

Direct Comparison of CN^- and CO as Ligands in Iron(II) Porphyrinates**

Supporting Information

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Experimental Section

General Information. All reactions and manipulations were carried out under argon using a double-manifold vacuum line, Schlenkware and cannula techniques. THF¹ and hexanes were distilled over sodium/benzophenone and dichloromethane over CaH₂. Chlorobenzene was washed with concentrated sulfuric acid, then with water until the aqueous layer was neutral, dried with MgSO₄, and distilled twice over P₂O₅ under argon. KCN was recrystallized and purified by a literature procedure.² Ethanethiol and Kryptofix 222 (Aldrich) were used as received. The free-base porphyrin ligand *meso*-tetraphenylporphyrin (H₂TPP) were prepared according to Adler et al.³ [Fe(TPP)]₂O and [Fe(TTP)]₂O was prepared according to a modified Fleischer preparation.⁴ UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis/near-IR spectrometer and IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer as KBr pellets. Mössbauer measurements were performed on a constant acceleration spectrometer from 4.2 K to 300 K with optional small field (Knox College). Samples for Mössbauer spectroscopy were prepared by immobilization of the crystalline material in Apiezon M grease.

Synthesis of [K(222)][Fe(TPP)(CN)] (Forms # 1 and # 2). [Fe(II)(TPP)] was prepared by reduction of [Fe(TPP)]₂O (27.1 mg, 0.02 mmol) with ethanethiol (0.5 mL) in benzene (8 mL) for 24 hours. Vacuum evaporation of the solvent yielded a dark purple solid to which KCN (2.9 mg, 0.044 mmol) and Kryptofix 222 (16.6 mg, 0.044 mmol) in THF or PhCl (~ 4 mL) was added by cannula and the mixture was stirred overnight. X-ray quality crystals were finally obtained in 8 mm × 250 mm sealed glass tubes by liquid diffusion using hexanes as non-solvent. Two different polymorphs were yielded by different reactions. Crystal form # 1 was obtained from THF or PhCl, whereas crystal form # 2 was obtained from PhCl. Very strong C–N stretches were found for iron(II) cyanide porphyrinates compared to the iron(III)

analogues which are much weaker. IR $\nu(\text{C-N})$: 2070 (strong) and 2105 cm^{-1} (weak) for form # 1; 2072 (strong) and 2106 $^{-1}$ (weak) for form # 2.

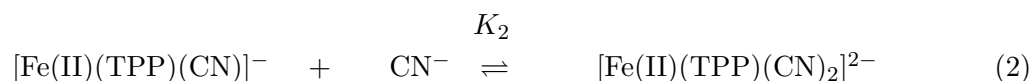
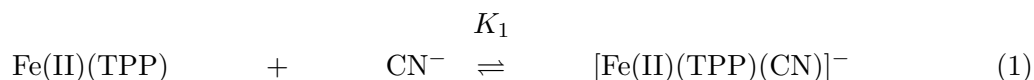
Synthesis of $[\text{K}(\mathbf{222})][\text{Fe}(\mathbf{TPP})(\mathbf{CN})(\mathbf{1-MeIm})]$. 1-Methylimidazole (0.1 mL, 1.2 mmol) was added to a solution of $[\text{K}(\mathbf{222})][\text{Fe}(\mathbf{TPP})(\mathbf{CN})]$ (44.4 mg, 0.04 mmol) in CH_2Cl_2 (9 mL). The mixture was stirred for 30 mins. Hexanes was allowed to diffuse slowly into the solution. Single crystals of $[\text{K}(\mathbf{222})][\text{Fe}(\mathbf{TPP})(\mathbf{CN})(\mathbf{1-MeIm})]$ (yield 20 mg) was obtained. IR $\nu(\text{C-N})$: 2076 cm^{-1} .

Synthesis of $[\text{K}(\mathbf{222})]_2[\text{Fe}(\mathbf{TPP})(\mathbf{CN})_2]$. Similar reaction procedures and conditions had been conducted as the synthesis of $[\text{K}(\mathbf{222})][\text{Fe}(\mathbf{TPP})(\mathbf{CN})]$. $[\text{Fe}(\text{II})(\mathbf{TPP})]$ was prepared by reduction of $[\text{Fe}(\mathbf{TPP})]_2\text{O}$ (40 mg, 0.03 mmol) with ethanethiol (0.8 mL) in benzene for 24 hours. Vacuum evaporation of benzene yielded a dark purple solid, to which fresh PhCl (~ 6 mL) was introduced to dissolve the solid. Then the dark red solution was transferred to KCN (8 mg, 0.12 mmol) and Kryptofix 222 (48 mg, 0.13 mmol) by cannula and the mixture was stirred overnight. After 3-4 weeks standing, crystals were obtained in sealed glass tubes by liquid diffusion using hexanes as non-solvent. Two different polymorphs were yielded by different reactions. They are $[\text{K}(\mathbf{222})]_2[\text{Fe}(\mathbf{TPP})(\mathbf{CN})_2]\cdot 4\text{PhCl}$ and $[\text{K}(\mathbf{222})]_2[\text{Fe}(\mathbf{TPP})(\mathbf{CN})_2]\cdot \text{PhCl}$. IR $\nu(\text{C-N})$: $[\text{K}(\mathbf{222})]_2[\text{Fe}(\mathbf{TPP})(\mathbf{CN})_2]\cdot 4\text{PhCl}$, 2069 cm^{-1} ; $[\text{K}(\mathbf{222})]_2[\text{Fe}(\mathbf{TPP})(\mathbf{CN})_2]\cdot \text{PhCl}$, 2069 cm^{-1} .

Synthesis of $[\text{K}(\mathbf{222})]_2[\text{Fe}(\mathbf{TTP})(\mathbf{CN})_2]$. $[\text{Fe}(\text{II})(\mathbf{TTP})]$ was prepared by reduction of $[\text{Fe}(\mathbf{TTP})]_2\text{O}$ (80 mg, 0.05 mmol) with ethanethiol (2 mL) in benzene (10 mL) for 24 hours. Vacuum evaporation of the solvent yielded a dark purple solid to which KCN (20 mg, 0.20 mmol) and Kryptofix 222 (90 mg, 0.20 mmol) in CH_2Cl_2 was added by cannula and the mixture was stirred overnight. X-ray quality crystals were finally obtained in 8 mm \times 250 mm sealed glass

tubes by liquid diffusion using hexanes as non-solvent. Very strong C—N stretch was found, IR $\nu(\text{C-N})$: 2056 cm^{-1} .

Equilibrium Constant Determinations. UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis/near-IR spectrometer in a specially designed combined 1- and 10-mm inert atmosphere cell. A solution of the four-coordinate iron(II) porphyrin was prepared as above using PhCl as solvent. The ligand solution ($[\text{K}(222)]^+\text{CN}^-$) was prepared by dissolving equivalent amount of KCN and Kryptofix 222 in PhCl and the concentrations for UV-vis measurements is 0.02 mol/L. $[\text{K}(222)]^+\text{CN}^-$ solution was titrated into $[\text{Fe}(\text{II})(\text{TPP})]$ in a 2% EtSH/PhCl solution. UV-vis spectra of $\text{Fe}(\text{TPP})$ in different concentrations of $[\text{K}(222)]^+\text{CN}^-$ were measured. The equilibrium constants for these equilibria were calculated with the non-linear least-squares program SQUAD.⁵ SQUAD calculates best values for the equilibrium constants by employing multiple-wavelength absorption data for varying concentrations of the reactants. Absorbance data, at 10-nm increments spanning the visible region, were input into SQUAD. The calculated results are $K_1 = 4.3 \times 10^5 \text{ M}^{-1}$ and $K_2 = 3.1 \times 10^3 \text{ M}^{-1}$.



X-ray Structure Determinations. Single crystal experiments were carried out on a Bruker Apex system with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXS-97⁶ and refined against F^2 using SHELXL-97;^{7, 8} subsequent difference Fourier syntheses led to the location of most of the remaining non-hydrogen atoms. For the structure refinement all data were used including negative intensities. All nonhydrogen atoms were refined anisotropically if not remarked otherwise be-

low. Hydrogen atoms were idealized with the standard SHELXL-97 idealization methods. The program SADABS⁹ was used to apply an absorption correction. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and fixed hydrogen atom coordinates are given in the Supporting Information for the four structures.

[K(222)][Fe(TPP)(CN)] (100, 296, 325, 400K; # 1). see reference 11.

[K(222)][Fe(TPP)(CN)] (100, 296, 325, 400K; # 2). A dark purple crystal with the dimensions $0.36 \times 0.33 \times 0.30$ mm³ was used for the temperature-dependent structure determination. The crystal was mounted in a sealed capillary. Measurement temperatures were 100, 296, 325 and 400 K. The asymmetric unit contains one porphyrin complex and one potassium cation coordinated with Kryptofix 222. Although several carbon atoms (*e. g.* C28 and C29) on Kryptofix 222 show large anisotropic displacement parameters (ADP) especially at high temperatures, no constrain/restrain conditions have been applied.

[K(222)][Fe(TPP)(CN)(1-MeIm)]·2CH₂Cl₂. A dark red crystal with the dimensions $0.40 \times 0.30 \times 0.14$ mm³ was used for the structure determination. The asymmetric unit contains one porphyrin complex, one potassium cation coordinated by Kryptofix 222 and two dichloromethane solvent molecules. One of the three arms of Kryptofix 222 is disordered and refined as two orientations. In both of the dichloromethane solvates, one of the chloride atoms is disordered and refined over two positions.

[K(222)]₂[Fe(TPP)(CN)₂]·4PhCl. A black crystal with the dimensions $0.27 \times 0.19 \times 0.17$ mm³ was used for the structure determination. The asymmetric unit contains one bis-liganded porphyrin complex, two potassium cations coordinated by Kryptofix 222, and four chlorobenzene solvent molecules. All the atoms are ordered.

