

Infinite Three-Dimensional Polymeric Metalloporphyrin Network via Six-Coordinate Zn(II) and Two Axial Oxygen Donors

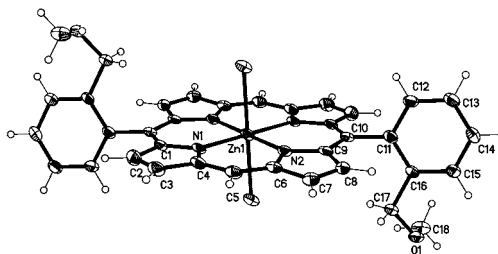
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ABSTRACT



An X-ray crystallographic study of zinc(II) 5,15-di(2-methoxymethylphenyl)porphyrin indicates that it forms a coordination polymer through ligation of the ether oxygen atoms on the porphyrin peripheries to the metal centers of two identical adjacent porphyrins. This gives a novel extensively linked, three-dimensional polymeric structure in which the zinc(II) metal forms a six-coordination center. The uniquely structured network has cavities between 4.81 and 9.27 Å, which makes it resemble molecular sieve materials.

Multiporphyrin architectures reveal enormous versatility in photoactivity, electron transfer, and redox properties.^{1–3} In particular, functional assemblies of multiporphyrin arrays have been designed for the development of new molecular electronic devices,⁴ molecular machines, and catalysts.^{5,6} Although many elegant structures of such arrays have been constructed via direct covalent bonding, they are difficult to realize on a practical scale.⁷ Molecular self-assembly offers a good alternative to a wide variety of one-, two-, and three-dimensional arrays through various associations and orientations. Self-assembly of zinc porphyrins via a molecular

recognition approach proved to be successful when external nitrogen donors were used to form a series of intermolecular Zn–N coordinations.⁸ Extension into a one-dimensional (1D) network was achieved in a series of tetra(4-pyridyl)porphyrins.⁹ A five-coordinate Zn(II) with one intermolecular Zn–N(pyridyl) coordination was preferred due to steric reasons. Three-dimensional (3D) coordination polymers involving six-coordinate Zn(II) with two axial N(pyridyl) donors was only formed after more extensive crystallization experiments.⁹ Coordination polymers of Zn(II) porphyrins with one axial O donor from functional groups attached to peripheral phenyl rings have also been reported.¹⁰ These examples are, however, limited to five-coordinate Zn(II), thus restricting the formation to only a 1D polymer network. To

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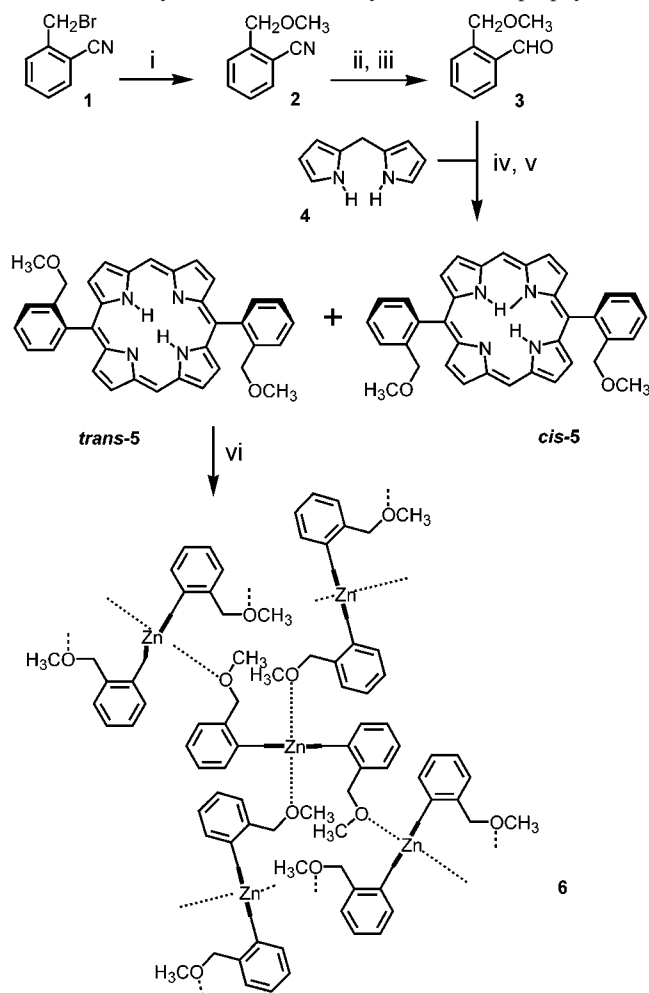
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the best of our knowledge, six-coordinate Zn(II) porphyrin complexes with two axial O donors forming a 3D polymer network were not known before our work. The ability of the central metal ion to accommodate two axial ligands is important in obtaining extensive multilayered arrays. From molecular modeling observations, we predicted that the porphyrin **5** (Scheme 1) with ortho-substituted benzylic

