

Zinc-Coordination Oligomers of Phenanthrolylporphyrins

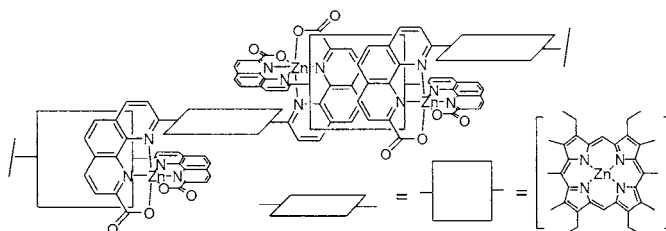
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ABSTRACT



We report the synthesis of mono- and bisphenanthrolylporphyrins 5-(9-carboxy-1,10-phenanthroline-2),15-(*p*-tolyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (MPPc) and 5,15-bis(9-carboxy-1,10-phenanthroline-2)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (BPPc), respectively. The formation of dimers and oligomers, with MPPc and BPPc, respectively, upon exposure to zinc acetate is described. Oligomerization of the porphyrins was monitored spectrophotometrically, and a kinetic study was performed to estimate the average oligomer chain length.

There is considerable current interest in porphyrinic assemblies and in identifying ways to exploit their multifaceted properties to prepare magnetic,¹ nonlinear optical,² conductive,^{3–6} oxygen transport,⁷ catalytic,⁸ artificial photosynthetic, and information storage devices.^{9,10,11} The synthetic versatility of porphyrins allows these assemblies to be tailored to

achieve a variety of properties, which makes them desirable building blocks for supramolecular systems. Strategies for the assembly of multiporphyrin constructs include non-bonded,⁴ hydrogen-bonded,¹² covalent,^{2,3,9,13} and metal-coordinative intramolecular forces and combinations of these.^{14,15}

Phenanthrolines are well-known for their metal-chelating abilities and have been previously used as linkers of porphyrins.^{15–17} Dimers were prepared upon chelation of various metal ions with the phenanthroline group from each porphyrin. The crystal structure of one of these dimers revealed that each phenanthroline was stacked over the adjacent porphyrin.¹⁷ This π -stacking led us to investigate polymeric analogues because of the potential to prepare materials with interesting magnetic and electronic properties. Such polymers

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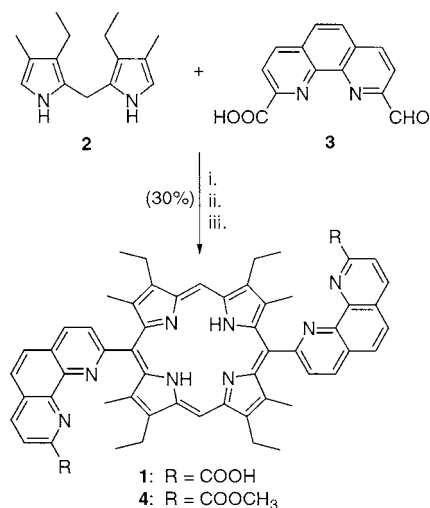
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could be formed from doubly substituted phenanthrolylporphyrins (BPP), as pictured in the graphical abstract. There are several potential advantages to using phenanthroline-substituted porphyrins of this type. These porphyrins assemble easily with different types of metal ions and do so quantitatively, an advantage over most of the known covalently linked systems, which in contrast do not produce very high yields of oligomers. Spectrophotometric, NMR, and mass spectral analyses were used to characterize monomers and dimers described here. Oligomer chain lengths were determined through a kinetic analysis of spectrophotometric changes.

BPPc **1** was synthesized in 30% yield using the dipyrromethane strategy shown in Scheme 1. Initial synthetic

Scheme 1. Synthesis of BPPc (**1**) and Its Ester (**4**)^a



^a Conditions: (i) *p*-toluene sulfonic acid in DMF; (ii) DDQ; (iii) HCl in MeOH.

attempts with pyrrole and a phenanthroline aldehyde under Adler or Lindsey-type conditions were unsuccessful in producing BPP with the desired 5,15-*meso* substitution.^{17,18} Compound **2** was prepared by the method of Sessler et al. and then condensed with **3** under the general method of Gunter and Mander.^{19,20} After oxidation of the porphyrinogen with *p*-chloranil, the carboxyl groups were esterified (compound **4**) to facilitate chromatographic purification and then restored. Note that α,α -atropisomers could not be separated chromatographically and that the rotational activation barrier in **4** was estimated to be 13 kcal/mol with standard ¹H NMR coalescence experiments. MPPc **5** was also prepared in this manner when tolylaldehyde was added to the condensation mixture. A 17% yield of **5** was obtained when a 1:1:2 ratio of tolylaldehyde/**3**/**2** was used. This dipyrromethane strategy also improved the yield of MPP by 10% over the Adler-type method.¹⁷