[K(222)]₂[Fe(TPP)(CN)₂]·PhCl. A black crystal with the dimensions $0.19 \times 0.12 \times$

0.11 mm³ was used for the structure determination. The asymmetric unit contains two bis-liganded porphyrin complexes, two potassium cations coordinated by Kryptofix 222, and two chlorobenzene solvent molecules. The two K(222) cations coordinate to cyanide ligands by Fe–CN–K linkages. Part of the ethylene bridges of two K(222) are disordered, which are constrained by DFIX commands. PLATON suggests a higher pseudo space group P21/c, but 11% of the atoms don't fit this symmetry. More disordered parts were found at the cations (K(222)) under the symmetry of P21/c, and the best refinement gave $R_1 > 0.10$, $wR_2 > 0.23$. So the space group $P\bar{1}$ was used.

[K(222)]₂[Fe(TTP)(CN)₂]·5.8CH₂Cl₂. A dark purple crystal with the dimensions 0.42 × 0.27 × 0.09 mm³ was used for the structure determination. The crystal was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. The asymmetric unit contains one half-porphyrin anion with required inversion symmetry and an ordered Kryptofix-222 molecule. There are three methylene chloride solvent molecules and one of them is ordered. For the second one, both of the chlorine atoms are refined over two positions. For the third methylene chloride, entire molecule is refined over two positions and the occupancies are restrained to 0.9.

Table S1. Complete Crystallographic Details for [K(222)][Fe(TPP)(CN)] # 2, [K(222)][Fe(TPP)(CN)(1-Melm)]·2CH₂Cl₂, [K(222)]₂[Fe(TPP)(CN)₂]·4PhCl, [K(222)]₂[Fe(TPP)(CN)₂]·PhCl and [K(222)]₂[Fe(TTP)(CN)₂]·5.8CH₂Cl₂

	[K(222)][Fe(TPP)(CN)] # 2	[K(222)][Fe(TPP)(CN)] # 2	[K(222)][Fe(TPP)(CN)] # 2	[K(222)][Fe(TPP)(CN)] # 2
chemical formula	C ₆₃ H ₆₄ FeKN ₇ O ₆	C ₆₃ H ₆₄ FeKN ₇ O ₆	C ₆₃ H ₆₄ FeKN ₇ O ₆	C ₆₃ H ₆₄ FeKN ₇ O ₆
FW	1110.16	1110.16	1110.16	1110.16
<i>a</i> , Å	12.7867(2)	12.8711(2)	12.8817(3)	12.9228(2)
<i>b</i> , Å	18.9525(3)	19.0847(3)	19.0987(4)	19.1592(3)
<i>c</i> , Å	23.3107(4)	23.6317(4)	23.6892(5)	23.9039(3)
α , deg	90.00	90.00	90.00	90.00
β , deg	99.411(1)	99.702(1)	99.751(1)	99.890(1)
γ , deg	90.00	90.00	90.00	90.00
<i>V</i> , Å ³	5573.08(16)	5721.89(16)	5743.9(2)	5830.43(15)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4	4	4	4
temp, K	100	296	325	400
<i>D</i> _{calcd} , g cm ⁻³	1.323	1.289	1.284	1.265
μ , mm ⁻¹	0.405	0.394	0.393	0.387
final <i>R</i> indices	<i>R</i> ₁ = 0.0545	<i>R</i> ₁ = 0.0442	<i>R</i> ₁ = 0.0442	<i>R</i> ₁ = 0.0406
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> ₂ = 0.1310	<i>wR</i> ₂ = 0.1014	<i>wR</i> ₂ = 0.1018	<i>wR</i> ₂ = 0.1000
final <i>R</i> indices	<i>R</i> ₁ = 0.0839	<i>R</i> ₁ = 0.1006	<i>R</i> ₁ = 0.1014	<i>R</i> ₁ = 0.0767
(all data)	<i>wR</i> ₂ = 0.1494	<i>wR</i> ₂ = 0.1255	<i>wR</i> ₂ = 0.1238	<i>wR</i> ₂ = 0.1180

Table S1. continued

	[K(222)] ₁ [Fe(TPP)(CN)- (1-MeIm)]·2CH ₂ Cl ₂	[K(222)] ₂ [Fe(TPP)- (CN) ₂]·PhCl	[K(222)] ₂ [Fe(TPP)- (CN) ₂]·4PhCl	[K(222)] ₂ [Fe(TPP)- (CN) ₂]·5.8CH ₂ Cl ₂
chemical formula	C ₆₉ H ₇₄ Cl ₄ FeKN ₉ O ₆	C ₈₈ H ₁₀₅ ClFeK ₂ N ₁₀ O ₁₂	C ₁₀₆ H ₁₂₀ Cl ₄ FeK ₂ N ₁₀ O ₁₂	C _{91.8} H _{121.6} Cl _{11.6} FeKN ₁₀ O ₁₂
FW	1362.12	1664.32	2001.97	1049.37
<i>a</i> , Å	12.9598(2)	14.9763(11)	15.5352(11)	13.090(6)
<i>b</i> , Å	18.9279(4)	21.2657(16)	15.8391(13)	14.679(6)
<i>c</i> , Å	27.3297(5)	26.944(2)	22.0815(16)	14.950(7)
α , deg	90.00	100.912(4)	83.820(4)	83.76(3)
β , deg	97.694(1)	90.461(4)	77.934(4)	65.70(2)
γ , deg	90.00	90.416(5)	68.686(4)	76.51(3)
<i>V</i> , Å ³	6643.7(2)	8425.4(11)	4947.0(6)	2545.5(19)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	4	4	2	1
temp, K	100	100	100	100
<i>D</i> _{calcd} , g cm ⁻³	1.362	1.312	1.344	1.369
μ , mm ⁻¹	0.510	0.377	0.412	0.595
final <i>R</i> indices	<i>R</i> ₁ = 0.0698	<i>R</i> ₁ = 0.0622	<i>R</i> ₁ = 0.0496	<i>R</i> ₁ = 0.0647
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> ₂ = 0.1736	<i>wR</i> ₂ = 0.1585	<i>wR</i> ₂ = 0.1445	<i>wR</i> ₂ = 0.1708
final <i>R</i> indices	<i>R</i> ₁ = 0.1039	<i>R</i> ₁ = 0.0829	<i>R</i> ₁ = 0.0799	<i>R</i> ₁ = 0.0757
(all data)	<i>wR</i> ₂ = 0.1827	<i>wR</i> ₂ = 0.1745	<i>wR</i> ₂ = 0.1699	<i>wR</i> ₂ = 0.1787

Table S2. Selected Structural Parameters of Related Iron(II) Porphyrinates^a

Complex	Δ^b	AN_4^c	(Fe-N _p) _{av}	Fe-C	Fe-N _L	C-N/O	Fe-C-N/O	τ^d	ref.
Five-coordinate Porphyrinates									
[K(222)][Fe(TPP)(CN)] (100K, # 1)	0.23	0.17	1.986(7)	1.8783(10)		1.1662(14)	177.19(10)	6.3	11
[K(222)][Fe(TPP)(CN)] (296K, # 1)	0.42	0.35	2.047(8)	2.028(3)		1.153(4)	175.7(2)	6.9	11
[K(222)][Fe(TPP)(CN)] (325K, # 1)	0.47	0.39	2.064(8)	2.103(3)		1.134(3)	175.8(2)	7.2	11
[K(222)][Fe(TPP)(CN)] (400K, # 1)	0.54	0.45	2.089(8)	2.108(3)		1.122(3)	175.8(2)	7.4	11
[K(222)][Fe(TPP)(CN)] (100K, # 2)	0.22	0.16	1.984(8)	1.869(2)		1.152(3)	178.1(2)	3.1	tw
[K(222)][Fe(TPP)(CN)] (296K, # 2)	0.35	0.28	2.019(10)	1.917(5)		1.127(4)	178.4(4)	2.9	tw
[K(222)][Fe(TPP)(CN)] (325K, # 2)	0.40	0.33	2.036(8)	1.990(5)		1.106(4)	177.5(4)	3.0	tw
[K(222)][Fe(TPP)(CN)] (400K, # 2)	0.50	0.42	2.070(9)	2.068(4)		1.099(4)	176.5(4)	2.8	tw
[Fe(OEP)(CO)]·C ₆ H ₆	0.22	0.20	1.984(3)	1.7077(13)		1.1259(16)	177.20(11)	2.4	10
Six-coordinate bis(ligand) Porphyrinates									
[K(222)] ₂ [Fe(TPP)(CN) ₂] ₄ PhCl	0.01	0.00	1.990(4)	1.971(4)		1.156(5)	175.4(3)	3.4	tw
				1.966(4)		1.158(5)	178.3(3)	0	
[K(222)] ₂ [Fe(TPP)(CN) ₂] ₂ ·PhCl	0.03	0.01	1.974(11)	1.988(3)		1.157(4)	177.5(2)	1.6	tw
<i>molecule 1</i>				1.989(3)		1.162(3)	178.7(2)	0	
[K(222)] ₂ [Fe(TPP)(CN) ₂] ₂ ·PhCl	0.05	0.01	1.975(9)	1.991(3)		1.157(4)	176.0(2)	1.4	tw
<i>molecule 2</i>				1.985(3)		1.157(4)	177.9(2)	3.3	
[K(222)] ₂ [Fe(TPP)(CN) ₂]	0.00	0.00	1.999(6)	1.976(4)		1.159(5)	176.8(3)	3.8	tw
[Fe(OEP)(CO) ₂]	0.00	0.00	2.0133(7)	1.8558(10)		1.1216(13)	173.95(9)	5.9	13
Six-coordinate mixed-ligand Porphyrinates									
[K(222)][Fe(TPP)(CN)(1-Melm)]	0.04	0.03	1.990(3)	1.932(4)	2.046(3)	1.169(5)	176.6(3)	2.3	tw
[Fe(TPP)(CO)(1-Melm)]	-0.02	0.02	2.005(6)	1.7600(17)	2.0503(14)	1.139(2)	177.03(15)	1.0	12
[Fe(OEP)(CO)(1-Melm)]	0.02	0.03	2.010(4)	1.7733(12)	2.0544(9)	1.1413(15)	175.67(11)	3.9	10

^a Distance values in Å, Angle values in deg., tw = this work. ^b Displacement of iron atom from the 24-atom mean plane. the positive numbers indicate a displacement toward the C-N/O. ^c Displacement of iron atom from the mean plane of the four pyrrole nitrogen atoms. the positive numbers indicate a displacement toward the C-N/O. ^d The angle of Fe-C vector tilted from the normal to the 24-atom mean plane.