Scheme 1. Synthetic Route to Polymeric Metalloporphyrin **6**^a



^a Reaction conditions: (i) Na/CH₃OH; (ii) DIBAL/benzene; (iii) HCl/H₂O; (iv) CF₃COOH/CH₂Cl₂; (v) chloranil; (vi) Zn(OAc)₂·2H₂O/ethanol.

oxygen donors (earlier examples involved phenolic oxygen donors) should have an appropriate metal–oxygen distance suitable for rigid, stable, and extensively linked 3D metalloporphyrin arrays as in **6** with tolerable steric demand. The ether function is preferred over a hydroxyl group, as the latter may favor intermolecular hydrogen bonding instead of metal coordination.¹¹

The synthesis of **6** involved a five-step reaction pathway as summarized in Scheme 1. The methoxymethyl group was introduced by a nucleophilic substitution in **1** to give **2**. The

latter was reduced by DIBAL to provide the aldehyde function in **3** needed for the construction of the porphyrin template. The other building block, namely, **4**, was formed by a condensation reaction between pyrrole and paraformaldehyde according to a literature method.¹² The porphyrins **5** were prepared from **3** and **4** via a MacDonald [2 + 2] condensation reaction¹³ and subsequent oxidation of the intermediate porphyrinogens by chloranil.

Earlier work¹⁴ on the synthesis of 5,15-diarylporphyrins indicated the presence of atropisomers in examples involving ortho substituents in the aryl rings. More recently, discrete atropisomers of a series of *meso*-tetraarylporphyrins having *ortho*-aryl rings were successfully separated by chromatography.¹⁵ The ¹H NMR (CDCl₃) spectrum of the product mixture immediately isolated from the reaction between **3** and **4** clearly suggested the presence of *trans*- and *cis*-**6**. Two separate signals 0.07 ppm apart in a 1:1 ratio were observed for the methylene protons of the two isomers, respectively, although their corresponding pairs of other proton signals are identical. Use of a 1:1 solvent mixture of cyclohexane/chloroform allowed the isolation of a pure sample of *trans*-**5** by fractional crystallization. The mother liquor was further purified by chromatography on silica gel to provide a pure sample of *cis*-**5** that eluted slower than the *trans* isomer. The two isomers show almost identical ¹³C NMR and EI-mass spectra. Use of their methyl protons as a probe gave results from dynamic ¹H NMR studies of separate isomers of **5** that indicated no isomeric interchange up to 100 °C.

Suitable single crystals of *trans*-**5** could be obtained for X-ray crystallographic analysis. The asymmetric unit of *trans*-**5** consists of half of the molecule, and its ORTEP diagram is shown in Figure 1. The porphyrin ring is nearly

