

POLYMERIC METALLOPORPHYRINS FOR FIELD RESPONSIVE MATERIALS.

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INTRODUCTION

Metalloporphyrins and related macrocycles provide an extremely versatile synthetic base from which to design molecules with specific physical and chemical properties. Molecular engineering in this field has had dramatic successes in the syntheses of reversible O₂ binders¹, shape selective catalysts², molecular receptors³, and one-dimensional conductors and semiconductors^{4,5}. The use of porphyrinic arrays in the photosynthetic reaction center has lead to an intensive study of energy transfer in synthetic systems⁶. However, the investigation of their field-responsive properties has been extremely limited^{7,8}. We have been interested in the exploration of metalloporphyrin assemblies as field responsive materials, particularly as ferroelectrics and as non-linear optical devices. To do so, it is necessary to generate the inter-porphyrin interactions that will show a cooperative effect in response to the applied field. There are five general classes of macrocyclic assemblies in which such interactions might occur: 1) π - π stacked arrays, 2) ligand-bridged coordination polymers, 3) metal-bridged polymers, 4) porphyrin-bound polymers, and 5) porphyrin-inclusion solids. This report will present our preliminary results on the second class of porphyrin assemblies, including the synthesis with full spectroscopic and crystallographic characterization of pure isolated solids.

As depicted in Fig. 1, polymeric metalloporphyrins, in which each subunit is connected with suitable bridge-ligands, X-D, have a net and aligned dipole moment. The direction of bulk polarization may switch in a strong field (electric or possibly electromagnetic), thus, exhibiting ferroelectric properties. It has already been demonstrated that in metalloporphyrin complexes the position of the metal with respect to the porphyrin can have a double-well potential⁹ and show cooperative behavior in ligand binding in solid state¹⁰. Furthermore, bridge-ligands whose donor and acceptor groups are properly oriented along the polymeric metalloporphyrin chain may provide for non-linear optical properties in the polymer.

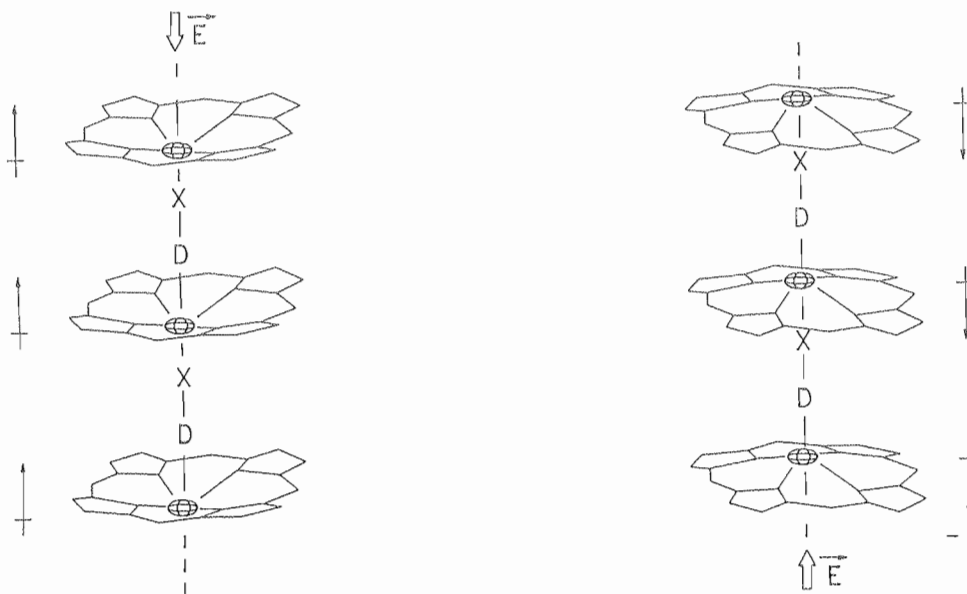


Fig. 1 Schematic representation of a stacked metalloporphyrin polymer and the switching of the dipole moment under the influence of an external force.