Table S3. Mössbauer Parameters of Related Porphyrinates

Complex	T (K)	ΔE_Q (mm/s)	δ (mm/s)	ref.
[K(222)][Fe(TPP)(CN)] # 1	25	1.83	0.37	11
	100	1.83	0.36	11
	200	1.82	0.35	11
	270	1.31	0.31	11
	280	1.20	0.35	11
	290	1.12	0.38	11
	295	0.87	0.48	11
	300	0.85	0.47	11
	[Fe(OEP)(CO)]	4.2	1.84	0.27
25		1.84	0.23	10
100		1.84	0.23	10
225		1.84	0.20	10
250		1.83	0.20	10
298		1.81	0.14	10
[K(222)] ₂ [Fe(TPP)(CN) ₂]	20	0.27	0.31	tw
	100	0.24	0.31	tw
	200	0.21	0.28	tw
	296	0.14	0.23	tw
	296	0.13	0.22	tw
[K(222)] ₂ [Fe(TTP)(CN) ₂]	15	0.15	0.29	tw
	100	0.13	0.29	tw
	200	0.09	0.27	tw
	298	0.07	0.22	tw
[Fe(OEP)(CO) ₂]	4.2	0	0.31	10
	15	0.09	0.28	10
	100	0.10	0.28	10
	200	0.11	0.27	10
	298	0.18	0.18	10
[K(222)][Fe(TPP)(CN)(1-MeIm)]	4.2	0.53	0.36	tw
	16	0.60	0.39	tw
	100	0.61	0.37	tw
	200	0.62	0.32	tw
	298	0.62	0.26	tw
[Fe(OEP)(CO)(1-MeIm)]	15	0.34	0.24	12
	100	0.37	0.23	12
	200	0.37	0.25	12
	293	0.40	0.18	12
[Fe(TPP)(CO)(1-MeIm)]	15	0.30	0.26	12
	100	0.32	0.25	12
	200	0.32	0.24	12
	293	0.35	0.16	12

References and Notes

- (1) Abbreviations: Porph, generalized porphyrin dianion; N_p , porphyrinato nitrogen; N_L , ligand nitrogen; TPP, dianion of *meso*-tetraphenylporphyrin; TTP, *meso*-tetra-*p*-tolylporphyrin; OEP, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; THF, tetrahydrofuran; 1-MeIm, 1-methylimidazole; Kryptofix-222 or 222, 4,7,13,16,21,24-hexaoxo-1,10-diazabicyclo[8.8.8]hexacosane.
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- (8) $R_1 = \sum \| |F_o| - |F_c| \| / \sum |F_o|$ and $wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4] \right\}^{1/2}$. The conventional *R*-factors R_1 are based on F , with F set to zero for negative F^2 . The criterion of $F^2 > 2\sigma(F^2)$ was used only for calculating R_1 . *R*-factors based on F^2 (wR_2) are statistically about twice as large as those based on F , and *R*-factors based on ALL data will be even larger.
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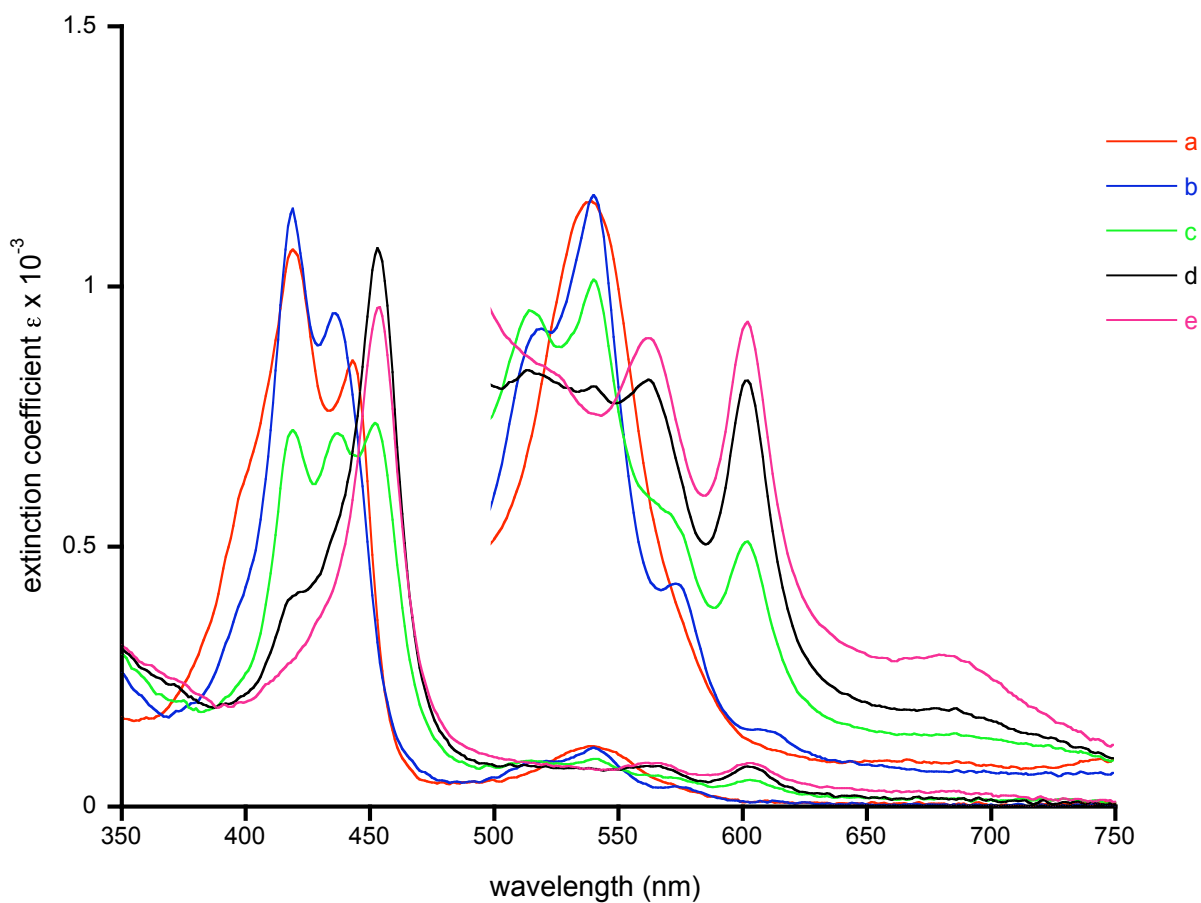


Figure S1. Selected UV-vis spectra taken in chlorobenzene under argon. a) Fe(II)(TPP) (9.0×10^{-5} mol/L) b) Fe(II)(TPP) in 1.0×10^{-4} mol/L [K(222)(CN)] solution. c) Fe(II)(TPP) in 1.8×10^{-4} mol/L [K(222)(CN)] solution. d) Fe(II)(TPP) in 2.2×10^{-4} mol/L [K(222)(CN)] solution. e) Fe(II)(TPP) in 2.8×10^{-4} mol/L [K(222)(CN)] solution. The enlarged spectra from 500 to 750 nm are measured in the 10-mm UV cell.

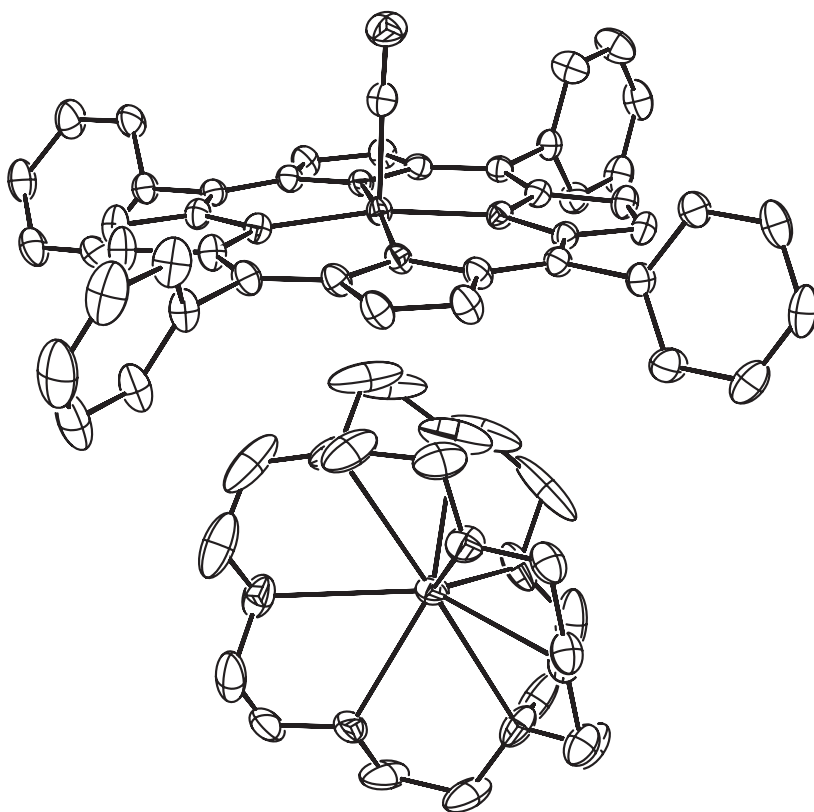


Figure S2. ORTEP diagram of asymmetric unit of $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 100K. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