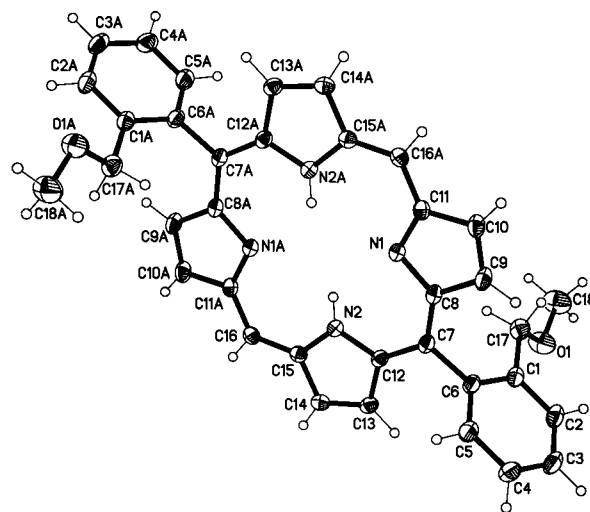


Figure 1. ORTEP drawing of *anti*-**5** (thermal ellipsoids are drawn at their 30% probability level).

planar, and the two substituted aromatic rings are confirmed to be in *trans* conformation. All the hydrogen atoms are

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located directly, and the thermal ellipsoids indicate a relatively rigid core structure with somewhat dangling side chains. The two aryl rings are oriented at an angle of 71.1° with respect to the molecular plane of the porphyrin ring with only a negligible deviation of 0.0024 \AA . This orientation is comparable to values reported for tetraaryl-substituted porphyrin systems.¹⁶

Complex formation was attempted by stirring a concentrated ethanol solution of *trans*-**5** and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ over 5 days. The product isolated was purified on a short chromatographic column of silica gel using a mixture of hexane/dichloromethane as the eluant. This sample exhibited interesting time-dependent ^1H NMR spectra as illustrated in Figure 2. The initial spectrum showed that the benzylic,

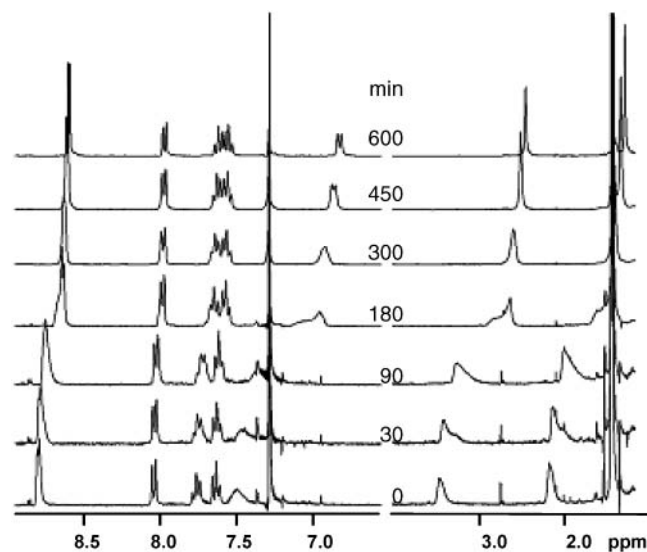


Figure 2. Time-dependent ^1H NMR spectra (in CDCl_3) of a freshly isolated sample of polymeric complex **6**.

methyl, one of the pyrrolic, and phenyl protons appeared as significantly broadened signals. As time progressed, these signals shifted to higher fields and sharpened. There were essentially no further changes observed after the final spectrum was taken after 10 h. In fact, this spectrum was reproducible even after solvent removal and redissolving the residue in the same solvent. A similar phenomenon was observed in experiments using deuterated toluene as a solvent.

By comparing the final ^1H NMR spectrum of the product in the time-dependent study and that of the ligand *anti*-**5**, the methylene and methyl protons, and the aryl proton on the carbon next to that carrying the CH_2OCH_3 group of the product, are significantly shifted upfield (Table 1). The observed shifts are too large to be due to solvent effects

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Table 1. Selected Proton Chemical Shifts (δ) of *anti*-**5** and **6**

	PhH^a	CH_2O	OCH_3
<i>anti</i> - 5	7.68	4.11	2.80
6	6.89	2.61	1.50

^a Proton on carbon adjacent to carbon carrying CH_2OCH_3 .