RESULTS AND DISCUSSION

We have isolated and crystallographically characterized the first ligand-bridged polymers with a non-symmetric bridge. Specifically, we have synthesized and obtained single-crystal x-ray diffraction structures of $[\text{Fe}^{\text{II}}(\text{TPP})(\text{CNpy})]_n$ (1), $[\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2)]_n$ (2), $[\text{Fe}^{\text{III}}(\text{TPP})(\text{OpyCO}_2)]_n$ (3), and $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_n$ (4). It is rarely a successful endeavor to grow single crystals of a polymer. However, due to a unique property of these polymers, namely their ability to dissociate into the corresponding metalloporphyrin subunits in solution and regain the polymeric forms when the solvent is removed, single crystals of 1-4 suitable for x-ray diffraction were easily obtained by ordinary crystal-growing methods.

The solid-state structure of these polymers may come in several structural types; as shown schematically in Fig. 2, these include disordered, anti-parallel, and polar classes. We have examples of all three classes: 1 is disordered; 2 and 3 are anti-parallel, and 4 is polar. In Fig. 3, the neutral bridge-ligand, CNpy, coordinates to one $\text{Fe}^{\text{II}}\text{TPP}$ through the pyridine and to the next $\text{Fe}^{\text{II}}\text{TPP}$ through the nitrile nitrogen atom. The alignment of CNpy along the polymer chain is disordered with 180° difference (two sets of CNpy are shown in solid and hollow bonds, respectively, in Fig. 3 representing different orientations¹²). This of course precludes any net dipole in the crystal, and hence, no field responsive (ferroelectric, non-linear optical) properties will be expected from it. It appears that the pyridine and nitrile coordination are insufficiently different to induce a strong orientational preference.

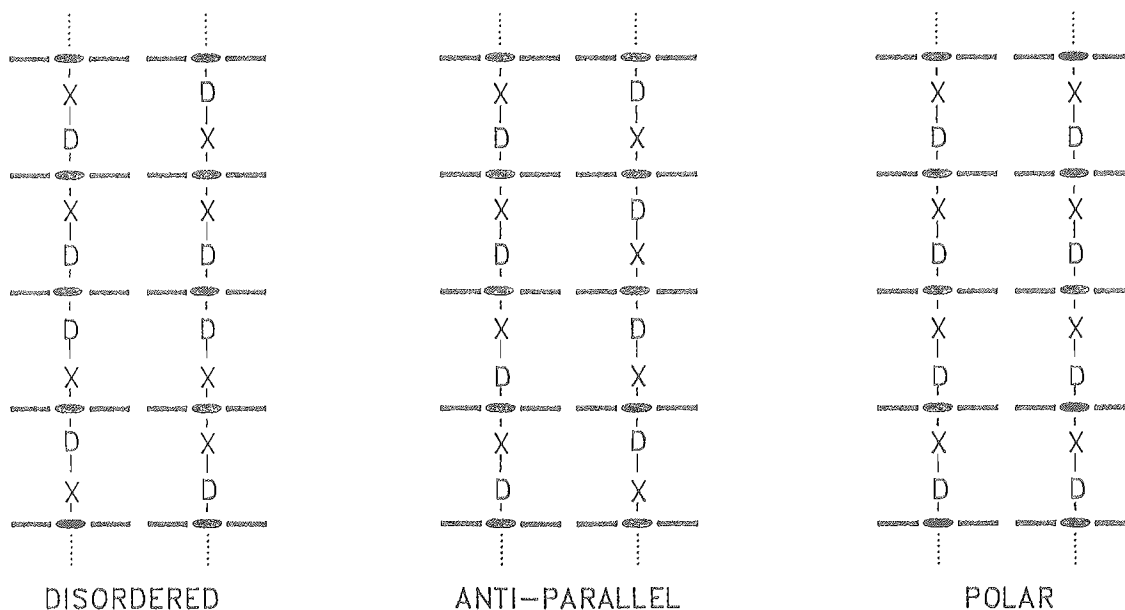


Fig. 2 Three idealized types of alignment of the bridge-ligand in polymer chains.