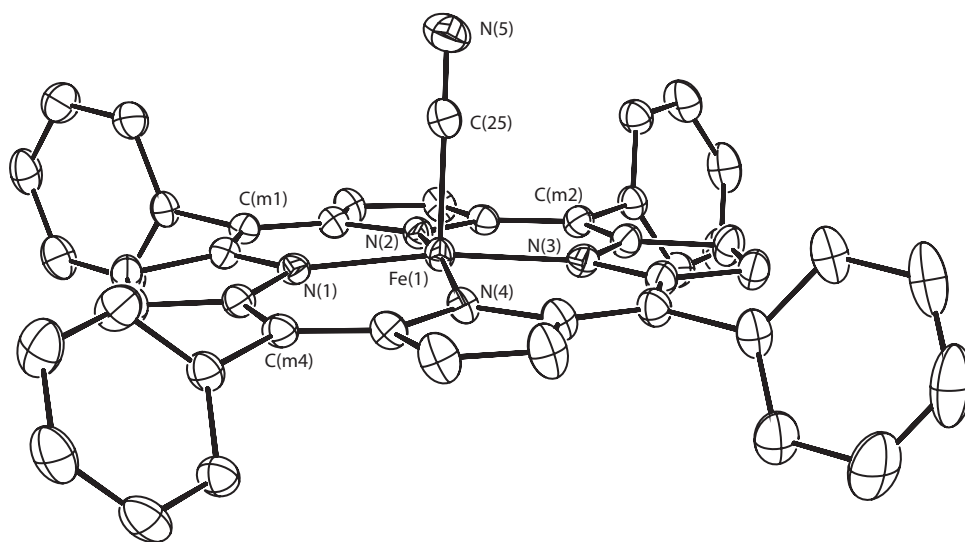


Figure S3. ORTEP diagram of the $[\text{Fe}(\text{TPP})(\text{CN})]^-$ anion in $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 100K displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

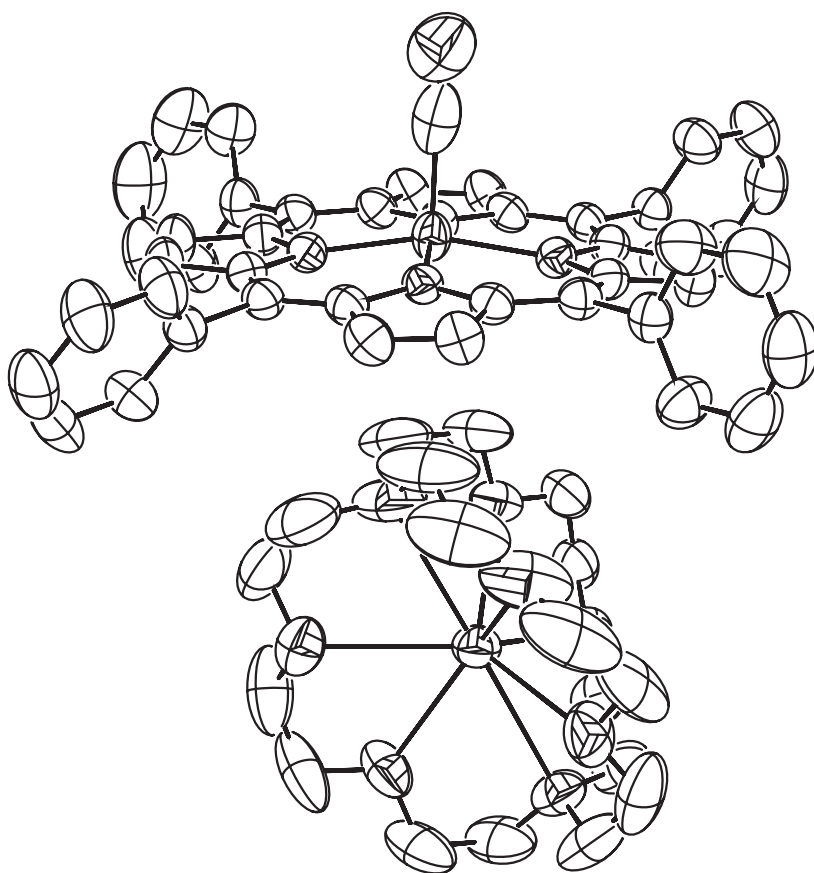


Figure S4. ORTEP diagram of asymmetric unit of $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 296K. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

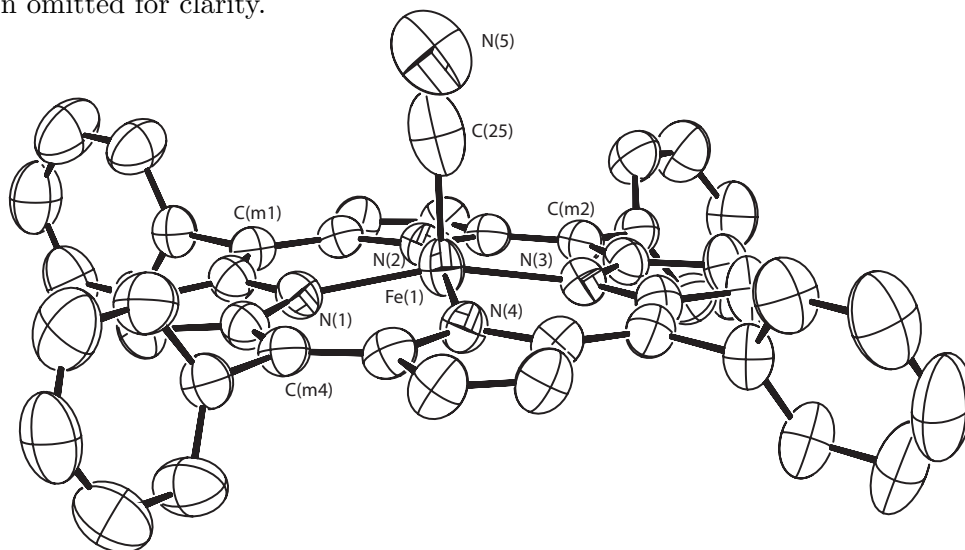


Figure S5. ORTEP diagram of the $[\text{Fe}(\text{TPP})(\text{CN})]^-$ anion in $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 296K displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

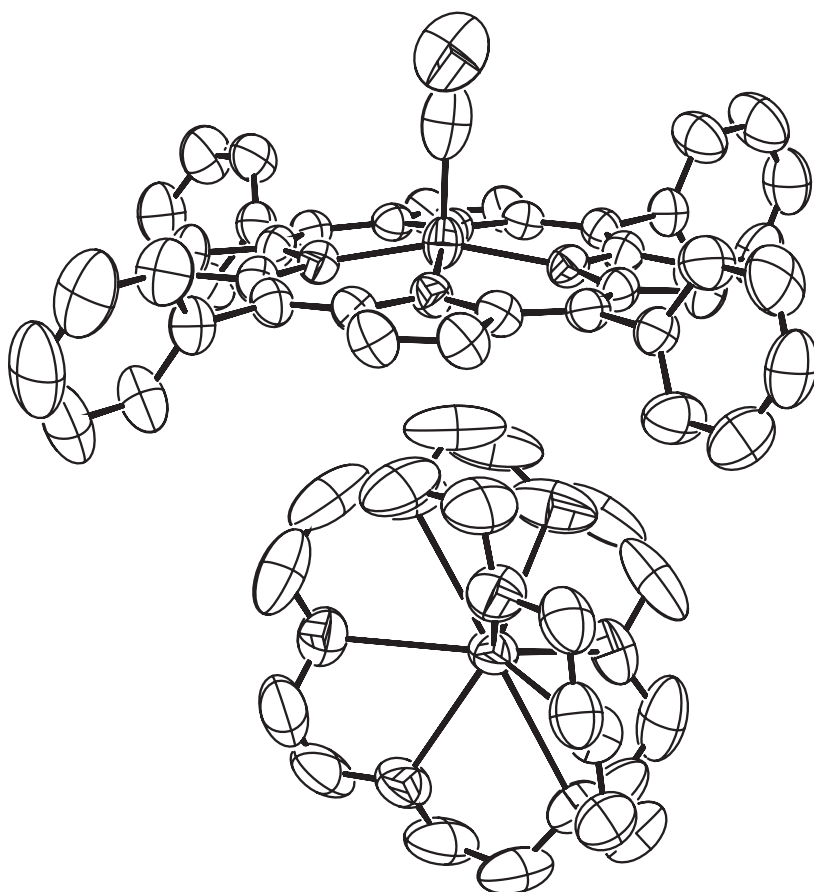


Figure S6. ORTEP diagram of asymmetric unit of $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 325K. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