alone. These results we believe were derived from coordination of O donor to zinc, thus locating the protons concerned within the shielding zone of the adjacent aromatic porphyrin macroring, accounting for the strong shielding effect observed. Such geometric arrangement(s) in solution could be similar to that of the polymeric **6** (Figures 3 and 4). The

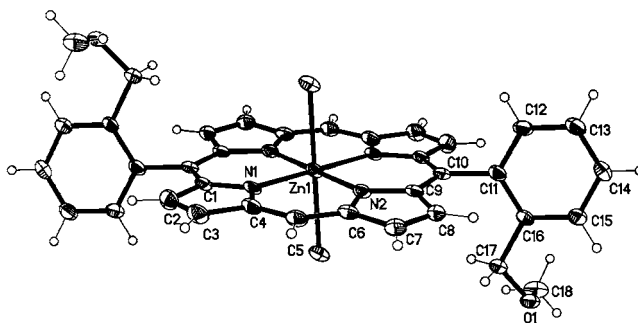


Figure 3. ORTEP view of the asymmetric unit of complex **6**.

time-dependent ^1H NMR spectra could suggest an initial solution of monomer and different conformational framework

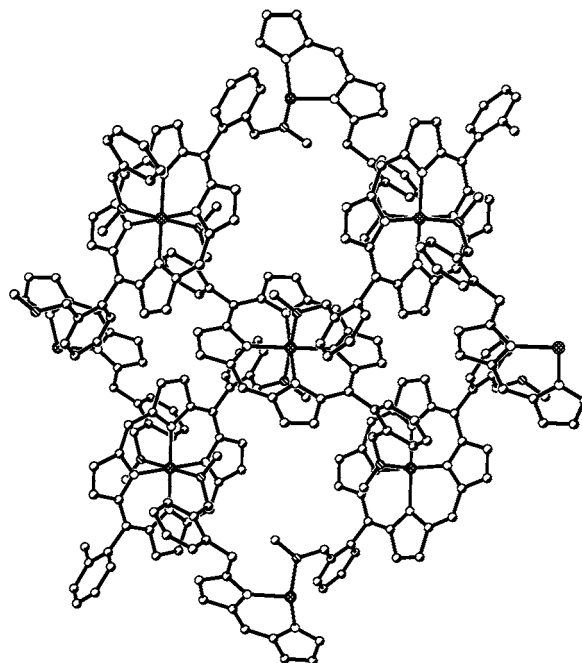


Figure 4. Segment of the coordination polymer **6**.

of oligomers as reflected in the rather broad and relatively less shielded signals. Slow aggregation processes would eventually result in an optimum and relatively more rigid polymeric framework that was still soluble, allowing rapid diffusion of solvent in and out of the network, resulting in sharp averaged signals in the ^1H NMR spectrum. In the recrystallization process, concentration of the solution was associated with further aggregation to form the infinite 3D network as described for **6** in the solid state (refer to later discussion on X-ray crystallographic analysis). Redissolving the infinite coordination polymer in the same solvent gave an identical ^1H NMR spectrum due to breaking down of the polymeric framework into the soluble aggregate as observed earlier.

The aggregation pattern of the Zn(II) porphyrin complex **6** was elucidated by X-ray crystallographic study. Intensely pink single crystals of **6** were successfully grown by slow evaporation of a solution of **6** in a cyclohexane/chloroform mixture. Complex **6** is a 3D coordination polymer, and the ORTEP drawing of its fundamental building unit is shown in Figure 3. Each Zn(II) metal ion forms a square plane (angles are perfect at 180.0°) with the four pyrrolic nitrogen atoms, and coordination to two neighboring oxygen atoms of the methoxymethyl functions completes a distorted octahedral geometry of the metal ion with angles ranging from 87.58 to 92.42° . The average equatorial Zn–N distance is 2.049 Å. This value is very similar to those reported for related porphyrin systems,^{8–10} thus indicating that there is little geometric strain/changes in the porphyrin units of the polymeric framework of **6**. The two axial methoxy groups are in trans orientation with an identical Zn–O bond distance of 2.434 Å. This value, as expected, is slightly longer than those reported for a number of five-coordinated zinc porphyrins,¹⁰ but it is shorter than that (2.536 Å) of the Zn–O bond distance reported for a six-coordinated Zn(THF)₂ complex.¹⁷ Thus, the identical Zn–O distances in **6** undoubtedly correspond to actual Zn–O coordination bonds. This serves as evidence for a true six-coordinated system in **6** and rules out any solid-state phenomenon based on some cooperative interaction that physically places the oxygen groups above and below the plane of the porphyrin. A segment of the coordination polymer **6** is shown in Figure 4.