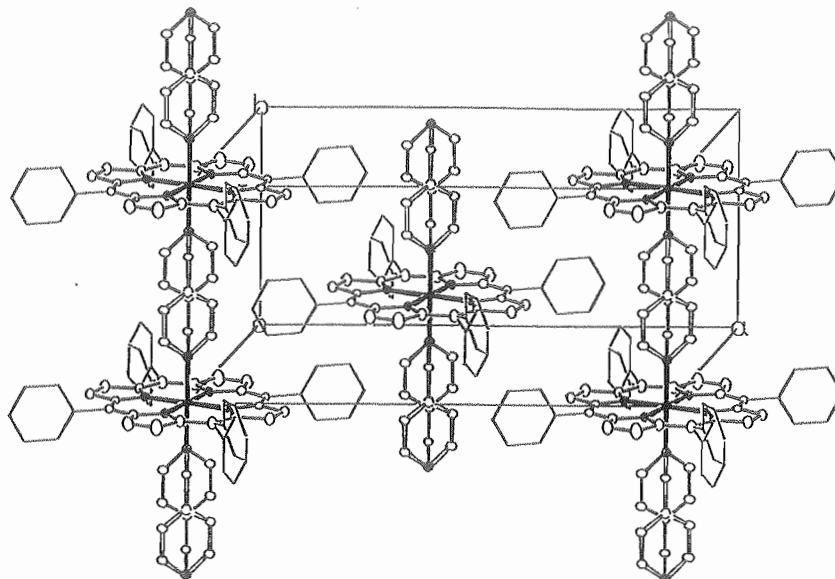


Fig. 3 An ORTEP plot of the packing diagram of $[\text{Fe}^{\text{III}}(\text{TPP})(\text{CNpy})\cdot 2\text{C}_6\text{H}_6]_n$. The solvent molecules and hydrogen atoms are omitted for clarity.

For the structures of 2, 3, and 4, well-aligned chains are found. The alignment patterns of the bridge-ligands in crystals of polymer chains 2 and 3, however, are both antiparallel¹⁶ shown in Fig. 4a and 4b. In contrast, the crystal of 4 (Fig. 4c) is polar and has the non-centrosymmetric space group, $Pna2_1$. All three of these crystals have a normal $\text{Fe}^{\text{III}}\text{-X}$ bond distance (X is the donor atom of the anionic group of these bridge-ligand, i.e., carboxylate O for 2 and 3; phenoxide O for 4)¹⁷, and a rather long $\text{Fe}^{\text{III}}\text{-L}$ (L is the donor atom of the neutral group on the bridge-ligand, i.e., pyridine N for 2, N-oxide O for 3, and imidazole N for 4)¹⁹. The weak $\text{Fe}^{\text{III}}\text{-L}$ bonds in 2, 3, and 4 allow the polymers dissociate easily in solution.

Normally, one would expect the metal atom to be out of the porphyrin plane toward the anionic group of the bridge-ligand; one would also expect the porphyrin to accommodate this with some doming in the same direction. For 2 and 3, this is the case: the metal is 0.154(2) Å and 0.168(1) Å out of the mean porphyrin plane and the porphyrin is domed²² 0.013 Å and 0.039 Å for 2 and 3, respectively. For 4, however, this is not the case and there is an unusual displacement of the metal and the pyrrole nitrogen atoms in *opposite* directions. The iron atom is 0.049(1) Å out of the mean porphyrin plane toward the phenoxide, but the porphyrin is reverse domed 0.074 Å.

In summary, we have synthesized and crystallographic characterized the first polymeric metalloporphyrins in which each subunit is bridged by a non-symmetric ligand. One of them, $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_n$, has a non-centrosymmetric crystal structure. The unusual metal atom displacement implies the core of metalloporphyrin ring in 4 is flexible and that the relative position of the metal atom to the porphyrin ring may change under the influence of an external force. 4 is our best candidate to date for field responsive properties, and studies of its ferroelectric properties are underway.

