 porphyrin equivalent of N-benzylmethylamine) δ 10.31 (s, 2H, *meso* -H); 8.75 (m, 2H, phen); 8.70 (d, J=8.07, 1H, phen); 8.47 (d, J=8.73, 1H, phen); 8.21(d, J=8.74, 1H, phen); 8.15 (d, J=8.74, 1H, phen); 7.96 (m, 2H, tolyl); 7.59 (d, J=8.07, 2H, tolyl); 4.05 (m, 4H, methylene of ethyl); 3.99 (m, 2H, methylene of ethyl); 3.90 (m, 2H, methylene of ethyl); 2.75 (s, 3H, methyl of tolyl); 2.55 (s, 6H, methyl of β -pyrrole); 2.19 (s, 6H, methyl of β -pyrrole); 1.81 (t, J=7.39, 6H, methyl of ethyl); 1.70 (t, J=7.39, 6H, methyl of ethyl) ppm; FAB MS m/z 791 ($\text{M}+\text{H}^+$, 100), 746 ($\text{M}-\text{CO}_2$,80); λ_{max} (CH_2Cl_2) 412, 508, 542, 576, 622 nm.

Bis[ZnMPPc(-1)-*N,N',O*] zinc(II), $[\text{Zn}(\text{ZnMPPc})_2]$, **7**.

A solution of MPPc, **5**, (5 mg, 6.3 μmol) in 5ml of CHCl_3 was stirred with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (500 mg, 2.3 mmol) in 5 ml of water for 24 h at room temperature. The organic layer was then isolated, washed three times with water and concentrated. A dimer with 3 Zn^{2+} ions $[\text{Zn}(\text{ZnMPPc})_2]$ was isolated in quantitative yield and was the only product detected by ^1H NMR. (500 MHz, CDCl_3) δ 10.22 (s, 2H, *meso*-H); 9.95 (s, 2H, *meso*-H); 8.56 (d, J=7.70, 2H, phen); 8.40 (d, J=8.06, 2H, phen); 8.14 (d, J=8.06, 2H, tolyl); 8.07 (d, J=7.69, 2H, tolyl); 7.68 (d, J=7.33, 2H, tolyl); 7.64 (d, J=7.70, 2H, tolyl); 7.52 (d, J=8.79, 2H, phen); 5.94 (d, J=8.79, 2H, phen); 4.21 (m, 4H, methylene of ethyl); 4.06 (m, 2H, methylene of ethyl); 3.93 (m, 4H, methylene of ethyl); 3.91 (d, J=9.89, 2H, phen); 3.81 (m, 2H, methylene of ethyl); 3.72 (d, J=8.06, 2H, phen); 3.65 (m, 2H, methylene of ethyl); 3.45 (m, 2H, methylene of ethyl); 2.81 (s, 3H, methyl of tolyl); 2.70 (s, 3H, methyl of β -pyrrole); 2.56 (s, 3H, methyl of β -pyrrole); 2.37 (s, 3H, methyl of β -pyrrole); 2.09 (m, 3H, methyl of ethyl); 1.78 (m, 3H, methyl of ethyl); 1.65 (m, 3H, methyl of ethyl); 1.59 (m, 3H, methyl of ethyl); 1.51 (s, 3H, methyl of β -pyrrole) ppm; FAB MS m/z 1772 ($\text{M}+1$); λ_{max} (CH_2Cl_2) 416, 550, 582 nm.

Bis[MPPc(1-)-N,N',O] zinc(II), [Zn(MPPc)₂], **6**.

A solution of MPPc, **5**, (2 mg, 2.5 μ mol) in 5 ml of CHCl₃ was stirred with Zn(OAc) $\cdot$ 2H₂O (500 mg, 2.3 mmol) in 3 ml of water for 40 minutes at room temperature. The reaction was monitored by UV-Vis spectrophotometry and was complete when the porphyrin Soret band shifted 6nm from 412 nm to 418 nm (in CH₂Cl₂). The organic layer was then isolated, washed three times with H₂O and concentrated to yield **5** quantitatively. FAB MS indicated that only one porphyrin dimer was present. FAB MS *m/z* 1647 (M+2); λ_{max} (CH₂Cl₂) 418, 512, 548, 578, 630 nm.

References

- ¹ Dong L-C, Ph.D. Thesis; Princeton University, Princeton, NJ, 1991.
- ² Johnson AW, Markham E, Price R, Shaw KB. *J. Chem. Soc.* 1958: 4254.
- ³ Sessler JL, Hugdahl J, Johnson MR. *J.Org.Chem* . 1986: **51**, 2838.
- ⁴ Gunter, MJ, Mander LN. *J. Org. Chem* . 1981: **46**, 4792.