For Zn(II) metalloporphyrins, five-coordinate examples^{8–10} are common, and the six-coordinate zinc(II) polymer **6** is, we believed, the first zinc(II) porphyrin 3D framework successfully assembled through two axial Zn(II)–O coordination.¹⁰ Examples reported earlier involved phenoxy functions with a Zn(II)–O distance too short for construction of a 3D framework. Our modeling studies indicated that extending the oxygen function to a methoxymethyl group at the ortho position should have the [Zn(II)–O]–[Zn(II)–O]' coordination from two adjacent units adopting an ideal "square planar" arrangement with appropriate Zn(II)–O distances. This is clearly confirmed in the crystallographic 3D framework of **6** (Figures 3 and 4). Compared to *anti*-**5**, the phenyl rings in **6** are tilted at a relatively larger angle (76.7°) with respect to the porphyrin molecular plane to facilitate coordination to the central metal.

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Along the *a*-axis of the polymeric structure of **6** (Figure 5a), two different alignments of the units are visible. One

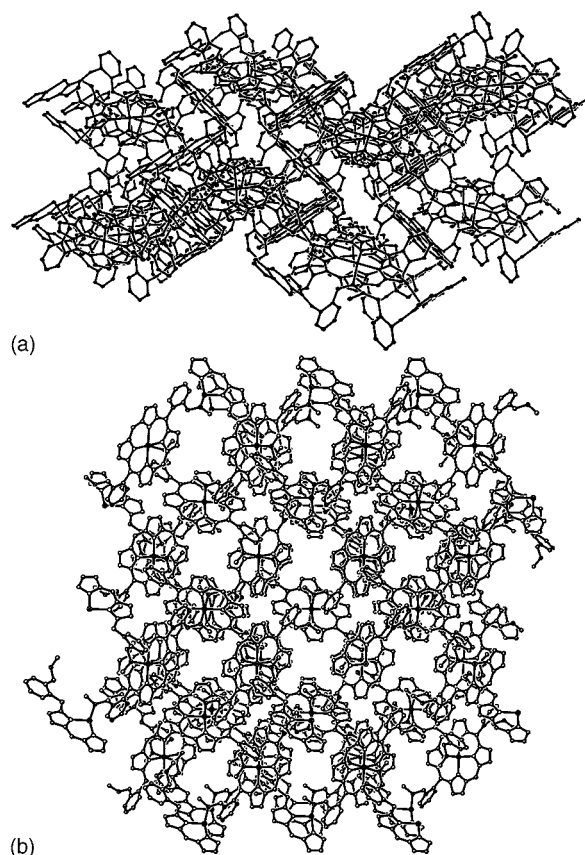


Figure 5. View of **6** along the (a) *a*-axis and (b) *c*-axis.

array is flat, and another array is slanted; thus, a 3D coordination network polymer resulted. There is no appreciable aromatic interaction in the chains on the basis of the estimated inter-ring distances. Along the *c*-axis, a clearer overview of the 3D network architecture is observed (Figure 5b) and the packing creates the flowerlike cavities as shown. The shortest and longest non-hydrogen atomic distances across the channel are about 4.81 and 9.27 Å, respectively (Figure 5b). These cavities and channels should be involved in the solvent diffusion phenomenon observed in the time-dependent NMR study described earlier. Applications of the 3D polymer **6** in selective trapping of organic molecules and inorganic ions and serving as a polymer assembly for catalytic organic reactions are in progress in our laboratory.

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Supporting Information Available: CIF files for *anti*-**5** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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