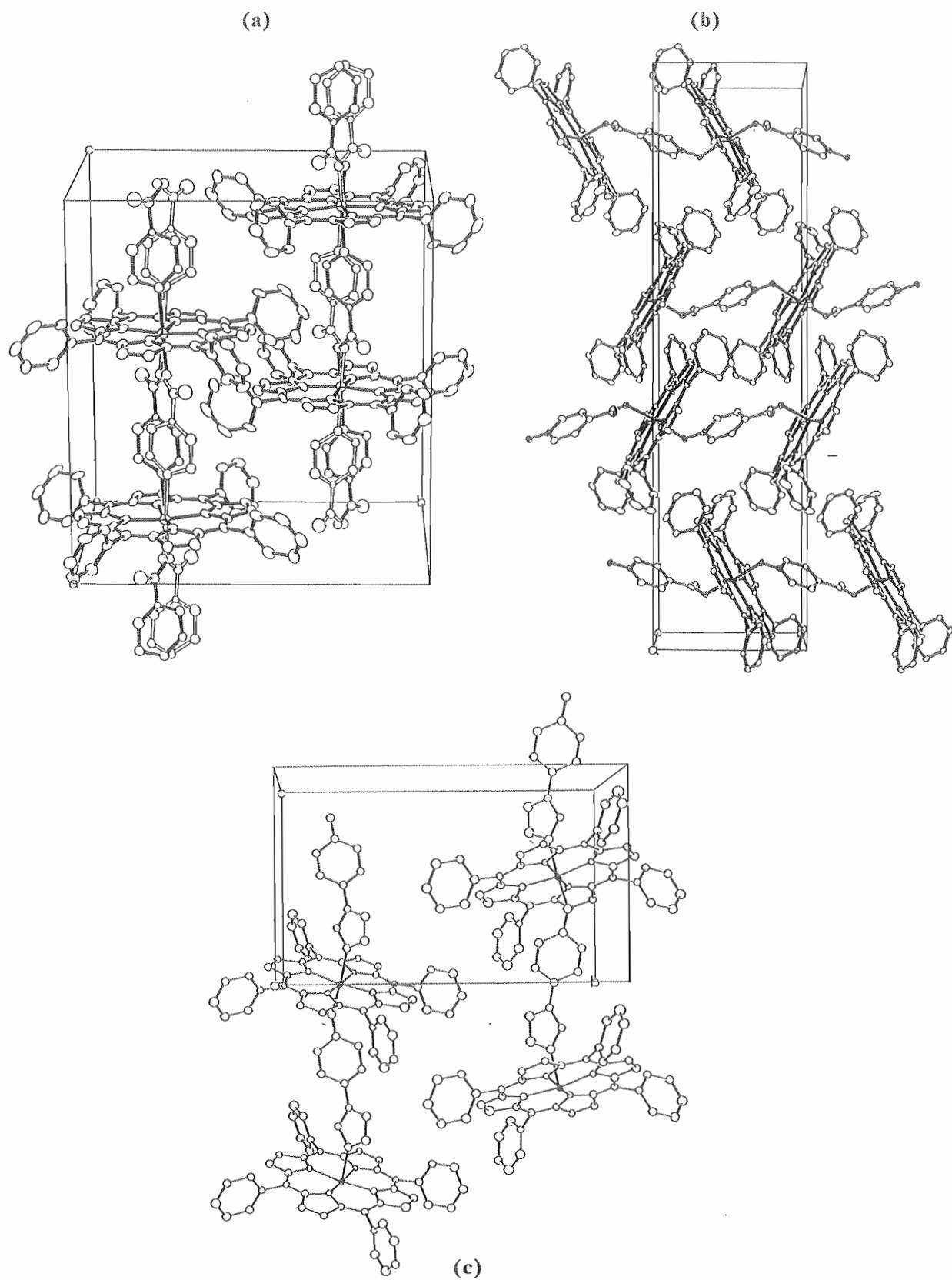


Fig. 4 ORTEP plots of packing diagram of $[\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2)\cdot\text{C}_7\text{H}_8]_n$, (a), $[\text{Fe}^{\text{III}}(\text{TPP})(\text{OpyCO}_2)\cdot\text{C}_7\text{H}_8]_n$, (b), $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_n$, (c); solvent molecules and hydrogen atoms are omitted for clarity.