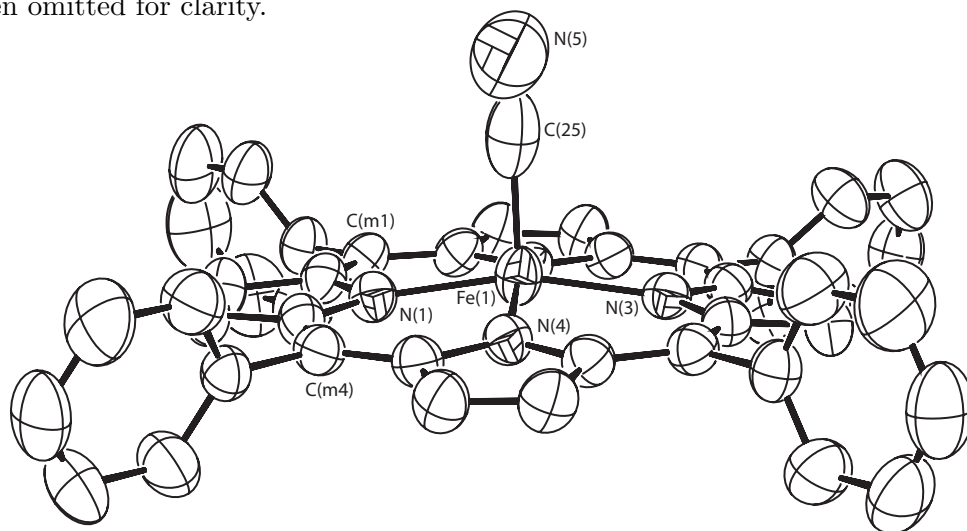


Figure S7. ORTEP diagram of the $[\text{Fe}(\text{TPP})(\text{CN})]^-$ anion in $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 325K displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

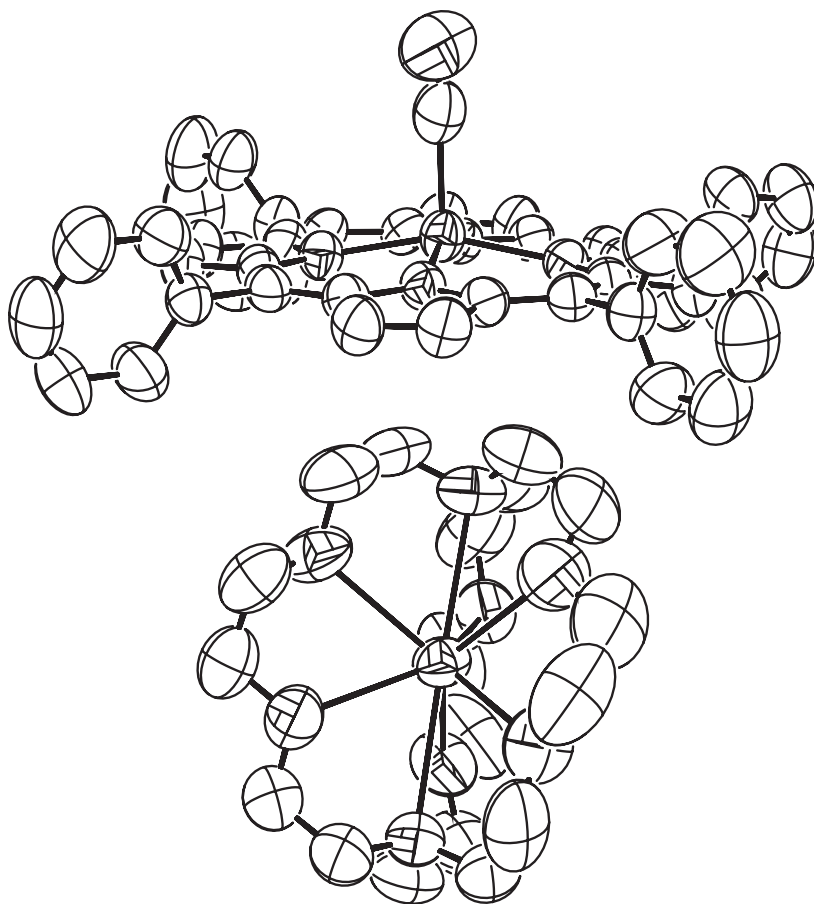


Figure S8. ORTEP diagram of asymmetric unit of $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 400K. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

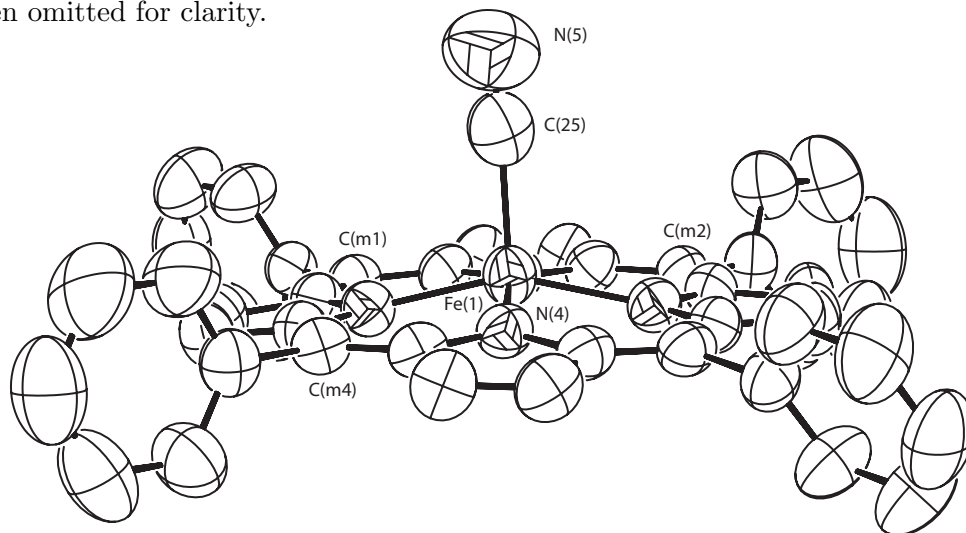


Figure S9. ORTEP diagram of the $[\text{Fe}(\text{TPP})(\text{CN})]^-$ anion in $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})]$ # 2 at 400K displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

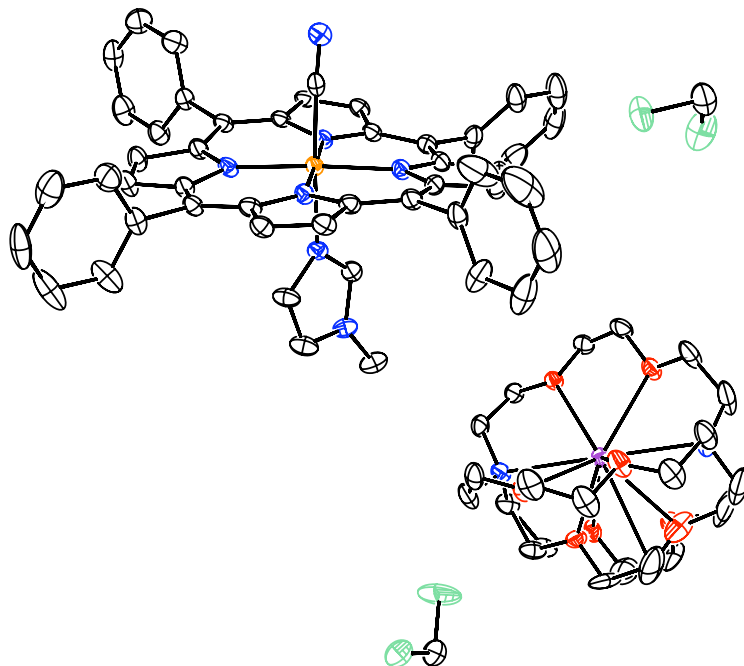


Figure S10. ORTEP diagram of asymmetric unit of $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})(1\text{-MeIm})]\cdot 2\text{CH}_2\text{Cl}_2$. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

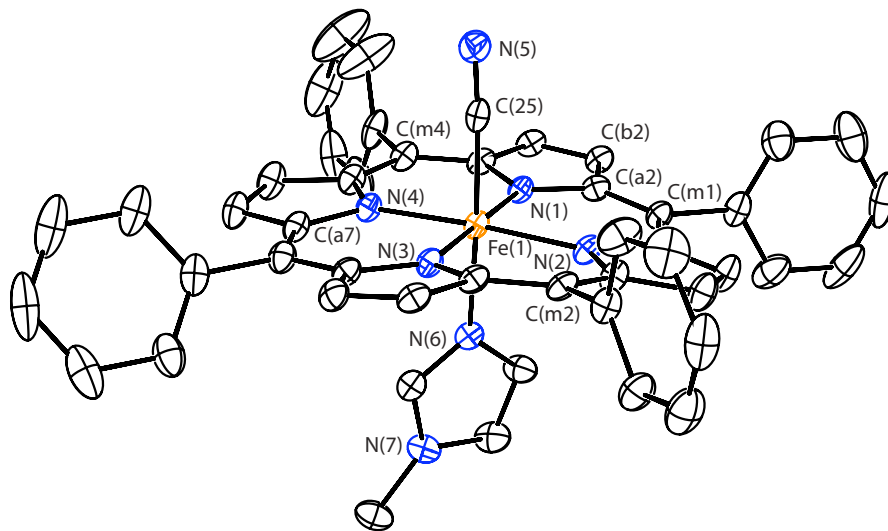


Figure S11. ORTEP diagram of the $[\text{Fe}(\text{TPP})(\text{CN})(1\text{-MeIm})]^-$ anion in $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})(1\text{-MeIm})]\cdot 2\text{CH}_2\text{Cl}_2$ displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