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Dimers were prepared quantitatively by stirring a chloroform solution of MPPc (**5**) against an aqueous solution of Zn(OAc)₂. After dimer formation was complete, as determined spectrophotometrically, the aqueous layer was removed and the organic layer washed several times with water to remove residual metal ions. During dimerization, the porphyrin macrocycle was also subject to metalation, the extent of which could be controlled by varying both the concentration of the metal ion solution and the stirring time. Lower concentrations of Zn(OAc)₂ and shorter reaction times favored the formation of a dimer with one Zn²⁺ ion [Zn(MPPc)₂] (**6**), while higher concentrations of Zn(OAc)₂ and longer reaction times favored the formation of a dimer with three Zn²⁺ ions [Zn(ZnMPPc)₂] (**7**).

Dimer formation was monitored spectrophotometrically and accompanied by 4–6 nm bathochromic shifts of the porphyrin Soret band (Table 1, Figure 1). The magnitude of

Table 1. UV–Visible Absorption Data for MPPc, BPPc and Their Metal-Ion Complexes in CH₂Cl₂ at Room Temperature

porphyrin species	λ_{max} (nm) Soret and Q-bands				
MPPc (5)	412	508	542	576	622
BPPc (1)	416	510	542	578	628
Zn(MPPc) ₂ (6)	418	512	548	578	630
Zn(ZnMPPc) ₂ (7)	416	550	582		
Zn(<i>n</i> –1)(BPPc) _{<i>n</i>}	440	518	554	582	634
Zn(<i>n</i> –1)(ZnBPPc) _{<i>n</i>}	418	552	586		

the Soret shift can be masked when the porphyrin macrocycle also becomes metalated. Since the rate of dimer formation was distinctly faster than metalation of the porphyrin macrocycle, the progress of the two different events could be monitored sequentially. Upon addition of Zn(OAc)₂ to MPPc (**5**), the Soret band first shifted bathochromically 6 nm and then hypsochromically 2 nm. The hypsochromic shift of the Soret was also accompanied by changes in the Q-band region that were indicative of porphyrin macrocycle metalation. Mass spectral analyses of the Zn²⁺ dimer solution were recorded before and after the hypsochromic shift of the Soret band. Before the hypsochromic shift, only Zn(MPPc)₂ (**6**) was detected.

After the hypsochromic shift of the Soret and the disappearance of two of the four Q-bands, Zn(ZnMPPc)₂ (**7**) had formed. Spectral red-shifted Soret bands are known to occur upon formation of porphyrin dimers in a head-to-tail geometry.²¹ Such shifts have been explained in terms of exciton coupling theory.²² Metalation of porphyrin macrocycles can also cause shifts in the porphyrin Soret band. With the Zn²⁺ ion, porphyrin metalation and dimerization were observed independently during spectrophotometric monitoring of the reaction. Note that in the reaction of MPPc with a second row transition metal ion such as Cd²⁺, metalation of the porphyrin ring does not occur and only dimerization is observed spectrophotometrically.

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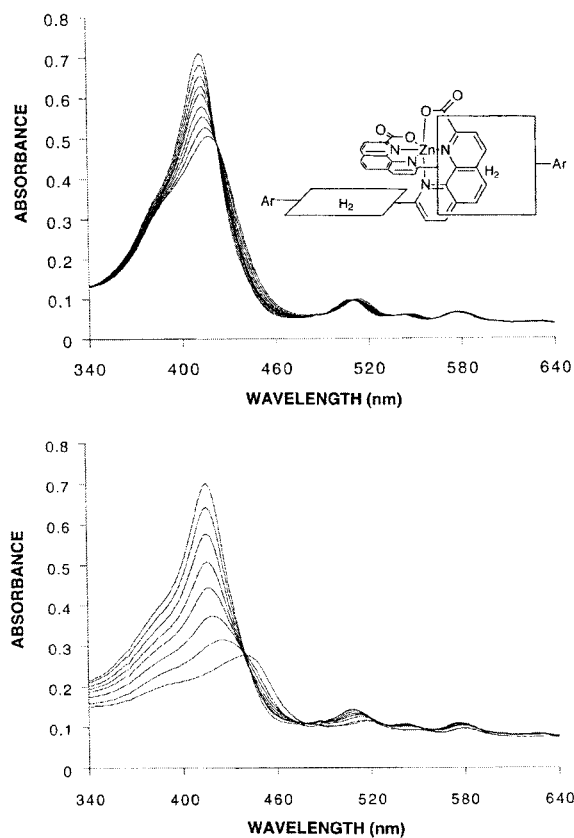


Figure 1. Overlaid UV–visible absorption spectra of MPPc (top) and BPPc (bottom) in methylene chloride that demonstrate the spectral changes (bathochromic shifts) upon exposure to zinc acetate during oligomerization.