EXPERIMENTAL

Materials and Equipment

All reactions were carried out in a Vacuum Atmospheres inert atmosphere box with $[O_2] < 2$ ppm. All polymer samples were found to be air stable after isolation as crystalline solids. Solvents were dried by distillation from sodium/benzophenone (benzene, pentane, and tetrahydrofuran), or sodium (toluene, heptane) except for methanol, which was run through a column of Linde 4 Å molecular sieve. All solvents were degassed by the way of three freeze-pump-thaw cycles before use. $Fe(TPP)^{23}$ and $Fe(TPP)(ClO_4)^{24}$ were prepared by literature methods. All bridge-ligands were used as received (Aldrich), and were deprotonated in the following methods: sodium hydroxide in aqueous solution ($OpyCO_2^-$), KH or NaH in tetrahydrofuran ($pyCO_2^-$), and $NaOCH_3$ in methanol ($ImPhO^-$). Elemental analyses and x-ray crystallographic studies were performed by the School of Chemical Science Microanalysis Laboratory and X-ray Crystallographic Laboratory, respectively, at University of Illinois.

Synthesis of Polymers

$[Fe^{II}(TPP)(CNpy)]_n$, 1. $Fe(TPP)$ (0.3 g, 0.45 mmol) and $CNpy$ (0.05 g, 0.48 mmol) were added to toluene (80 mL). The solution was stirred at about 80°C for 10 h, and slowly cooled to ambient temperature without disturbing in 10 h. A dark purple crystalline solid was collected by filtration and dried under vacuum. Yield, 65%–75%. Anal. Calcd for $C_{50}H_{32}N_6Fe$: C, 77.71; H, 4.18; N, 10.88; Fe, 7.23. Found: C, 77.26; H, 4.19; N, 10.74; Fe, 7.38.

$[(Fe^{III}(TPP)(pyCO_2))]_n$, 2. $Fe(TPP)ClO_4 \cdot 0.5C_7H_8$ (0.2 g, 0.25 mmol) and $K(pyCO_2)$ (0.0396 g, 0.25 mmol) were added to toluene (80 mL). The solution was stirred under reflux for 5 h. $KClO_4$ was removed from the solution by filtration through a medium frit while the solution was still hot. Heptane or pentane (350 mL) was then added to the filtrate, and the mixture was set aside for 2 days. A dark purple crystalline solid was collected by filtration and dried under vacuum. The yield of toluene solvate was 85%. Anal. Calcd for $C_{57}H_{40}N_5O_2Fe$: C, 77.55; H, 4.57; N, 7.94; Fe, 6.33. Found: C, 77.38; H, 4.61; N, 7.89; Fe, 6.30.

$[Fe^{III}(TPP)(OpyCO_2)]_n$, 3. In a fashion similar to that described for $[(Fe^{III}(TPP)(OpyCO_2))]_n$ except sodium salt of $OpyCO_2^-$ was used instead of $K(pyCO_2)$. A toluene solvate product was isolated in 80% yield. Anal. Calcd for $C_{57}H_{40}N_5O_3Fe$: C, 76.17; H, 4.49; N, 7.79; Fe, 6.21. Found: C, 76.13; H, 4.47; N, 7.60; Fe, 6.12.

$[(Fe^{III}(TPP)(ImPhO))]_n$, 4. In a fashion similar to that described for $[(Fe^{III}(TPP)(OpyCO_2))]_n$ except sodium salt of $ImphO^-$ was used instead of $K(pyCO_2)$ and the time of reflux was extended to 20 h. Product without solvate isolated in 63% yield. Anal. Calcd for $C_{53}H_{35}N_6OFe$: C, 76.90; H, 4.26; N, 10.16; Fe, 6.75. Found: C, 76.57; H, 4.44; N, 9.85; Fe, 6.24.

Crystallographic Analysis

The crystal of **1** suitable for x-ray structure analysis was picked from the product isolated from the reaction solution in benzene and those crystals of **2-4** were all obtained by letting pentane (or heptane) slowly diffuse into toluene solutions. Crystal data for each polymer are listed as followings:

$[(\text{Fe}^{\text{II}}(\text{TPP})(\text{CNpy})\cdot 2\text{C}_6\text{H}_6)]_n$ ($T = -75$ °C): space group $C2/m$, $a = 20.110(9)$ Å, $b = 9.356(9)$ Å, $c = 13.049(4)$ Å, $\beta = 103.30(3)^\circ$, $V = 2389(3)$ Å³, $Z = 8$, $R_{\text{F}} = 6.9\%$, $R_{\text{wF}} = 8.9\%$ on 158 variables and 2115 unique data with $I > 2.58\sigma(I)$. Neither refinement of a polar model in $C2$ nor refinement of a similarly disordered model in Cm significantly improved agreement between observed and calculated structure factors.