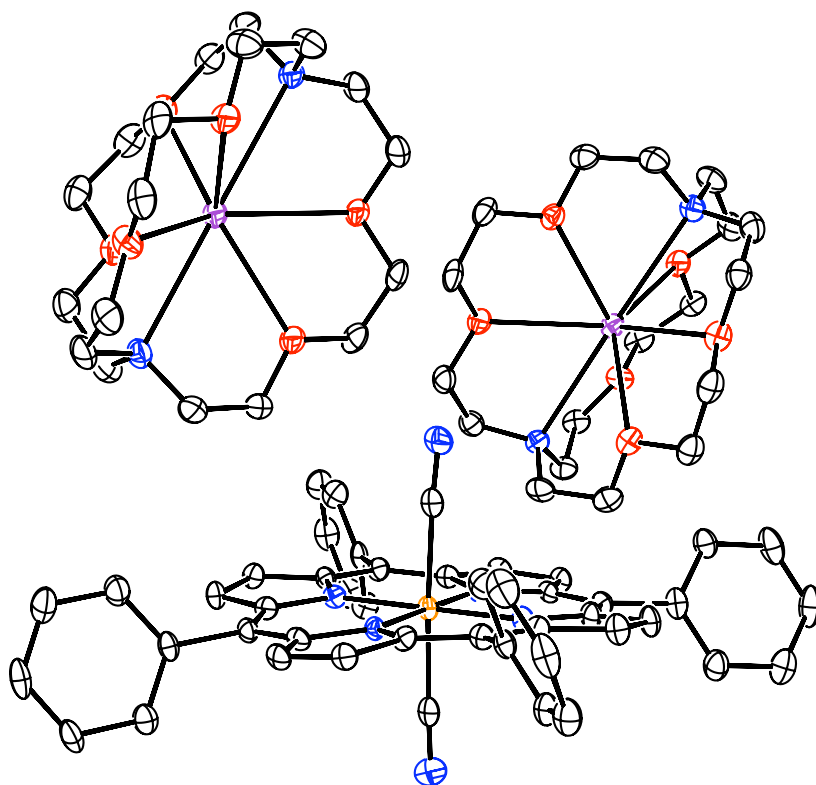


Figure S12. ORTEP diagram of asymmetric unit of $[\text{K}(222)]_2[\text{Fe}(\text{TPP})(\text{CN})_2] \cdot 4\text{PhCl}$. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

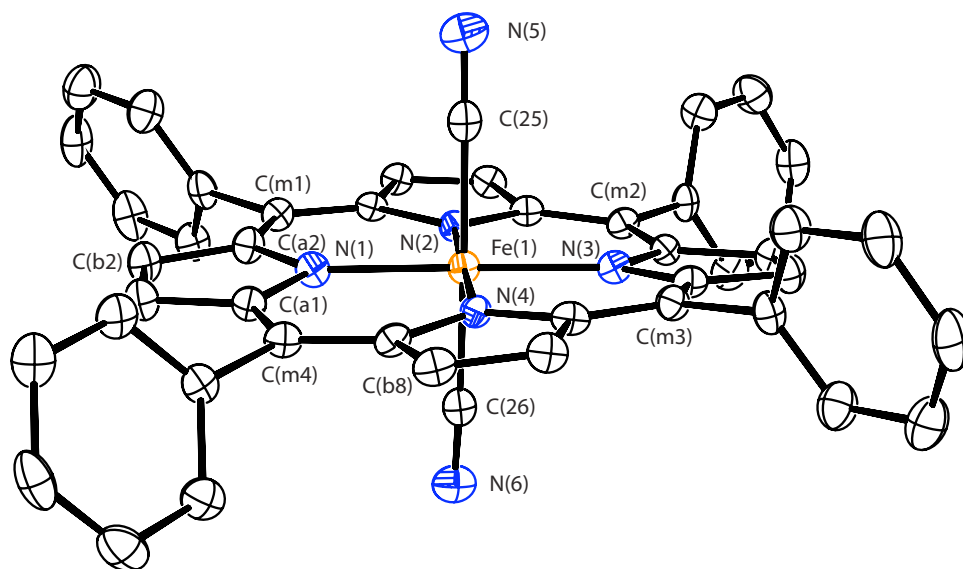


Figure S13. ORTEP diagram of the $[\text{Fe}(\text{TPP})(\text{CN})_2]^{2-}$ anion in $[\text{K}(222)]_2[\text{Fe}(\text{TPP})(\text{CN})_2] \cdot 4\text{PhCl}$ displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

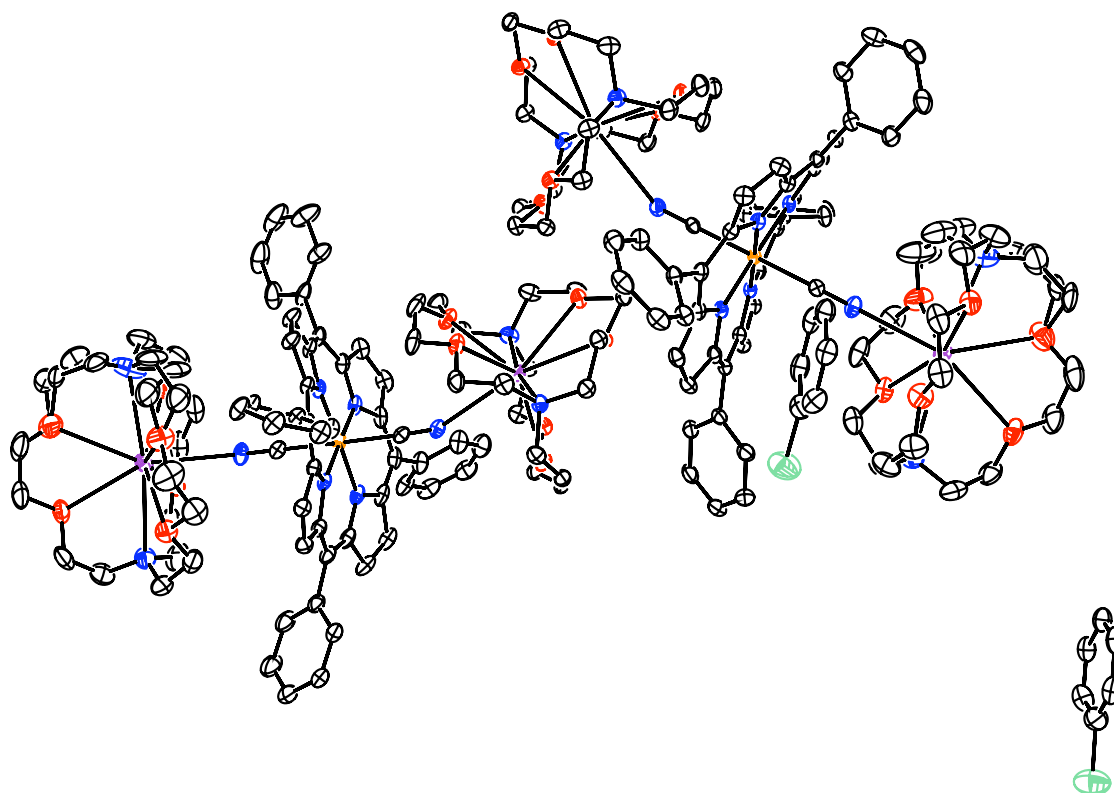


Figure S14. ORTEP diagram of asymmetric unit of $[\text{K}(222)]_2[\text{Fe}(\text{TPP})(\text{CN})_2] \cdot \text{PhCl}$. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

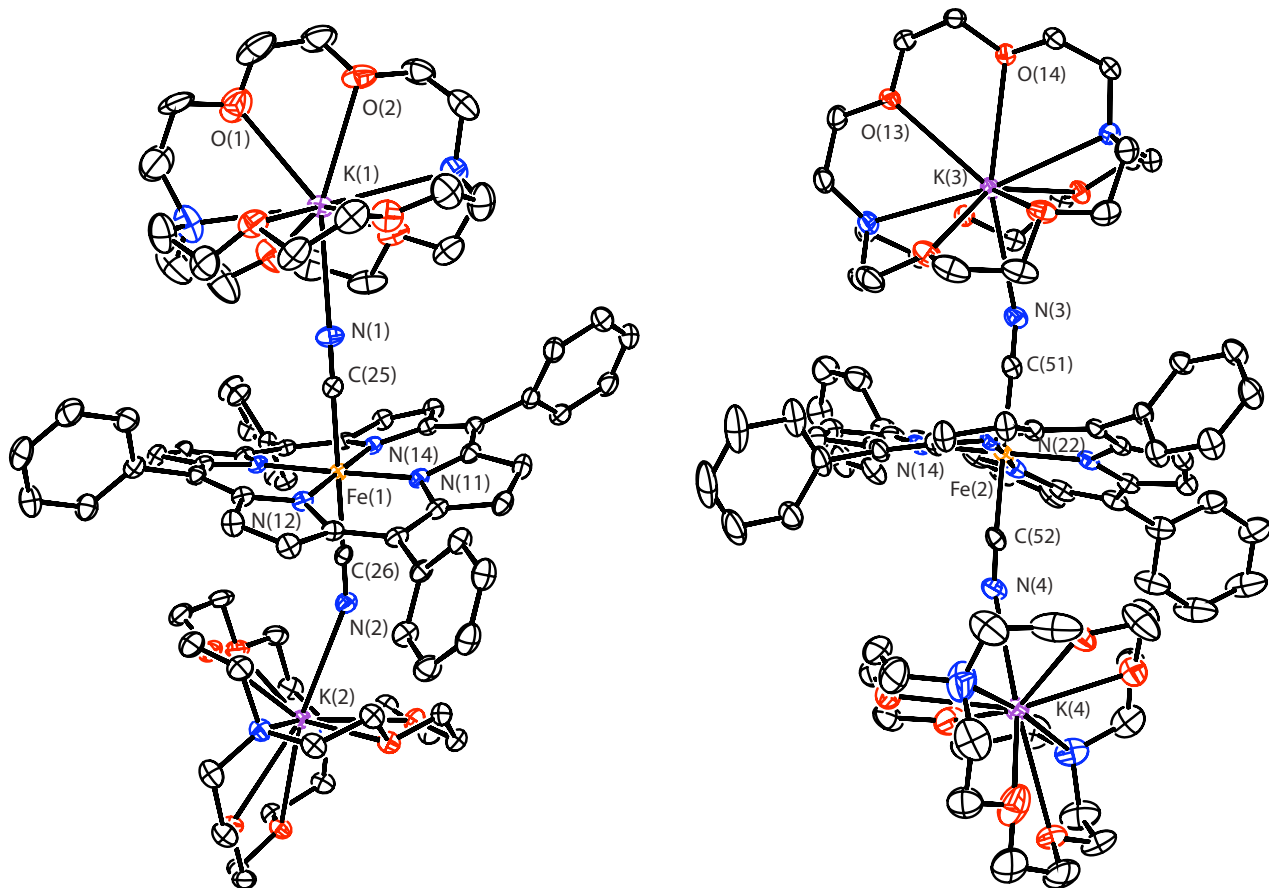


Figure S15. ORTEP diagram of two $[\text{Fe}(\text{TPP})(\text{CN})_2]^{2-}$ anions in $[\text{K}(222)]_2[\text{Fe}(\text{TPP})(\text{CN})_2] \cdot \text{PhCl}$ displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