The effects of dimerization were evident upon comparison of the ^1H NMR spectra of $\text{Zn}(\text{ZnMPPc})_2$ (**7**) and MPPc (**5**) (Figure 2). The most striking differences observed upon dimerization were the four upfield-shifted phenanthroline protons. Two of the six phenanthroline resonances were shifted upfield by at least 4 ppm upon dimerization. Also affected by the ring current of the adjacent porphyrin was one β -pyrrole methyl resonance that was shifted upfield ~ 1 ppm due to its proximity to the phenanthroline appendage and the site of dimer formation.

Dimers have also been prepared from MPP without carboxyl groups; however, they were found to be less robust than those formed from MPPc (**5**). These dimers would frequently dissociate upon exposure to H-bonding solvents or solvents with trace acid impurities. Thus, the carboxyl groups enhanced the stability of the dimer by providing two additional coordination sites for the metal ion.

When millimolar solutions of BPPc in chloroform were combined with aqueous $\text{Zn}(\text{OAc})_2$, porphyrinic material immediately began to precipitate. Eventually, two clear solution phases resulted after the solids were isolated upon vacuum filtration. At micromolar concentrations of BPPc, the reaction products remained in solution and, thus, oligomer formation could be monitored spectrophotometrically. Typically the

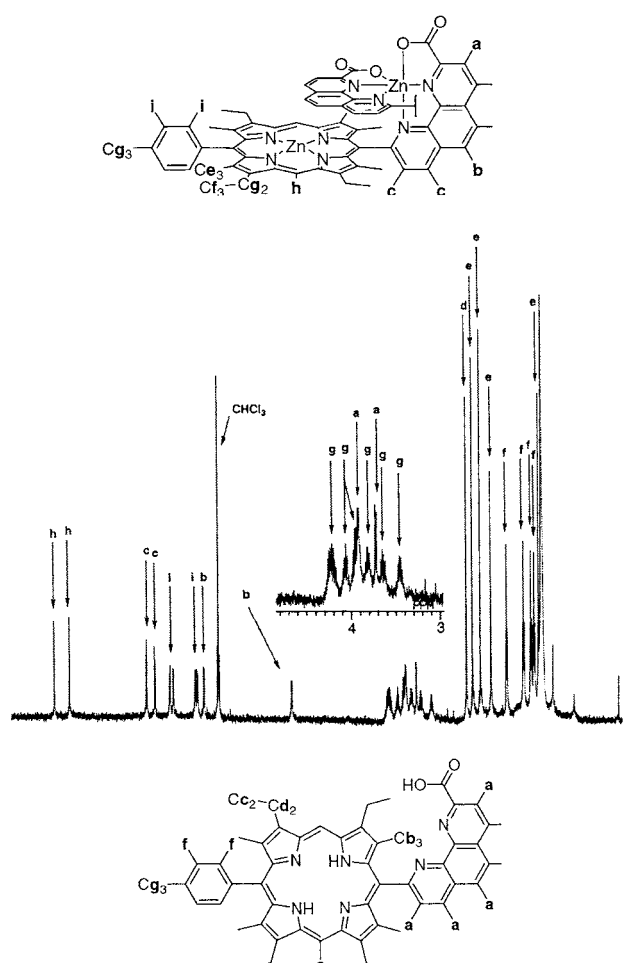


Figure 2. ^1H NMR spectra of **7** (top) in CDCl_3 and of **5** (bottom) in CDCl_3 with 1 equiv of *N*-benzylmethylamine.

Soret band shifted to the red and became unevenly broadened and almost split (Table 1, Figure 1). Note the simple selection rules for spectral changes in the UV–visible absorption of dye molecules given by Kasha: red shifts for a head-to-tail geometry, blue shifts for a face-to-face geometry, and band splitting for an oblique arrangement.²³ The BPPc oligomer may be described as having both head-to-tail and oblique

geometries since the linearly arranged porphyrin units are not coplanar but orthogonal. This description coincides with the predicted absorption characteristics according to Kasha's rules. Also note that the magnitude of the spectral shifts upon introduction of metal ions is much larger with BPPc than with MPPc. A 24 nm bathochromic shift of the Soret was observed when Zn(OAc)₂ and BPPc were reacted (before metalation of the porphyrin macrocycle) compared to a 6 nm shift produced with MPPc. It has been suggested with other linear porphyrin oligomers that an increase in the magnitude of a spectral absorption change correlates with an increase in the number of pigments.²⁴ Finally, as observed with MPPc, the bathochromic shift was followed by a hypsochromic shift of the Soret and Q-band.

A kinetic study of the oligomerization of MPPc and BPPc upon addition of Zn²⁺ was performed to estimate an average polymer chain length. Reactions were performed in a glass cuvette suitable for spectrophotometric monitoring. After a methylene chloride solution of porphyrin was added to the cuvette, an aqueous solution of metal ion was layered on top of the organic phase. The porphyrin solution was stirred to accelerate mass transfer to and from the organic/aqueous solution interface and to provide a homogeneous concentration of porphyrin species. The concentration of metal ion was always greater than that of the porphyrin. The uptake of metal ions by the phenanthrolylporphyrins was observed spectrophotometrically by monitoring changes in the porphyrin Soret band absorption. A clear isosbestic point was discovered from analysis of overlaid spectra, which indicated that the conversion from monomer to oligomer occurred without accumulation of intermediates or byproducts.

The binding of metal ions by phenanthrolylporphyrins was found to be pseudo-first order in porphyrin over a wide range (from 0.1 M to 10 μM) of metal ion concentrations. Monitoring the progress of a polymer-forming reaction allows the average length of the polymer chain to be determined.^{25,26} If the rate constant for the condensation is assumed to be independent of the chain length, the average chain length (χ) can then be calculated from the following expression:

$$\chi = 1 + kt[A]_0$$

where k is the second-order rate constant (M⁻¹ s⁻¹) independent of chain length, t is the reaction time (s), and $[A]_0$ is the initial concentration of monomer. To obtain a second-order rate constant (k), the pseudo-first-order rate constant for a dimerization of MPPc was divided by the initial concentration. This estimate was envisioned to be a better

representation of the rate constant because it is independent of chain length in comparison to the uncontrolled oligomerization of BPPc. The parameter t was obtained by multiplying the reaction half-life of the oligomerization of BPPc by ten.²⁵ The half-life was calculated from the experimentally determined pseudo-first-order rate constant ($t_{1/2} = \ln 2/k$). These modifications of the first equation are represented below:

$$\chi = 1 + (k_{\text{MPPc}}/[MPPc])(10 \times \ln 2/k_{\text{BPPc}})[BPPc]$$

where k_{MPPc} and k_{BPPc} must be compared at identical metal-ion concentrations. Note that the mechanisms for dimerization and oligomerization appear to be similar as supported by the ΔG values and rate constants being comparable ($k_{\text{MPPc}} = 1 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{BPPc}} = 6 \times 10^{-4} \text{ s}^{-1}$, ΔG for dimerization and oligomerization = 4 kcal).

The average value of χ calculated for the reaction of BPPc (μM) with three different concentrations of Zn(OAc)₂ (1, 10, and 100 mM) was 12.3 ± 0.5 . A χ value of 12 corresponded to an average molecular weight in the 11 768–12 524 range, depending on the degree of metalation of the porphyrin macrocycle. The average chain length determined for the Zn-coordinated oligomer is within ranges reported in the literature for metal–ligand bound porphyrinic polymers. Mercury-bridged phthalocyanine oligomers reported by George and co-workers were determined to be an average of 11 units long with a vapor pressure osmometer.²⁷ Collman and co-workers reported average chain lengths in the 25–40 unit range for pyrazine-bridged iron, ruthenium, and osmium octaethylporphyrin coordination polymers using an IR end-group analysis.⁵ Michelsen and Hunter reported *meso*-pyridyl, Co²⁺porphyrin oligomers in the 10–100 unit range that were characterized by size exclusion chromatography.²⁸

Phenanthrolylporphyrins were prepared from dipyrromethane, rather than pyrrole, to reduce the number of products formed upon condensation with phenanthroline aldehyde. MPPc was also prepared from dipyrromethane and could sequester Zn²⁺ ions from aqueous solution to form zinc-linked dimers. Oligomers were characterized by monitoring their formation spectrophotometrically and are believed to have a head-to-tail, oblique geometry. The average oligomer chain length for zinc-coordinated oligomers was estimated from kinetic studies to be 12 units long.

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Supporting Information Available: Experimental procedures for the synthesis and characterization of compounds described in this manuscript, along with selected precursors and related compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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