$[(\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2)\cdot \text{C}_7\text{H}_8)]_n$ ($T = -75$ °C): space group $Pccn$, $a = 13.348(5)$ Å, $b = 17.338(7)$ Å, $c = 18.841(4)$ Å, $V = 4361(5)$ Å³, $Z = 8$, $R_{\text{F}} = 7.0\%$, $R_{\text{wF}} = 7.7\%$ on 273 variables and 1634 unique data with $I > 2.58\sigma(I)$.

$[(\text{Fe}^{\text{III}}(\text{TPP})(\text{OpyCO}_2)\cdot \text{C}_7\text{H}_8)]_n$ ($T = -100$ °C): space group $P2_1/n$, $a = 13.175(5)$ Å, $b = 9.339(3)$ Å, $c = 35.023(16)$ Å, $\beta = 93.55(4)^\circ$, $V = 4301(5)$ Å³, $Z = 4$, $R_{\text{F}} = 5.0\%$, $R_{\text{wF}} = 5.5\%$ on 1206 variables and 4272 unique data with $I > 2.58\sigma(I)$.

$[(\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO}))_n$ ($T = -75$ °C): space group $Pna2_1$, $a = 19.132(5)$ Å, $b = 18.217(3)$ Å, $c = 11.223(4)$ Å, $V = 3912(2)$ Å³, $Z = 4$, $R_{\text{F}} = 5.4\%$, $R_{\text{wF}} = 4.0\%$ on 251 variables and 1525 unique data with $I > 2.58\sigma(I)$.

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11. Abbreviations used are as follows: TPP, 5,10,15,20-tetraphenylporphyrinate; CNpy, 4-cyanopyridine; pyCO₂⁻, pyridine-4-carboxylate; OpyCO₂⁻, N-oxide of pyridine-4-carboxylate; ImPhO⁻, 4-(imidazol-1-yl)phenoxide; py, pyridine.
12. One of the two unique phenyl rings on porphyrin is also disordered above and below the porphyrin plane coupled to the disorder of bridge-ligand about a parallel symmetry plane. The Fe^{II} atom is coplanar with the mean plane of 24-atom core of the porphyrin ring, which is planar due to the mirror plane symmetry. The distance of Fe^{II}-N (pyridine or nitrile) is 1.982(4) Å and is comparable to the corresponding bond of other known low-spin ferrous porphyrins¹³⁻¹⁵.
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16. The bridge-ligand of **2** is drawn in two types of bonding, the solid and the hollow, to present the disorder about the 2-fold symmetry axis.
17. The bond distances of Fe^{III}-X are 2.051(7), 1.982(3), and 1.899(9) Å for **2**, **3**, **4** respectively. The distances found for **2** and **3** are about 0.1 Å longer than the 1.82-1.97 Å range of the corresponding distance in high-spin ferric porphyrins¹⁸. This elongation is also found for Ga-Cl bond in Ga^{III}(TPP)(py)Cl²⁵ due to the coordination of the second axial ligand (pyridine) on the other side of TPP.
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19. The bond distance of Fe^{III}-L is 2.350(9) Å in **2** and 2.21(1) Å in **4**. 2.53(9) Å is comparable to 2.442(2) Å of the corresponding bond in high-spin Fe^{III}(OEP)(py)(NCS)²⁰ which has a "semicoordinated" pyridine, and 2.22(1) Å is longer than 2.068(4) Å found in high-spin [Fe^{III}(OEP)(2-MeHIm)](ClO₄)²¹ which has a steric hindered imidazole.
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22. The distances of the metal to the mean plane of 24-atom porphyrinato core (M--P_C) are 0.154(2), 0.168(1), and 0.049(1) Å for **2**, **3**, and **4**, respectively. The distances of the metal to the mean plane of four nitrogen atoms (M--P_N) are 0.141(2), 0.129(1), and 0.123(1) Å for **2**, **3**, and **4**, respectively. The difference of the M--P_C and M--P_N distances serves as a measure of the "net doming" of the core²⁶.
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