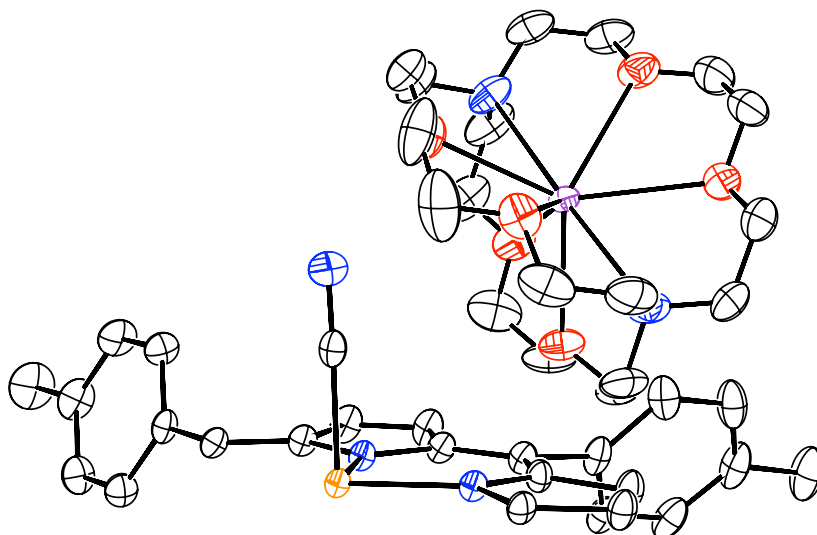


Figure S16. ORTEP diagram of asymmetric unit of $[\text{K}(222)]_2[\text{Fe}(\text{TTP})(\text{CN})_2] \cdot 5.8\text{CH}_2\text{Cl}_2$. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms and solvents have been omitted for clarity.

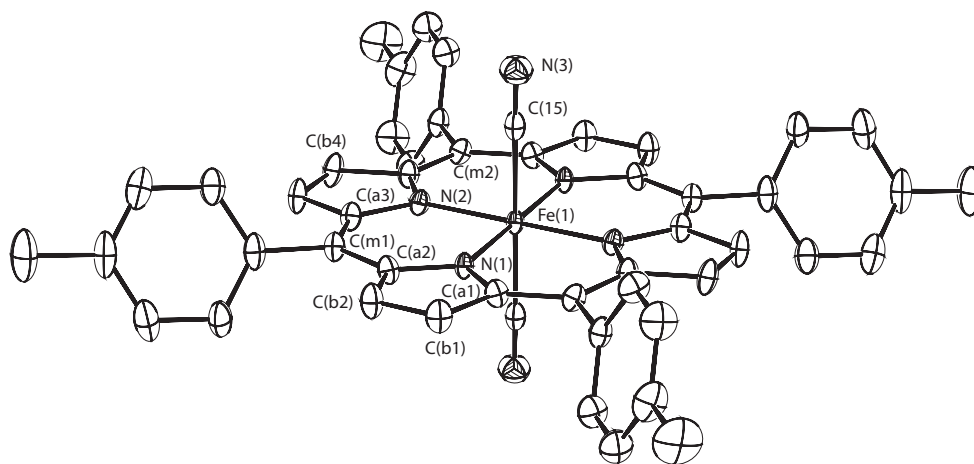


Figure S17. ORTEP diagram of the $[\text{Fe}(\text{TTP})(\text{CN})_2]^{2-}$ anion in $[\text{K}(222)]_2[\text{Fe}(\text{TTP})(\text{CN})_2] \cdot 5.8\text{CH}_2\text{Cl}_2$ displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

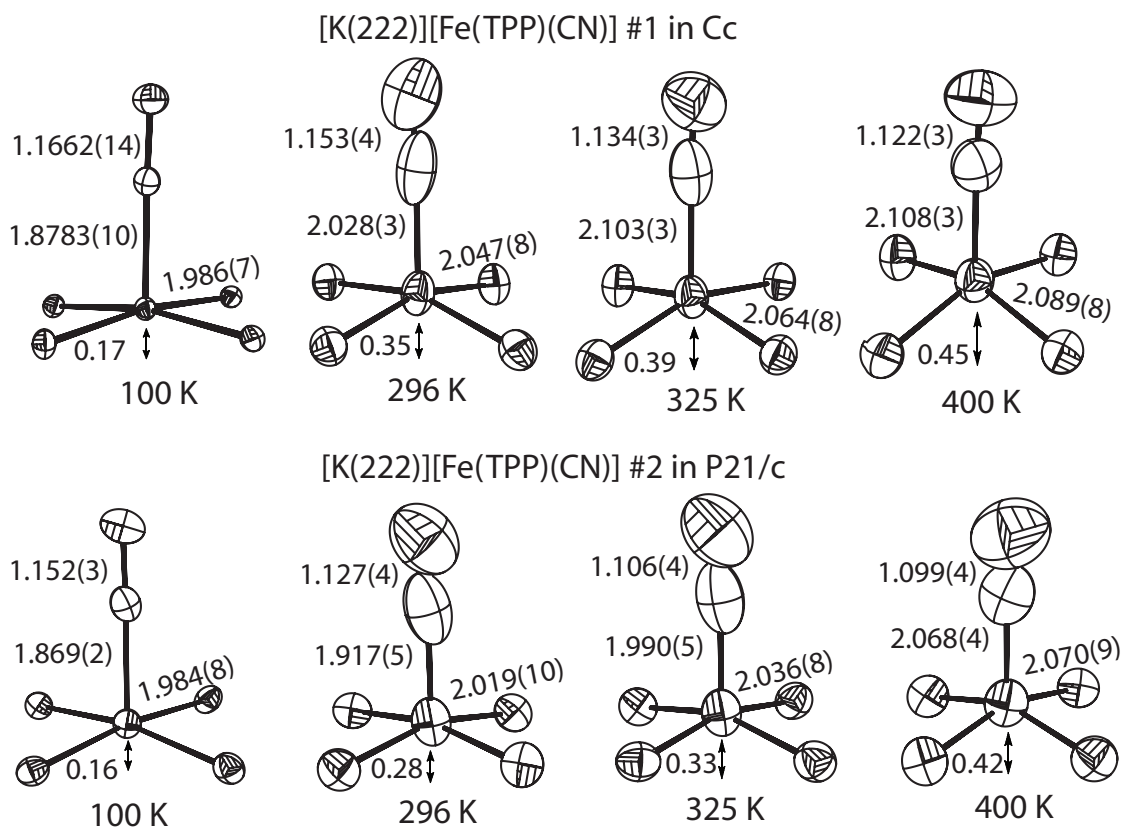


Figure S18. ORTEP diagrams of [K(222)][Fe(TPP)(CN)] # 1 and 2 displaying the cyanide groups and the core atoms of porphyrin (Fe and four pyrrole N atoms). Values of axial ligand and average equatorial bond distances are given as well as the iron displacement from the mean N_4 plane. Thermal ellipsoids are contoured at the 50% probability level.

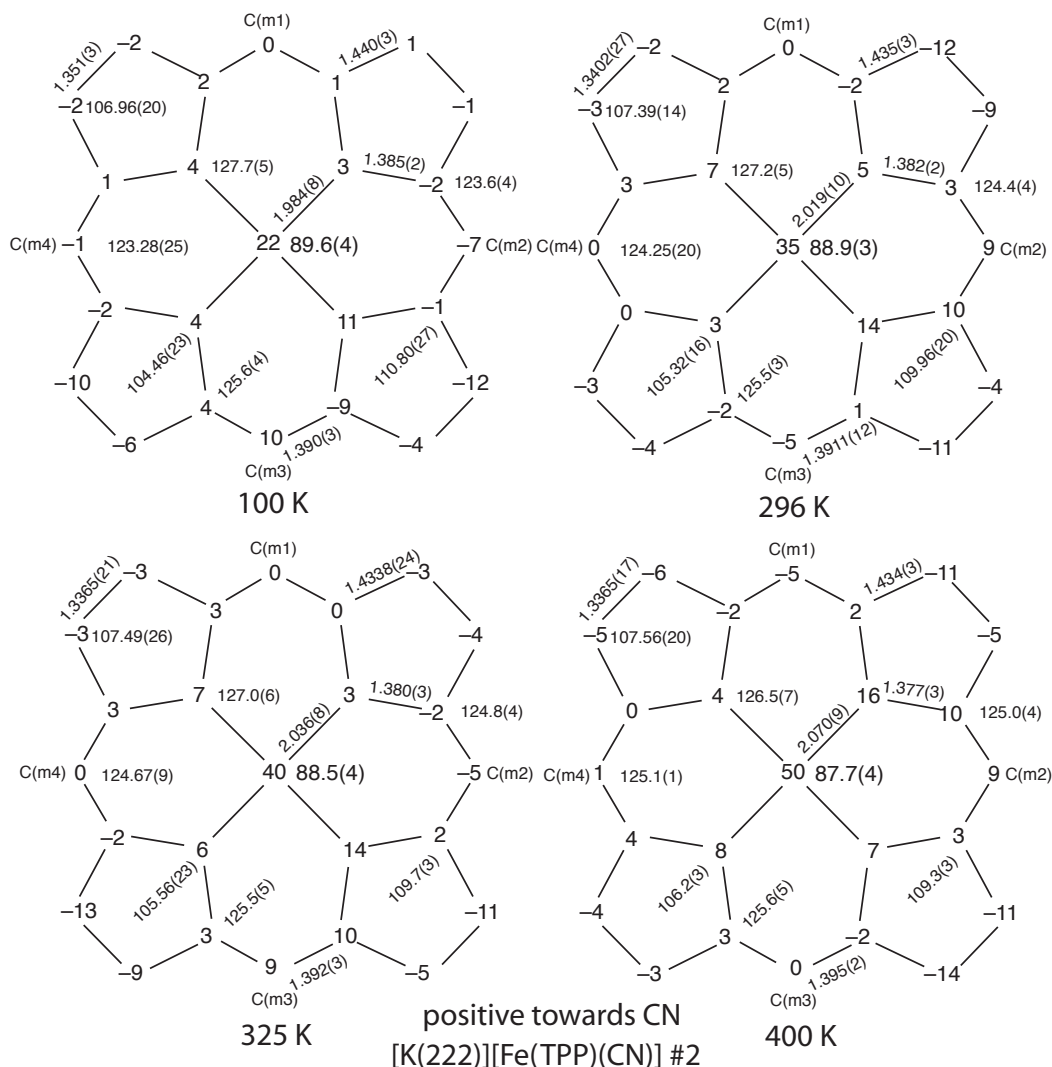


Figure S19. Formal diagram of the porphyrin cores of $[\text{K}(\text{222})][\text{Fe}(\text{TPP})(\text{CN})] \# 2$ at 100, 296, 325 and 400K structures. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed.

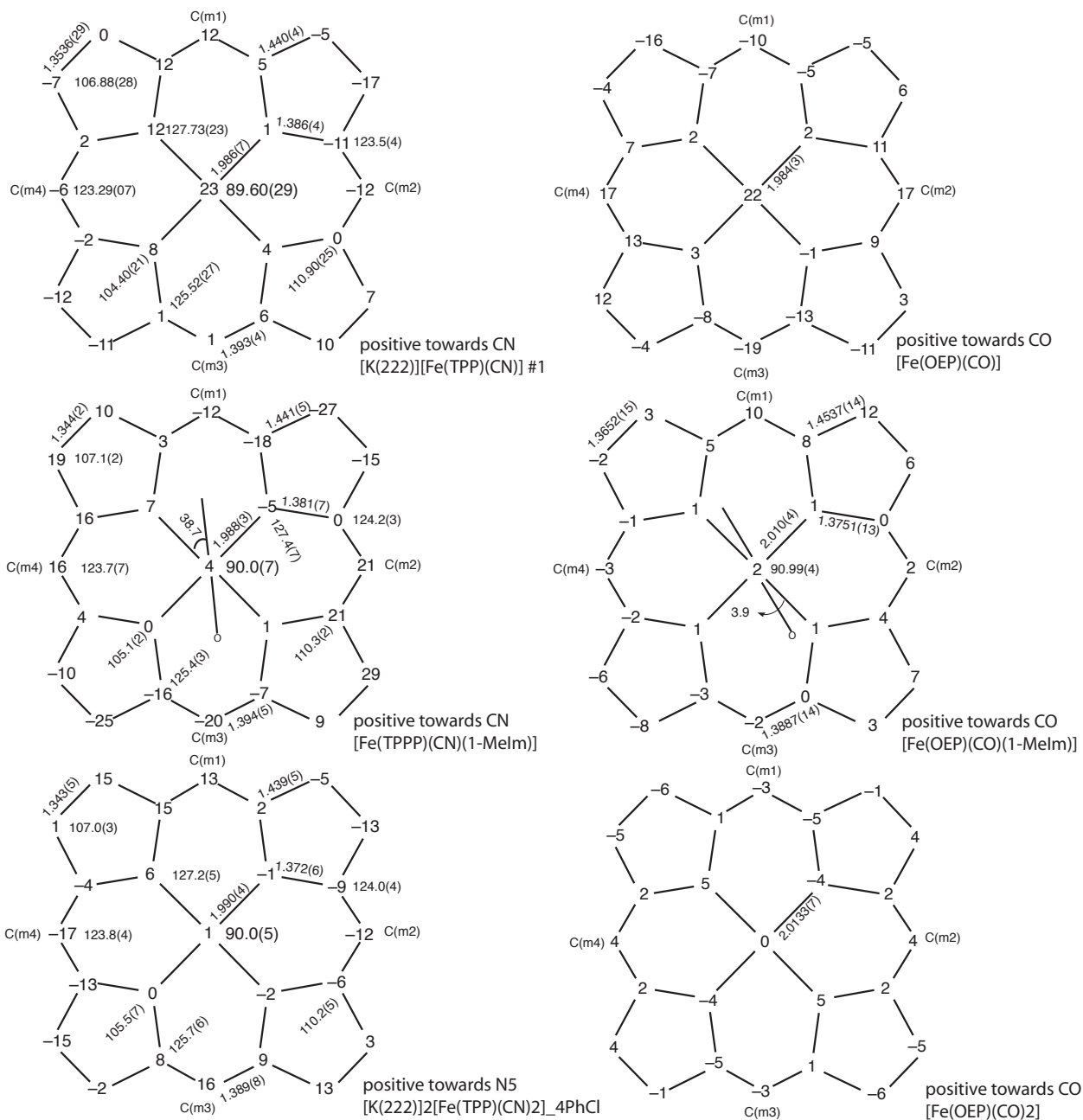


Figure S20. Formal diagram of the porphyrin cores of $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})] \# 1$, $[\text{K}(222)][\text{Fe}(\text{TPP})(\text{CN})(1\text{-MeIm})]$ and $[\text{K}(222)]_2[\text{Fe}(\text{TPP})(\text{CN})_2] \cdot 4\text{PhCl}$ structures. Three carbonyl structures are also presented for comparison. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed.

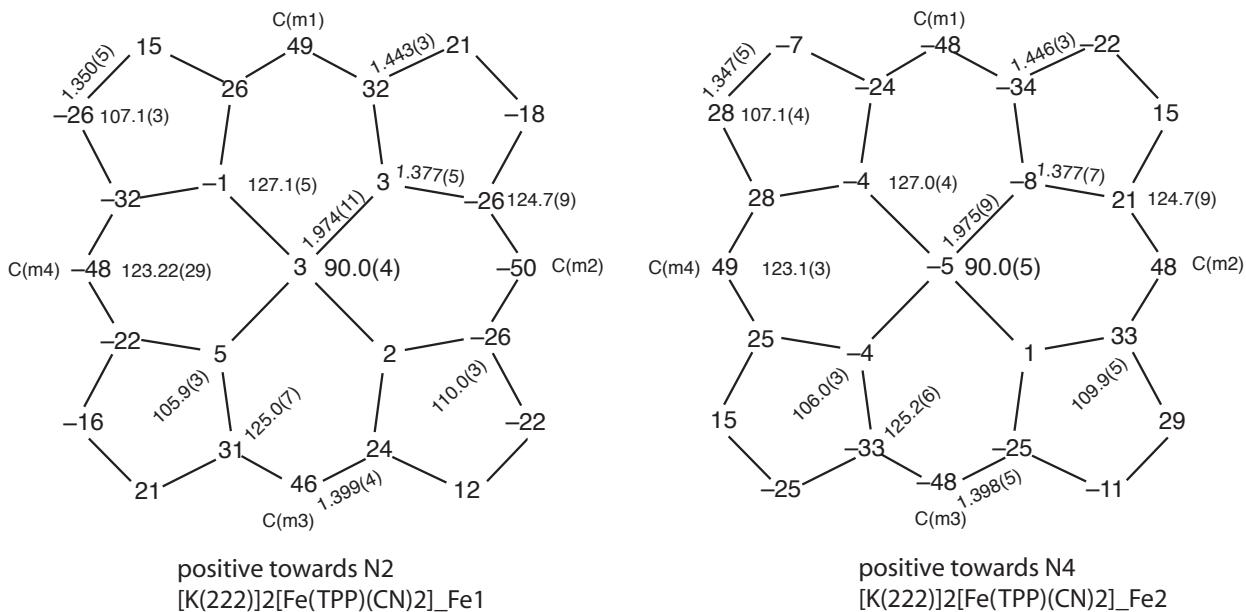


Figure S21. Formal diagram of the porphyrin cores of $[\text{K}(222)]_2[\text{Fe}(\text{TPP})(\text{CN})_2] \cdot \text{PhCl}$ structure. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed.

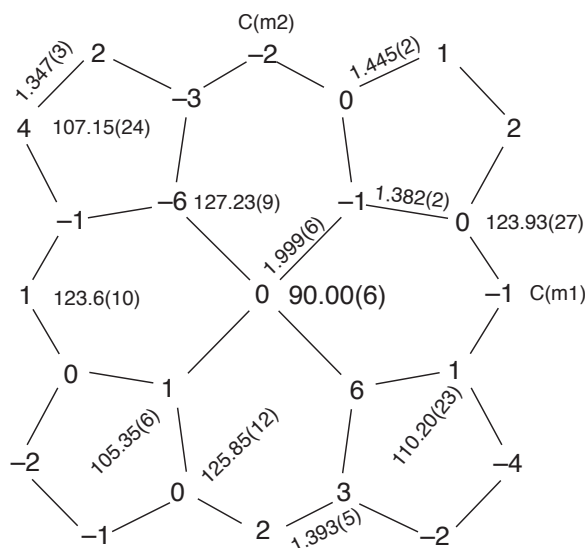


Figure S22. Formal diagram of the porphyrin cores of $[\text{K}(222)]_2[\text{Fe}(\text{TTP})(\text{CN})_2] \cdot 5.8\text{CH}_2\text{Cl}_2$ structure. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed.