Supporting Information for

Interplay of Structure and Vibrational Dynamics in Six-coordinate Heme Nitrosyls

Nathan J. Silvernail, Alexander Barabanschikov, Jeffrey W. Pavlik, Bruce C. Noll, Jiyong Zhao, E. Ercan Alp, Wolfgang Sturhahn, J. Timothy Sage, and W. Robert Scheidt*

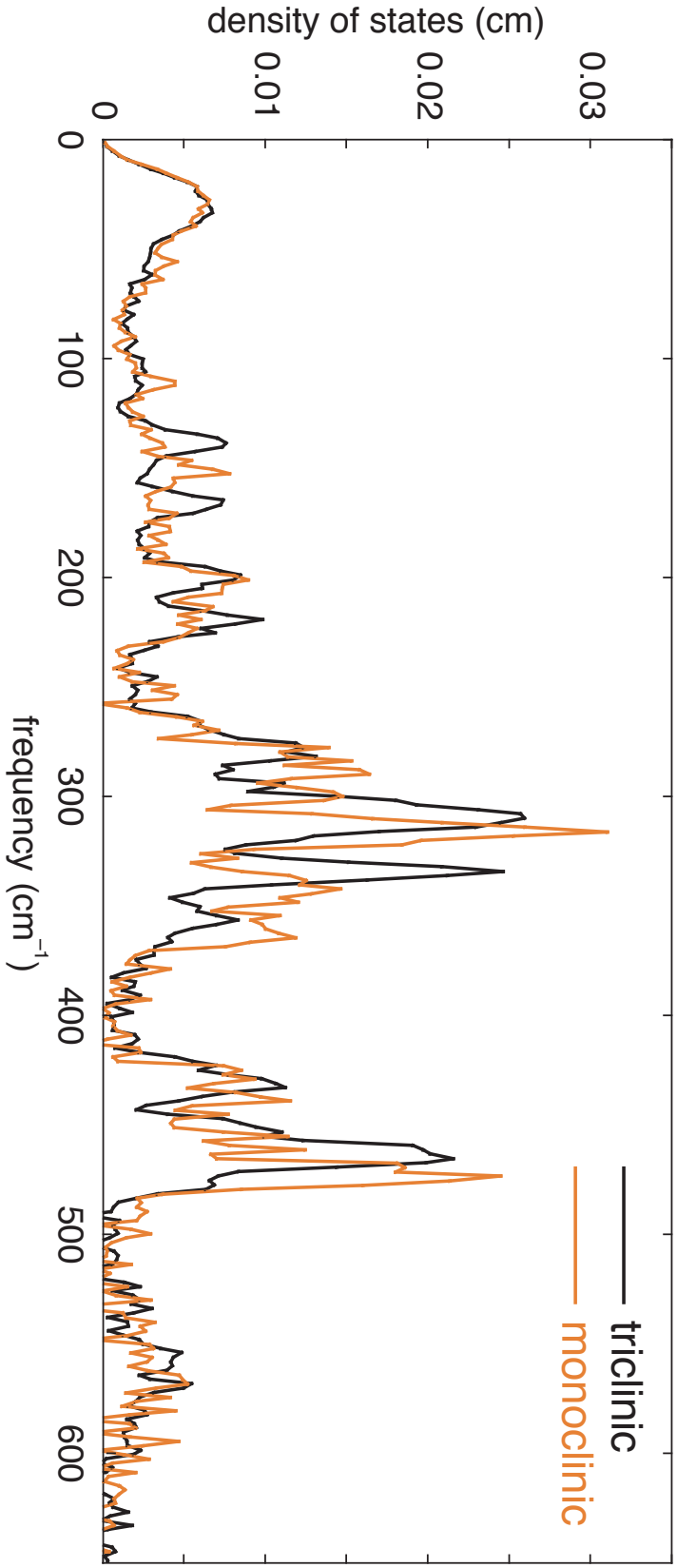

Figure 1. Comparison of the measured VDOS for powder samples of *mono*- and *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)].

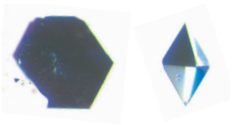

Figure 2. Illustration of the two crystalline forms of [Fe(T*p*FPP)(1-MeIm)(NO)]. The triclinic form is on the right.

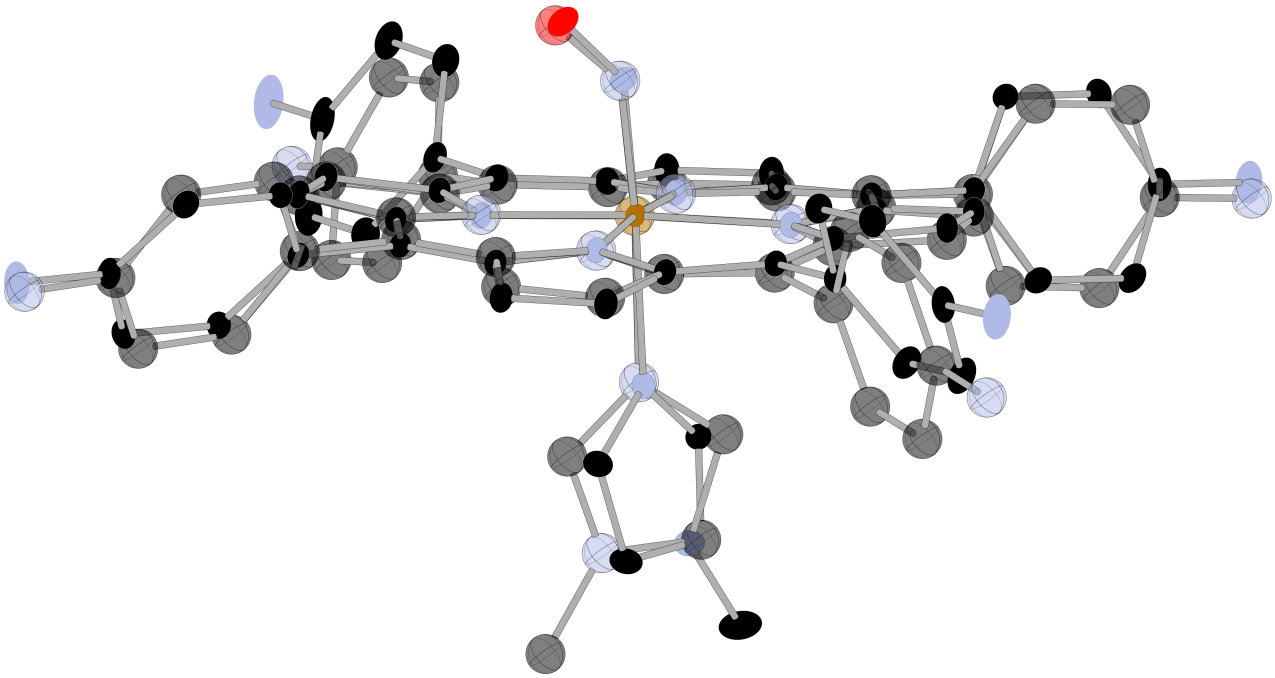

Figure 3. Diagram showing overlap of molecules of the two polymorphs. The two molecules are centered on the four porphyrin nitrogen atoms. The triclinic species is drawn with thermal ellipsoids contoured at the 50% probability level as solid surfaces, whereas atoms of the monoclinic form are drawn with translucent spheres of arbitary radius. Atoms of the NO and the porphyrin core are seen to be close to overlap, whereas the imidiazole and peripheral *p*-fluorophenyl groups are not.

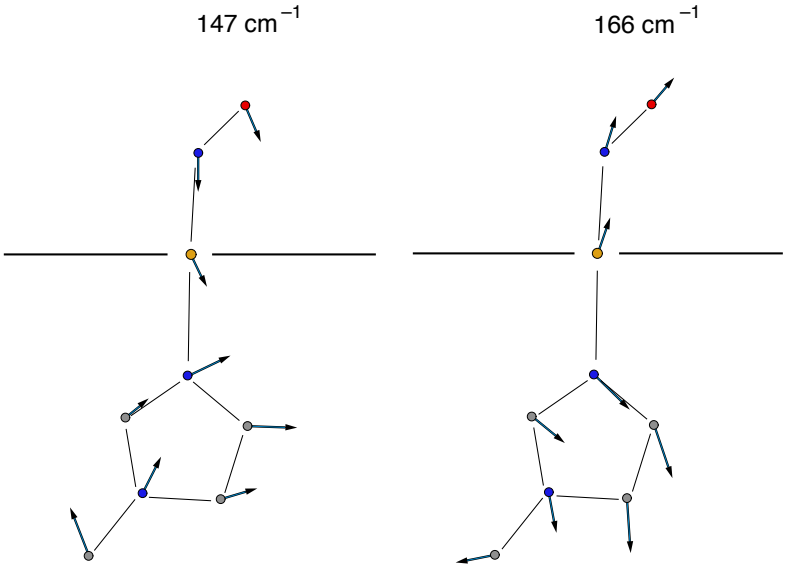

Figure 4. Predicted vibrational modes for *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] with frequencies of 147 $cm^{-1}$and 166 cm^{-1}.

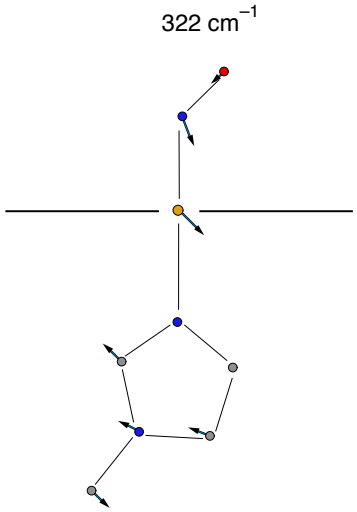

Figure 5. Predicted vibrational mode for the complex in-plane and out-of-plane motion of the FeNO group and the imidazole leading to changes in the Fe–N_{Im} bond at 322 cm^{-1}. The experimentally observed values are 315 cm^{-1} in *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] and 310 cm^{-1} in *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)].

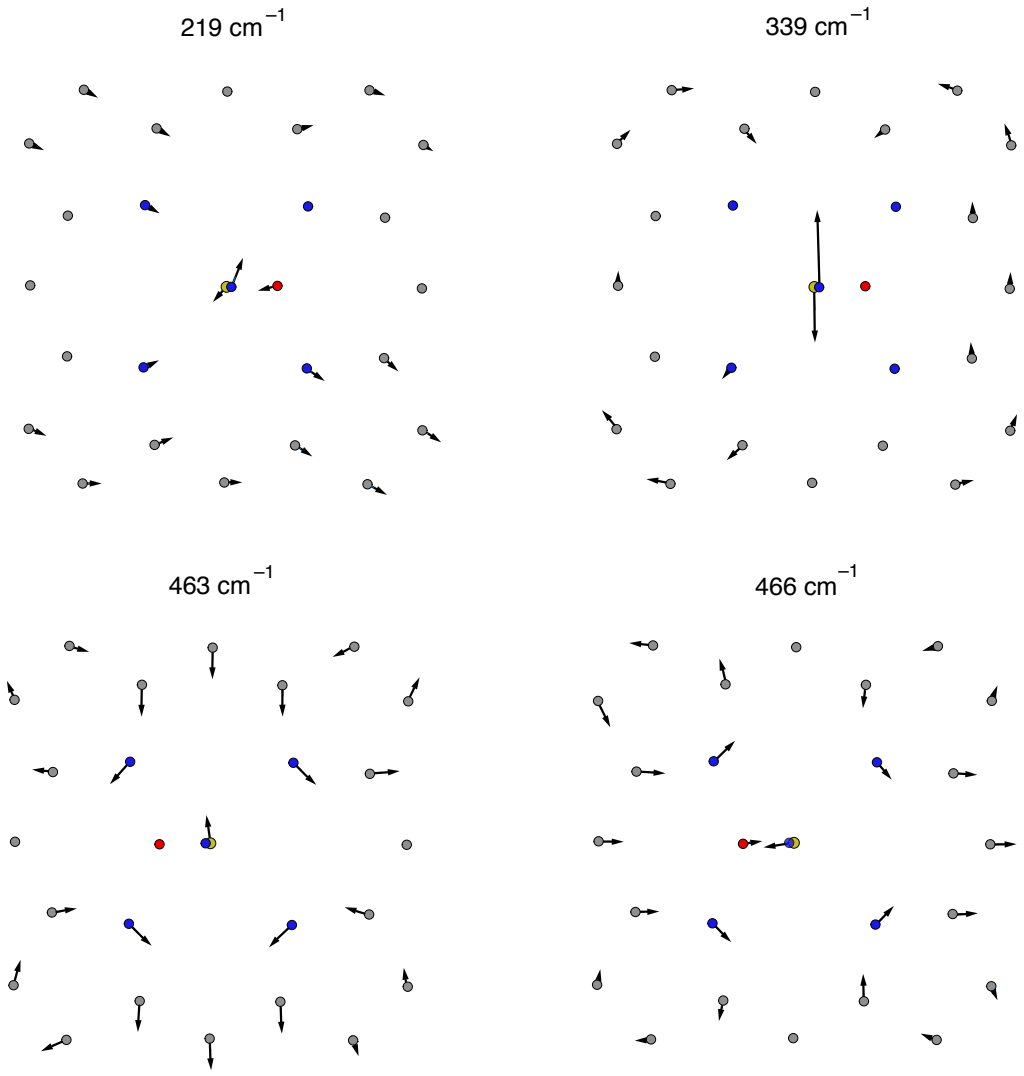

Figure 6. Predicted vibrational modes for the in-plane motion of the FeNO group. The imidazole group is omitted for clarity. The experimentally observed values that correspond to the calculated values in parentheses for *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] are 219 (219), 343 (339) and 456/471 (463/466) cm^{-1} and for *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] are 218 (219), 338 (339) and 457 (463/466) cm^{-1}.

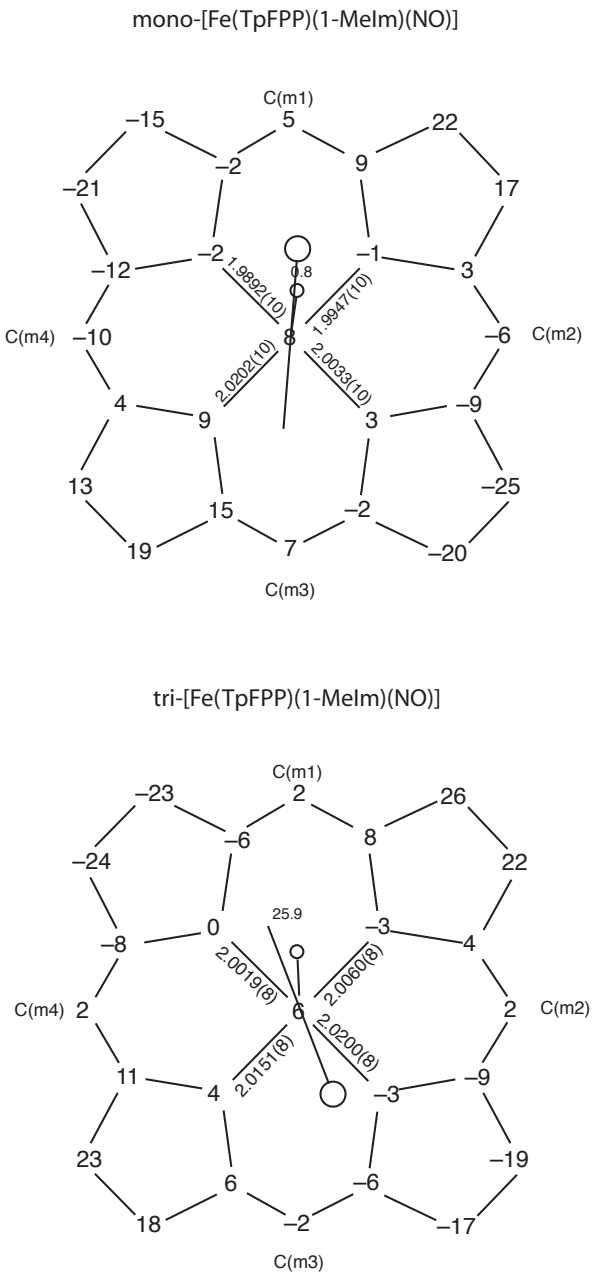

Figure 7. Formal diagram of the porphyrinato core of *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] (top) and *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] (bottom) both displaying the perpendicular displacements (in units of 0.01 Å) of the core atoms from the 24-atom mean plane. Positive displacements are toward the nitrosyl-coordinated face, while the imidazole ligand is displaced on the negative side of the porphyrin core. The orientation of the imidazole ligand with respect to the porphyrin core is also illustrated. The location of the 1-methyl group is represented by the large circle, while the location nitrosyl projection onto the porphyrin core is indicated by the small circle. Average bond distances (Å) and angles (degrees) are also displayed.

Experimental Section

General Information. All reactions were carried out under anaerobic conditions. Chloroform (Fisher), 1-propanol (Acros) and 1-methylimidazole (Acros) were used as received. Nitric oxide (Mittler Specialty Gases) was purified by passing it through a trap containing 4 Å molecular sieves immersed in an ethanol/dry ice slurry.[1] Free base T*p*FPPyrin [H_2T*p*FPP] was prepared according to Adler et al.[2] [Fe(T*p*FPP)(Cl)] was prepared according to the metalation procedure of Adler et al.[3] Infrared spectra were recorded on a Nicolet Nexus 870 FT-IR spectrometer. Solid state infrared samples were prepared by gently mulling a suitable crystal between two NaCl plates with a small amount of Nujol to allow dispersion. Samples were prepared for Mössbauer spectroscopy by weighing approximately 40 mg of selected crystals, grinding them in a small volume of Apiezon M grease to form a mull and placing them into a Mössbauer cup. Measurements were performed on a constant acceleration spectrometer from 15 K to 300 K.

Synthesis of [Fe(T*p*FPP)(NO)(1-MeIm)]. [Fe(T*p*FPP)(NO)(1-MeIm)] was prepared using modifications of a previously reported synthesis.[4] Approximately 30 mg of [Fe(T*p*FPP)(Cl)] was placed into a 10 mL beaker along with 3 mL of chloroform and 3 mL of 1-methylimidazole. This beaker was then placed into a crystallization jar along with 0.5 mL of 1-propanol, 2 ml of chloroform and 3 mL of 1-methylimidazole, then subsequently sealed with a rubber stopper. The system was purged with Ar for 10 min and NO was bubbled through the inner and outer solutions for 10 min. Crystals were found after 3 weeks.

X-Ray Crystallographic Studies. Crystal data were collected and integrated using a Bruker Apex system, with graphite monochromated Mo-Kα (λ= 0.71073 Å) radiation from 100–350 K (700 Series Oxford Cryostream). The program SADABS[5] was applied for absorption correction. All structures were solved using the Patterson method in SHELXS-97[7] and refined

using SHELXL-97.[8] All atoms were found after successive full-matrix least-squares refinement cycles on F^2 and refined with anisotropic thermal parameters. Hydrogen atom positions were idealized with a riding model and fixed thermal parameters [U_{ij} = 1.2Uij(eq) or 1.5Uij(eq)] for the atom to which they are bonded. Complete crystallographic details are given in the below.

Calculations. DFT calculations provided the optimized structures and detailed vibrational predictions for the six-coordinate porphyrins *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] and *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)]. DFT calculations were performed with Gaussian 03,[9] employing the B3LYP[10] hybrid functional. We used Ahlrich's VTZ[11] basis set for Fe atom and 6-31G* basis set for all other atoms.

References and Notes

(1) Dodd, R. E.; Robinson,P. L. *Experimental Inorganic Chemistry*, Elsevier: New York, 1957, p 253.

(2) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(3) Adler, A. D.; Longo, F. R.; Kampus, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(4) Wyllie, G. R. A.; Schulz, C. E.; Scheidt, W. R. *Inorg. Chem.* **2003**, *42*, 5722.

(5) Sheldrick, G. M.: Program for empirical absorption correction of area detector data. Universität Göttingen, Germany, 1996.

(6) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(7) Patterson, A. L. *Phys. Rev.* **1934**, *46*, 372.

(8) SHELXL-97: FORTRAN program for crystal structure refinement, © 1997, Sheldrick, G. M., Universität Göttingen, Germany.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.: Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.: Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03: Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.

(10) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5684. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785.

(11) Schafer, A.; Horn, H.; Ahlrich, R. *J. Phys. Chem.* **1992**, *97*, 2571.

Supporting Information

Table S1. Complete Crystallographic Details for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)]

formula	$C_{48}H_{30}F_4FeN_7O$
FW, amu	852.64
a, Å	11.4205(2)
b, Å	12.1603(2)
c, Å	14.3296(2)
α, deg	92.7890(10)
β, deg	102.6510(10)
γ, deg	99.5850(10)
V, Å^3	1907.12(5)
space group	$P\bar{1}$
Z	2
D_c, g/cm^3	1.485
F(000)	874
μ, mm^{-1}	0.465
crystal dimensions, mm	0.42 × 0.16 × 0.16
radiation	MoKα, $\bar{\lambda}$ = 0.71073 Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.46–33.14
index range	$-17 \leq h \leq 17$
	$-18 \leq k \leq 18$
	$-22 \leq l \leq 22$
total data collected	86150
absorption correction	Multiscan
relative transmission coefficients (I)	0.9297 and 0.8296
unique data	14421 (R_{int} = 0.033)
unique observed data [I > 2σ(I)]	12319
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	14421/0/551
goodness-of-fit (pased on F^2)	1.044
final R indices [I > 2σ(I)]	R_1 = 0.0346, wR_2 = 0.0936
final R indices (all data)	R_1 = 0.0432, wR_2 = 0.0995

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

atom	x	y	z	U(eq)
Fe(1)	0.37887(1)	0.12126(1)	0.25232(1)	0.0116(1)
N(1)	0.41016(8)	0.15916(7)	0.12453(6)	0.0132(1)
N(2)	0.23966(8)	−0.00058(7)	0.18726(6)	0.0136(1)
N(3)	0.33820(8)	0.09191(7)	0.38017(6)	0.0139(1)
N(4)	0.51118(8)	0.25020(7)	0.31725(6)	0.0135(1)
C(m1)	0.25724(9)	0.01086(8)	0.01891(7)	0.0136(2)
C(m2)	0.16876(9)	−0.06899(8)	0.32883(7)	0.0152(2)
C(m3)	0.49306(9)	0.23845(8)	0.48549(7)	0.0143(2)
C(m4)	0.58108(9)	0.31928(8)	0.17611(7)	0.0142(2)
C(a1)	0.49346(9)	0.24676(8)	0.10693(7)	0.0142(2)
C(a2)	0.34838(9)	0.10678(8)	0.03581(7)	0.0140(2)
C(a3)	0.21061(9)	−0.04032(8)	0.09169(7)	0.0135(2)
C(a4)	0.17014(9)	−0.07532(8)	0.23132(7)	0.0143(2)
C(a5)	0.24704(9)	0.01148(8)	0.39719(7)	0.0152(2)
C(a6)	0.39474(9)	0.14884(8)	0.46803(7)	0.0149(2)
C(a7)	0.54820(9)	0.28262(8)	0.41398(7)	0.0142(2)
C(a8)	0.58968(9)	0.31766(8)	0.27481(7)	0.0140(2)
C(b1)	0.47994(10)	0.25252(8)	0.00491(7)	0.0174(2)
C(b2)	0.39054(10)	0.16581(8)	−0.03893(7)	0.0171(2)
C(b3)	0.12261(9)	−0.14336(8)	0.07636(7)	0.0159(2)
C(b4)	0.09718(9)	−0.16446(8)	0.16263(7)	0.0167(2)
C(b5)	0.24476(10)	0.01977(9)	0.49774(7)	0.0193(2)
C(b6)	0.33663(10)	0.10436(9)	0.54150(7)	0.0188(2)
C(b7)	0.65441(9)	0.37031(8)	0.43271(7)	0.0166(2)
C(b8)	0.68091(9)	0.39107(8)	0.34665(7)	0.0171(2)
F(10)	0.06846(7)	−0.17639(7)	−0.36094(5)	0.0314(2)
C(11)	0.20708(9)	−0.03887(8)	−0.08199(7)	0.0138(2)
C(12)	0.28440(9)	−0.07000(8)	−0.13779(7)	0.0157(2)
C(13)	0.23876(10)	−0.11560(9)	−0.23256(7)	0.0182(2)
C(14)	0.11427(10)	−0.13133(9)	−0.26907(7)	0.0193(2)
C(15)	0.03446(10)	−0.10236(9)	−0.21670(8)	0.0193(2)
C(16)	0.08176(9)	−0.05508(8)	−0.12296(7)	0.0167(2)
F(20)	−0.16311(9)	−0.38986(7)	0.45370(6)	0.0390(2)
C(21)	0.08033(10)	−0.15501(8)	0.36121(7)	0.0172(2)

Table S2. Continued

atom	x	y	z	U(eq)
C(22)	0.12208(11)	−0.23148(9)	0.42420(8)	0.0211(2)
C(23)	0.04035(12)	−0.31227(9)	0.45502(8)	0.0253(2)
C(24)	−0.08232(12)	−0.31354(10)	0.42200(8)	0.0265(2)
C(25)	−0.12797(11)	−0.24042(11)	0.35922(9)	0.0271(2)
C(26)	−0.04558(11)	−0.16073(10)	0.32871(8)	0.0231(2)
F(30)	0.65379(8)	0.43566(7)	0.86469(5)	0.0321(2)
C(31)	0.53993(9)	0.29193(8)	0.58598(7)	0.0146(2)
C(32)	0.52427(10)	0.40082(9)	0.60886(7)	0.0191(2)
C(33)	0.56468(11)	0.45120(9)	0.70235(8)	0.0214(2)
C(34)	0.61875(11)	0.38961(9)	0.77249(7)	0.0206(2)
C(35)	0.63652(10)	0.28229(9)	0.75326(7)	0.0200(2)
C(36)	0.59698(10)	0.23378(8)	0.65902(7)	0.0175(2)
F(40)	0.92729(7)	0.62129(6)	0.04747(5)	0.0295(2)
C(41)	0.67278(9)	0.40065(8)	0.14233(7)	0.0155(2)
C(42)	0.67883(11)	0.51607(9)	0.15696(8)	0.0218(2)
C(43)	0.76489(12)	0.59115(9)	0.12512(9)	0.0249(2)
C(44)	0.84285(10)	0.54852(9)	0.07864(7)	0.0207(2)
C(45)	0.83972(10)	0.43549(9)	0.06150(8)	0.0207(2)
C(46)	0.75387(10)	0.36150(9)	0.09430(8)	0.0193(2)
N(5)	0.47556(8)	0.02285(7)	0.25752(6)	0.0160(2)
O(1)	0.49211(8)	−0.05039(7)	0.20746(6)	0.0225(2)
N(6)	0.25766(8)	0.24222(7)	0.23532(6)	0.0151(1)
N(7)	0.15344(9)	0.37146(8)	0.26668(7)	0.0210(2)
C(1)	0.22398(10)	0.29820(9)	0.30361(7)	0.0180(2)
C(2)	0.14186(11)	0.36243(10)	0.16936(8)	0.0231(2)
C(3)	0.20612(10)	0.28270(9)	0.15055(7)	0.0202(2)
C(4)	0.10199(16)	0.44965(14)	0.31907(10)	0.0376(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. The estimated standard deviations of the least significant digits are given in parentheses.

Table S3. Bond Lengths for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

bond	length (Å)	bond	length (Å)
Fe(1)–N(5)	1.7521(9)	C(13)–H(13)	0.9500
Fe(1)–N(1)	2.0019(8)	C(14)–C(15)	1.3780(15)
Fe(1)–N(2)	2.0060(8)	C(15)–C(16)	1.3894(14)
Fe(1)–N(4)	2.0151(8)	C(15)–H(15)	0.9500
Fe(1)–N(3)	2.0200(8)	C(16)–H(16)	0.9500
Fe(1)–N(6)	2.1689(9)	F(20)–C(24)	1.3633(13)
N(1)–C(a1)	1.3774(12)	C(21)–C(22)	1.3955(15)
N(1)–C(a2)	1.3778(12)	C(21)–C(26)	1.3999(16)
N(2)–C(a4)	1.3748(12)	C(22)–C(23)	1.3961(15)
N(2)–C(a3)	1.3792(12)	C(22)–H(22)	0.9500
N(3)–C(a6)	1.3752(12)	C(23)–C(24)	1.374(2)
N(3)–C(a5)	1.3766(12)	C(23)–H(23)	0.9500
N(4)–C(a8)	1.3744(12)	C(24)–C(25)	1.378(2)
N(4)–C(a7)	1.3748(12)	C(25)–C(26)	1.3904(16)
C(m1)–C(a3)	1.3982(13)	C(25)–H(25)	0.9500
C(m1)–C(a2)	1.4002(13)	C(26)–H(26)	0.9500
C(m1)–C(11)	1.4903(13)	F(30)–C(34)	1.3568(12)
C(m2)–C(a5)	1.3958(13)	C(31)–C(36)	1.3952(14)
C(m2)–C(a4)	1.3992(13)	C(31)–C(32)	1.3982(14)
C(m2)–C(21)	1.4934(13)	C(32)–C(33)	1.3922(14)
C(m3)–C(a6)	1.3977(13)	C(32)–H(32)	0.9500
C(m3)–C(a7)	1.3995(13)	C(33)–C(34)	1.3812(16)
C(m3)–C(31)	1.4961(13)	C(33)–H(33)	0.9500
C(m4)–C(a1)	1.3958(13)	C(34)–C(35)	1.3777(16)
C(m4)–C(a8)	1.3973(13)	C(35)–C(36)	1.3937(14)
C(m4)–C(41)	1.4946(13)	C(35)–H(35)	0.9500
C(a1)–C(b1)	1.4424(13)	C(36)–H(36)	0.9500
C(a2)–C(b2)	1.4421(13)	F(40)–C(44)	1.3621(12)
C(a3)–C(b3)	1.4441(13)	C(41)–C(42)	1.3970(14)
C(a4)–C(b4)	1.4402(13)	C(41)–C(46)	1.3972(15)
C(a5)–C(b5)	1.4457(14)	C(42)–C(43)	1.3950(15)
C(a6)–C(b6)	1.4434(14)	C(42)–H(42)	0.9500
C(a7)–C(b7)	1.4419(13)	C(43)–C(44)	1.3729(17)
C(a8)–C(b8)	1.4399(13)	C(43)–H(43)	0.9500

Table S3. Continued

bond	length (Å)	bond	length (Å)
C(b1)–C(b2)	1.3583(14)	C(44)–C(45)	1.3776(16)
C(b1)–H(b1)	0.9500	C(45)–C(46)	1.3931(14)
C(b2)–H(b2)	0.9500	C(45)–H(45)	0.9500
C(b3)–C(b4)	1.3570(14)	C(46)–H(46)	0.9500
C(b3)–H(b3)	0.9500	N(5)–O(1)	1.1819(12)
C(b4)–H(b4)	0.9500	N(6)–C(1)	1.3252(13)
C(b5)–C(b6)	1.3571(14)	N(6)–C(3)	1.3805(13)
C(b5)–H(b5)	0.9500	N(7)–C(1)	1.3494(14)
C(b6)–H(b6)	0.9500	N(7)–C(2)	1.3689(14)
C(b7)–C(b8)	1.3581(14)	N(7)–C(4)	1.4570(15)
C(b7)–H(b7)	0.9500	C(1)–H(1a)	0.9500
C(b8)–H(b8)	0.9500	C(2)–C(3)	1.3599(16)
F(10)–C(14)	1.3564(12)	C(2)–H(2a)	0.9500
C(11)–C(12)	1.3977(14)	C(3)–H(3a)	0.9500
C(11)–C(16)	1.3995(14)	C(4)–H(4a)	0.9800
C(12)–C(13)	1.3942(14)	C(4)–H(4b)	0.9800
C(12)–H(12)	0.9500	C(4)–H(4C)	0.9800
C(13)–C(14)	1.3804(15)		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S4. Bond Angles for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

angle	degree	angle	degree
N(5)–Fe(1)–N(1)	89.64(4)	C(13)–C(12)–H(12)	119.4
N(5)–Fe(1)–N(2)	88.27(4)	C(11)–C(12)–H(12)	119.4
N(1)–Fe(1)–N(2)	90.13(3)	C(14)–C(13)–C(12)	117.90(9)
N(5)–Fe(1)–N(4)	95.31(4)	C(14)–C(13)–H(13)	121.1
N(1)–Fe(1)–N(4)	89.97(3)	C(12)–C(13)–H(13)	121.1
N(2)–Fe(1)–N(4)	176.42(3)	F(10)–C(14)–C(15)	118.46(10)
N(5)–Fe(1)–N(3)	94.92(4)	F(10)–C(14)–C(13)	118.56(10)
N(1)–Fe(1)–N(3)	175.43(3)	C(15)–C(14)–C(13)	122.98(9)
N(2)–Fe(1)–N(3)	89.87(3)	C(14)–C(15)–C(16)	118.35(10)
N(4)–Fe(1)–N(3)	89.73(3)	C(14)–C(15)–H(15)	120.8
N(5)–Fe(1)–N(6)	176.08(4)	C(16)–C(15)–H(15)	120.8
N(1)–Fe(1)–N(6)	86.72(3)	C(15)–C(16)–C(11)	120.97(9)
N(2)–Fe(1)–N(6)	90.29(3)	C(15)–C(16)–H(16)	119.5
N(4)–Fe(1)–N(6)	86.14(3)	C(11)–C(16)–H(16)	119.5
N(3)–Fe(1)–N(6)	88.71(3)	C(22)–C(21)–C(26)	118.88(10)
C(a1)–N(1)–C(a2)	105.87(8)	C(22)–C(21)–C(m2)	120.41(10)
C(a1)–N(1)–Fe(1)	126.97(6)	C(26)–C(21)–C(m2)	120.71(10)
C(a2)–N(1)–Fe(1)	127.07(6)	C(21)–C(22)–C(23)	120.96(11)
C(a4)–N(2)–C(a3)	105.73(8)	C(21)–C(22)–H(22)	119.5
C(a4)–N(2)–Fe(1)	126.64(6)	C(23)–C(22)–H(22)	119.5
C(a3)–N(2)–Fe(1)	126.49(6)	C(24)–C(23)–C(22)	117.94(11)
C(a6)–N(3)–C(a5)	105.72(8)	C(24)–C(23)–H(23)	121.0
C(a6)–N(3)–Fe(1)	127.22(6)	C(22)–C(23)–H(23)	121.0
C(a5)–N(3)–Fe(1)	127.05(6)	F(20)–C(24)–C(23)	118.57(12)
C(a8)–N(4)–C(a7)	105.87(8)	F(20)–C(24)–C(25)	118.17(12)
C(a8)–N(4)–Fe(1)	126.89(6)	C(23)–C(24)–C(25)	123.25(10)
C(a7)–N(4)–Fe(1)	127.03(6)	C(24)–C(25)–C(26)	118.22(12)
C(a3)–C(m1)–C(a2)	123.41(9)	C(24)–C(25)–H(25)	120.9
C(a3)–C(m1)–C(11)	118.38(8)	C(26)–C(25)–H(25)	120.9
C(a2)–C(m1)–C(11)	118.22(8)	C(25)–C(26)–C(21)	120.75(11)
C(a5)–C(m2)–C(a4)	123.60(9)	C(25)–C(26)–H(26)	119.6
C(a5)–C(m2)–C(21)	118.61(9)	C(21)–C(26)–H(26)	119.6
C(a4)–C(m2)–C(21)	117.78(8)	C(36)–C(31)–C(32)	118.68(9)
C(a6)–C(m3)–C(a7)	123.75(9)	C(36)–C(31)–C(m3)	121.05(9)

Table S4. Continued

angle	degree	angle	degree
C(a6)–C(m3)–C(31)	118.05(8)	C(32)–C(31)–C(m3)	120.24(9)
C(a7)–C(m3)–C(31)	118.18(8)	C(33)–C(32)–C(31)	121.18(10)
C(a1)–C(m4)–C(a8)	123.66(9)	C(33)–C(32)–H(32)	119.4
C(a1)–C(m4)–C(41)	117.82(8)	C(31)–C(32)–H(32)	119.4
C(a8)–C(m4)–C(41)	118.49(8)	C(34)–C(33)–C(32)	118.02(10)
N(1)–C(a1)–C(m4)	126.08(9)	C(34)–C(33)–H(33)	121.0
N(1)–C(a1)–C(b1)	110.18(8)	C(32)–C(33)–H(33)	121.0
C(m4)–C(a1)–C(b1)	123.73(9)	F(30)–C(34)–C(35)	118.39(10)
N(1)–C(a2)–C(m1)	125.89(8)	F(30)–C(34)–C(33)	118.76(10)
N(1)–C(a2)–C(b2)	110.01(8)	C(35)–C(34)–C(33)	122.83(10)
C(m1)–C(a2)–C(b2)	124.10(9)	C(34)–C(35)–C(36)	118.33(10)
N(2)–C(a3)–C(m1)	125.83(8)	C(34)–C(35)–H(35)	120.8
N(2)–C(a3)–C(b3)	110.08(8)	C(36)–C(35)–H(35)	120.8
C(m1)–C(a3)–C(b3)	124.09(8)	C(35)–C(36)–C(31)	120.95(9)
N(2)–C(a4)–C(m2)	126.23(8)	C(35)–C(36)–H(36)	119.5
N(2)–C(a4)–C(b4)	110.38(8)	C(31)–C(36)–H(36)	119.5
C(m2)–C(a4)–C(b4)	123.39(9)	C(42)–C(41)–C(46)	118.78(9)
N(3)–C(a5)–C(m2)	125.77(9)	C(42)–C(41)–C(m4)	121.34(9)
N(3)–C(a5)–C(b5)	110.30(8)	C(46)–C(41)–C(m4)	119.88(9)
C(m2)–C(a5)–C(b5)	123.92(9)	C(43)–C(42)–C(41)	120.78(11)
N(3)–C(a6)–C(m3)	125.91(9)	C(43)–C(42)–H(42)	119.6
N(3)–C(a6)–C(b6)	110.30(8)	C(41)–C(42)–H(42)	119.6
C(m3)–C(a6)–C(b6)	123.77(9)	C(44)–C(43)–C(42)	118.22(10)
N(4)–C(a7)–C(m3)	126.12(9)	C(44)–C(43)–H(43)	120.9
N(4)–C(a7)–C(b7)	110.07(8)	C(42)–C(43)–H(43)	120.9
C(m3)–C(a7)–C(b7)	123.81(9)	F(40)–C(44)–C(43)	118.58(10)
N(4)–C(a8)–C(m4)	125.68(8)	F(40)–C(44)–C(45)	118.17(10)
N(4)–C(a8)–C(b8)	110.30(8)	C(43)–C(44)–C(45)	123.24(10)
C(m4)–C(a8)–C(b8)	123.97(9)	C(44)–C(45)–C(46)	117.91(10)
C(b2)–C(b1)–C(a1)	106.79(8)	C(44)–C(45)–H(45)	121.0
C(b2)–C(b1)–H(b1)	126.6	C(46)–C(45)–H(45)	121.0
C(a1)–C(b1)–H(b1)	126.6	C(45)–C(46)–C(41)	121.07(10)
C(b1)–C(b2)–C(a2)	107.08(8)	C(45)–C(46)–H(46)	119.5
C(b1)–C(b2)–H(b2)	126.5	C(41)–C(46)–H(46)	119.5

Table S4. Continued

angle	degree	angle	degree
C(a2)–C(b2)–H(b2)	126.5	O(1)–N(5)–Fe(1)	138.64(8)
C(b4)–C(b3)–C(a3)	106.88(8)	C(1)–N(6)–C(3)	105.48(9)
C(b4)–C(b3)–H(b3)	126.6	C(1)–N(6)–Fe(1)	127.77(7)
C(a3)–C(b3)–H(b3)	126.6	C(3)–N(6)–Fe(1)	126.61(7)
C(b3)–C(b4)–C(a4)	106.93(8)	C(1)–N(7)–C(2)	107.25(9)
C(b3)–C(b4)–H(b4)	126.5	C(1)–N(7)–C(4)	127.41(10)
C(a4)–C(b4)–H(b4)	126.5	C(2)–N(7)–C(4)	125.30(10)
C(b6)–C(b5)–C(a5)	106.70(9)	N(6)–C(1)–N(7)	111.32(9)
C(b6)–C(b5)–H(b5)	126.7	N(6)–C(1)–H(1a)	124.3
C(a5)–C(b5)–H(b5)	126.7	N(7)–C(1)–H(1a)	124.3
C(b5)–C(b6)–C(a6)	106.96(9)	C(3)–C(2)–N(7)	106.43(9)
C(b5)–C(b6)–H(b6)	126.5	C(3)–C(2)–H(2a)	126.8
C(a6)–C(b6)–H(b6)	126.5	N(7)–C(2)–H(2a)	126.8
C(b8)–C(b7)–C(a7)	106.96(8)	C(2)–C(3)–N(6)	109.52(9)
C(b8)–C(b7)–H(b7)	126.5	C(2)–C(3)–H(3a)	125.2
C(a7)–C(b7)–H(b7)	126.5	N(6)–C(3)–H(3a)	125.2
C(b7)–C(b8)–C(a8)	106.75(9)	N(7)–C(4)–H(4a)	109.5
C(b7)–C(b8)–H(b8)	126.6	N(7)–C(4)–H(4b)	109.5
C(a8)–C(b8)–H(b8)	126.6	H(4a)–C(4)–H(4b)	109.5
C(12)–C(11)–C(16)	118.60(9)	N(7)–C(4)–H(4C)	109.5
C(12)–C(11)–C(m1)	120.63(9)	H(4a)–C(4)–H(4C)	109.5
C(16)–C(11)–C(m1)	120.77(9)	H(4b)–C(4)–H(4C)	109.5
C(13)–C(12)–C(11)	121.19(9)		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S5. Anisotropic Displacement Parameters (Å^2) for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0122(1)	0.0110(1)	0.0116(1)	0.0004(1)	0.0040(1)	0.0003(1)
N(1)	0.0140(3)	0.0124(3)	0.0128(3)	0.0000(3)	0.0043(3)	−0.0002(3)
N(2)	0.0148(3)	0.0131(3)	0.0126(3)	0.0001(3)	0.0050(3)	0.0000(3)
N(3)	0.0146(3)	0.0139(3)	0.0128(3)	0.0005(3)	0.0042(3)	0.0002(3)
N(4)	0.0146(3)	0.0129(3)	0.0124(3)	0.0006(3)	0.0037(3)	0.0002(3)
C(M1)	0.0141(4)	0.0135(4)	0.0130(4)	−0.0007(3)	0.0043(3)	0.0009(3)
C(M2)	0.0152(4)	0.0150(4)	0.0156(4)	0.0012(3)	0.0061(3)	−0.0003(3)
C(M3)	0.0161(4)	0.0139(4)	0.0124(4)	0.0006(3)	0.0031(3)	0.0015(3)
C(M4)	0.0148(4)	0.0132(4)	0.0148(4)	0.0012(3)	0.0055(3)	0.0000(3)
C(A1)	0.0154(4)	0.0132(4)	0.0140(4)	0.0009(3)	0.0055(3)	0.0000(3)
C(A2)	0.0152(4)	0.0138(4)	0.0129(4)	0.0003(3)	0.0047(3)	0.0005(3)
C(A3)	0.0138(4)	0.0130(4)	0.0133(4)	−0.0006(3)	0.0042(3)	0.0003(3)
C(A4)	0.0146(4)	0.0132(4)	0.0149(4)	0.0007(3)	0.0052(3)	0.0002(3)
C(A5)	0.0159(4)	0.0154(4)	0.0144(4)	0.0009(3)	0.0059(3)	0.0002(3)
C(A6)	0.0170(4)	0.0152(4)	0.0124(4)	0.0007(3)	0.0047(3)	0.0011(3)
C(A7)	0.0153(4)	0.0133(4)	0.0131(4)	0.0006(3)	0.0029(3)	0.0006(3)
C(A8)	0.0142(4)	0.0130(4)	0.0144(4)	0.0004(3)	0.0042(3)	0.0001(3)
C(B1)	0.0201(4)	0.0167(4)	0.0142(4)	0.0016(3)	0.0056(3)	−0.0027(3)
C(B2)	0.0202(4)	0.0168(4)	0.0131(4)	0.0005(3)	0.0045(3)	−0.0015(3)
C(B3)	0.0170(4)	0.0140(4)	0.0154(4)	−0.0013(3)	0.0049(3)	−0.0015(3)
C(B4)	0.0177(4)	0.0145(4)	0.0171(4)	0.0006(3)	0.0058(3)	−0.0017(3)
C(B5)	0.0212(5)	0.0211(4)	0.0148(4)	0.0000(3)	0.0081(4)	−0.0028(4)
C(B6)	0.0218(5)	0.0202(4)	0.0136(4)	0.0000(3)	0.0069(3)	−0.0018(4)
C(B7)	0.0172(4)	0.0160(4)	0.0143(4)	0.0004(3)	0.0020(3)	−0.0015(3)
C(B8)	0.0164(4)	0.0165(4)	0.0161(4)	0.0003(3)	0.0033(3)	−0.0026(3)
F(10)	0.0323(4)	0.0398(4)	0.0164(3)	−0.0099(3)	0.0012(3)	−0.0002(3)
C(11)	0.0147(4)	0.0126(4)	0.0136(4)	−0.0002(3)	0.0042(3)	0.0004(3)
C(12)	0.0153(4)	0.0162(4)	0.0153(4)	−0.0007(3)	0.0044(3)	0.0018(3)
C(13)	0.0204(4)	0.0186(4)	0.0164(4)	−0.0018(3)	0.0070(4)	0.0030(3)
C(14)	0.0222(5)	0.0196(4)	0.0133(4)	−0.0027(3)	0.0023(3)	−0.0001(4)
C(15)	0.0162(4)	0.0211(4)	0.0179(4)	−0.0011(3)	0.0015(3)	0.0002(3)
C(16)	0.0155(4)	0.0181(4)	0.0164(4)	0.0000(3)	0.0048(3)	0.0022(3)
F(20)	0.0439(5)	0.0366(4)	0.0290(4)	−0.0004(3)	0.0160(4)	−0.0232(4)
C(21)	0.0189(4)	0.0168(4)	0.0153(4)	−0.0008(3)	0.0076(3)	−0.0024(3)

Table S5. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(22)	0.0253(5)	0.0197(4)	0.0178(4)	0.0019(3)	0.0082(4)	−0.0016(4)
C(23)	0.0361(6)	0.0195(5)	0.0186(4)	0.0015(4)	0.0104(4)	−0.0051(4)
C(24)	0.0332(6)	0.0231(5)	0.0198(5)	−0.0040(4)	0.0137(4)	−0.0133(4)
C(25)	0.0220(5)	0.0301(6)	0.0270(5)	−0.0023(4)	0.0105(4)	−0.0070(4)
C(26)	0.0201(5)	0.0237(5)	0.0252(5)	0.0022(4)	0.0088(4)	−0.0018(4)
F(30)	0.0448(5)	0.0303(4)	0.0152(3)	−0.0053(3)	0.0021(3)	−0.0018(3)
C(31)	0.0165(4)	0.0143(4)	0.0127(4)	0.0008(3)	0.0039(3)	0.0011(3)
C(32)	0.0256(5)	0.0164(4)	0.0159(4)	0.0020(3)	0.0049(4)	0.0055(4)
C(33)	0.0297(5)	0.0162(4)	0.0184(4)	−0.0008(3)	0.0068(4)	0.0038(4)
C(34)	0.0240(5)	0.0216(5)	0.0136(4)	−0.0017(3)	0.0036(4)	−0.0012(4)
C(35)	0.0222(5)	0.0209(4)	0.0147(4)	0.0023(3)	0.0009(4)	0.0020(4)
C(36)	0.0202(4)	0.0158(4)	0.0162(4)	0.0018(3)	0.0038(3)	0.0029(3)
F(40)	0.0314(4)	0.0287(4)	0.0241(3)	0.0007(3)	0.0121(3)	−0.0141(3)
C(41)	0.0159(4)	0.0154(4)	0.0139(4)	0.0012(3)	0.0041(3)	−0.0016(3)
C(42)	0.0259(5)	0.0160(4)	0.0250(5)	0.0016(4)	0.0120(4)	−0.0002(4)
C(43)	0.0323(6)	0.0164(4)	0.0257(5)	0.0011(4)	0.0120(5)	−0.0039(4)
C(44)	0.0208(5)	0.0225(5)	0.0149(4)	0.0024(3)	0.0046(4)	−0.0081(4)
C(45)	0.0178(4)	0.0242(5)	0.0198(4)	0.0022(4)	0.0074(4)	−0.0012(4)
C(46)	0.0198(4)	0.0177(4)	0.0209(4)	0.0023(3)	0.0078(4)	0.0001(3)
N(5)	0.0159(4)	0.0148(3)	0.0182(4)	0.0031(3)	0.0064(3)	0.0020(3)
O(1)	0.0249(4)	0.0173(3)	0.0288(4)	0.0006(3)	0.0124(3)	0.0056(3)
N(6)	0.0148(3)	0.0157(3)	0.0142(3)	0.0003(3)	0.0035(3)	0.0015(3)
N(7)	0.0249(4)	0.0235(4)	0.0166(4)	−0.0005(3)	0.0047(3)	0.0108(3)
C(1)	0.0207(4)	0.0186(4)	0.0147(4)	−0.0001(3)	0.0032(3)	0.0055(3)
C(2)	0.0271(5)	0.0284(5)	0.0166(4)	0.0035(4)	0.0045(4)	0.0132(4)
C(3)	0.0230(5)	0.0248(5)	0.0144(4)	0.0018(3)	0.0044(4)	0.0091(4)
C(4)	0.0524(9)	0.0432(8)	0.0251(6)	−0.0017(5)	0.0101(6)	0.0314(7)

[a]The estimated standard deviations of the least significant digits are given in parentheses. The anisotropic displacement factor exponent takes the form: $-2\,\pi\,[h^2\,U_{11}\,+...+\,2\,h\,k\,a^*\,b^*\,U_{12}]$.

Table S6. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

atom	x	y	z	U(eq)
H(B1	0.5249	0.3065	−0.0257	0.021
H(B2	0.3613	0.1475	−0.1062	0.021
H(B3	0.0890	−0.1879	0.0172	0.019
H(B4	0.0418	−0.2262	0.1753	0.020
H(B5	0.1896	−0.0253	0.5274	0.023
H(B6	0.3585	0.1295	0.6079	0.023
H(B7	0.6976	0.4066	0.4937	0.020
H(B8	0.7469	0.4438	0.3359	0.020
H(12)	0.3696	−0.0599	−0.1107	0.019
H(13)	0.2917	−0.1352	−0.2708	0.022
H(15)	−0.0508	−0.1144	−0.2440	0.023
H(16)	0.0283	−0.0334	−0.0861	0.020
H(22)	0.2074	−0.2285	0.4464	0.025
H(23)	0.0687	−0.3647	0.4975	0.030
H(25)	−0.2134	−0.2443	0.3374	0.033
H(26)	−0.0751	−0.1096	0.2853	0.028
H(32)	0.4854	0.4411	0.5597	0.023
H(33)	0.5553	0.5257	0.7175	0.026
H(35)	0.6748	0.2423	0.8030	0.024
H(36)	0.6091	0.1601	0.6443	0.021
H(42)	0.6237	0.5438	0.1890	0.026
H(43)	0.7694	0.6697	0.1353	0.030
H(45)	0.8944	0.4088	0.0284	0.025
H(46)	0.7504	0.2832	0.0838	0.023
H(1A)	0.2466	0.2881	0.3700	0.022
H(2A)	0.0977	0.4037	0.1239	0.028
H(3A)	0.2143	0.2586	0.0886	0.024
H(4A)	0.1143	0.4333	0.3865	0.056
H(4B)	0.0144	0.4419	0.2907	0.056
H(4C)	0.1426	0.5264	0.3153	0.056

Table S7. Complete Crystallographic Details for *mono-mono*-[Fe(T*p*FPP)(NO)(1-MeIm)]

formula	$C_{48}H_{30}F_4FeN_7O$
FW, amu	852.64
a, Å	14.1135(4)
b, Å	18.7149(6)
c, Å	14.8501(4)
β, deg	97.8247(10)
V, Å^3	3885.9(2)
space group	P 2_1/n
Z	4
D_c, g/cm^3	1.457
F(000)	1748
μ, mm^{-1}	0.457
crystal dimensions, mm	0.54 × 0.27 × 0.11
radiation	MoKα, $\bar{\lambda}$ = 0.71073 Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.76–32.03
index range	$-21 \leq h \leq 21$
	$-23 \leq k \leq 27$
	$-22 \leq l \leq 22$
total data collected	110943
absorption correction	Semi-empirical fromequiv
relative transmission coefficients (I)	0.9511 and 0.7915
unique data	13516 (R_{int} = 0.040)
unique observed data [I > 2σ(I)]	10958
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	13516/0/551
goodness-of-fit (pased on F^2)	1.040
final R indices [I > 2σ(I)]	R_1 = 0.0383, wR_2 = 0.0983
final R indices (all data)	R_1 = 0.0520, wR_2 = 0.1077

Table S8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for *mono*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

atom	x	y	z	U(eq)
Fe(1)	0.68933(1)	0.11124(1)	0.72332(1)	0.0104(1)
N(1)	0.63273(7)	0.11743(5)	0.59335(7)	0.0124(2)
N(2)	0.55910(7)	0.11927(5)	0.76037(7)	0.0122(2)
N(3)	0.74854(7)	0.11375(5)	0.85378(7)	0.0125(2)
N(4)	0.82182(7)	0.10820(5)	0.68633(7)	0.0126(2)
C(m1)	0.46165(8)	0.11691(6)	0.61027(8)	0.0130(2)
C(m2)	0.60246(8)	0.12186(6)	0.92650(8)	0.0133(2)
C(m3)	0.91974(8)	0.10797(6)	0.83632(8)	0.0135(2)
C(m4)	0.77953(9)	0.11818(6)	0.52087(8)	0.0139(2)
C(a1)	0.68098(9)	0.12140(6)	0.51948(8)	0.0135(2)
C(a2)	0.53741(8)	0.11925(6)	0.55936(8)	0.0131(2)
C(a3)	0.47341(8)	0.11500(6)	0.70470(8)	0.0133(2)
C(a4)	0.53719(8)	0.11804(6)	0.84745(8)	0.0131(2)
C(a5)	0.70115(8)	0.12129(6)	0.92776(8)	0.0133(2)
C(a6)	0.84399(8)	0.11474(6)	0.88709(8)	0.0135(2)
C(a7)	0.90754(8)	0.10328(6)	0.74195(8)	0.0131(2)
C(a8)	0.84430(9)	0.11000(6)	0.59946(8)	0.0137(2)
C(b1)	0.61441(9)	0.12727(7)	0.43735(8)	0.0163(2)
C(b2)	0.52578(9)	0.12575(7)	0.46196(8)	0.0159(2)
C(b3)	0.39614(9)	0.10980(7)	0.75834(8)	0.0161(2)
C(b4)	0.43559(9)	0.11217(7)	0.84662(8)	0.0159(2)
C(b5)	0.76849(9)	0.12873(7)	1.00943(8)	0.0164(2)
C(b6)	0.85672(9)	0.12441(7)	0.98398(8)	0.0165(2)
C(b7)	0.98513(9)	0.09929(7)	0.68862(8)	0.0166(2)
C(b8)	0.94591(9)	0.10326(7)	0.60015(8)	0.0165(2)
F(10)	0.09319(6)	0.13315(6)	0.41664(7)	0.0332(2)
C(11)	0.36280(9)	0.11969(7)	0.56020(8)	0.0146(2)
C(12)	0.32701(9)	0.06471(7)	0.50254(9)	0.0169(2)
C(13)	0.23602(9)	0.06870(7)	0.45372(9)	0.0192(2)
C(14)	0.18222(9)	0.12849(8)	0.46407(10)	0.0222(3)
C(15)	0.21497(11)	0.18412(9)	0.51998(12)	0.0344(4)
C(16)	0.30616(11)	0.17926(8)	0.56822(11)	0.0286(3)
F(20)	0.47922(6)	0.16166(5)	1.26474(5)	0.0226(2)
C(21)	0.56492(8)	0.12944(7)	1.01485(8)	0.0139(2)

Table S8. Continued

atom	x	y	z	U(eq)
C(22)	0.52183(9)	0.19324(7)	1.03505(8)	0.0158(2)
C(23)	0.49166(9)	0.20424(7)	1.11908(8)	0.0176(2)
C(24)	0.50541(9)	0.14987(7)	1.18185(8)	0.0170(2)
C(25)	0.54466(10)	0.08494(8)	1.16418(9)	0.0211(2)
C(26)	0.57463(10)	0.07519(7)	1.07975(9)	0.0199(2)
F(30)	1.29183(6)	0.12808(6)	1.02178(7)	0.0312(2)
C(31)	1.01899(8)	0.11199(7)	0.88578(8)	0.0139(2)
C(32)	1.07507(9)	0.05162(7)	0.90460(10)	0.0207(2)
C(33)	1.16753(10)	0.05675(8)	0.95044(11)	0.0244(3)
C(34)	1.20188(9)	0.12295(8)	0.97709(9)	0.0210(3)
C(35)	1.14845(10)	0.18399(8)	0.96166(11)	0.0267(3)
C(36)	1.05656(10)	0.17802(8)	0.91511(11)	0.0240(3)
F(40)	0.91244(7)	0.15106(6)	0.18520(6)	0.0296(2)
C(41)	0.81714(9)	0.12525(7)	0.43219(8)	0.0155(2)
C(42)	0.84860(10)	0.19118(8)	0.40601(9)	0.0212(2)
C(43)	0.88127(11)	0.20026(8)	0.32282(9)	0.0244(3)
C(44)	0.88129(9)	0.14205(8)	0.26711(9)	0.0212(3)
C(45)	0.85058(14)	0.07598(9)	0.28960(11)	0.0346(4)
C(46)	0.81835(14)	0.06787(9)	0.37323(11)	0.0324(4)
N(5)	0.67088(8)	0.01887(6)	0.71898(7)	0.0149(2)
O(1)	0.60694(7)	−0.02067(5)	0.69600(7)	0.0226(2)
N(6)	0.69902(7)	0.22488(6)	0.72480(7)	0.0136(2)
N(7)	0.66909(8)	0.34015(6)	0.70978(8)	0.0175(2)
C(1)	0.63309(9)	0.27352(7)	0.69922(9)	0.0176(2)
C(2)	0.76347(9)	0.33367(7)	0.74450(10)	0.0207(2)
C(3)	0.78109(9)	0.26256(7)	0.75326(10)	0.0199(2)
C(4)	0.61902(11)	0.40746(7)	0.69059(11)	0.0257(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. The estimated standard deviations of the least significant digits are given in parentheses.

Table S9. Bond Lengths for *mono*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

bond	length (Å)	bond	length (Å)
Fe(1)–N(5)	1.7481(11)	C(13)–H(13)	0.9500
Fe(1)–N(1)	1.9892(10)	C(14)–C(15)	1.372(2)
Fe(1)–N(2)	1.9947(10)	C(15)–C(16)	1.388(2)
Fe(1)–N(3)	2.0033(10)	C(15)–H(15)	0.9500
Fe(1)–N(4)	2.0202(10)	C(16)–H(16)	0.9500
Fe(1)–N(6)	2.1312(11)	F(20)–C(24)	1.3508(14)
N(1)–C(a1)	1.3697(15)	C(21)–C(22)	1.3912(17)
N(1)–C(a2)	1.3714(15)	C(21)–C(26)	1.3936(17)
N(2)–C(a4)	1.3702(15)	C(22)–C(23)	1.3875(17)
N(2)–C(a3)	1.3713(15)	C(22)–H(22)	0.9500
N(3)–C(a5)	1.3691(15)	C(23)–C(24)	1.3758(18)
N(3)–C(a6)	1.3704(15)	C(23)–H(23)	0.9500
N(4)–C(a8)	1.3701(15)	C(24)–C(25)	1.3754(19)
N(4)–C(a7)	1.3719(15)	C(25)–C(26)	1.3888(18)
C(m1)–C(a3)	1.3898(16)	C(25)–H(25)	0.9500
C(m1)–C(a2)	1.3918(17)	C(26)–H(26)	0.9500
C(m1)–C(11)	1.4898(16)	F(30)–C(34)	1.3535(15)
C(m2)–C(a5)	1.3906(16)	C(31)–C(32)	1.3861(18)
C(m2)–C(a4)	1.3918(16)	C(31)–C(36)	1.3910(18)
C(m2)–C(21)	1.4871(16)	C(32)–C(33)	1.3905(18)
C(m3)–C(a7)	1.3914(16)	C(32)–H(32)	0.9500
C(m3)–C(a6)	1.3953(17)	C(33)–C(34)	1.369(2)
C(m3)–C(31)	1.4924(16)	C(33)–H(33)	0.9500
C(m4)–C(a8)	1.3895(17)	C(34)–C(35)	1.371(2)
C(m4)–C(a1)	1.3896(17)	C(35)–C(36)	1.3886(19)
C(m4)–C(41)	1.4912(16)	C(35)–H(35)	0.9500
C(a1)–C(b1)	1.4388(16)	C(36)–H(36)	0.9500
C(a2)–C(b2)	1.4385(16)	F(40)–C(44)	1.3590(14)
C(a3)–C(b3)	1.4386(17)	C(41)–C(42)	1.3848(18)
C(a4)–C(b4)	1.4366(16)	C(41)–C(46)	1.3871(19)
C(a5)–C(b5)	1.4421(16)	C(42)–C(43)	1.3867(18)
C(a6)–C(b6)	1.4369(16)	C(42)–H(42)	0.9500
C(a7)–C(b7)	1.4380(17)	C(43)–C(44)	1.368(2)
C(a8)–C(b8)	1.4382(17)	C(43)–H(43)	0.9500

Table S9. Continued

bond	length (Å)	bond	length (Å)
C(b1)–C(b2)	1.3504(18)	C(44)–C(45)	1.367(2)
C(b1)–H(b1)	0.9500	C(45)–C(46)	1.388(2)
C(b2)–H(b2)	0.9500	C(45)–H(45)	0.9500
C(b3)–C(b4)	1.3535(17)	C(46)–H(46)	0.9500
C(b3)–H(b3)	0.9500	N(5)–O(1)	1.1808(14)
C(b4)–H(b4)	0.9500	N(6)–C(1)	1.3200(16)
C(b5)–C(b6)	1.3521(17)	N(6)–C(3)	1.3726(16)
C(b5)–H(b5)	0.9500	N(7)–C(1)	1.3475(16)
C(b6)–H(b6)	0.9500	N(7)–C(2)	1.3667(17)
C(b7)–C(b8)	1.3564(17)	N(7)–C(4)	1.4535(17)
C(b7)–H(b7)	0.9500	C(1)–H(1)	0.9500
C(b8)–H(b8)	0.9500	C(2)–C(3)	1.3568(18)
F(10)–C(14)	1.3572(15)	C(2)–H(2)	0.9500
C(11)–C(16)	1.3864(18)	C(3)–H(3)	0.9500
C(11)–C(12)	1.3889(17)	C(4)–H(4a)	0.9800
C(12)–C(13)	1.3882(17)	C(4)–H(4b)	0.9800
C(12)–H(12)	0.9500	C(4)–H(4C)	0.9800
C(13)–C(14)	1.373(2)		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S10. Bond Angles for *mono*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

angle	degree	angle	degree
N(5)–Fe(1)–N(1)	89.07(4)	C(13)–C(12)–H(12)	119.5
N(5)–Fe(1)–N(2)	86.93(5)	C(11)–C(12)–H(12)	119.5
N(1)–Fe(1)–N(2)	89.99(4)	C(14)–C(13)–C(12)	118.15(12)
N(5)–Fe(1)–N(3)	95.70(5)	C(14)–C(13)–H(13)	120.9
N(1)–Fe(1)–N(3)	175.22(4)	C(12)–C(13)–H(13)	120.9
N(2)–Fe(1)–N(3)	90.59(4)	F(10)–C(14)–C(15)	118.49(13)
N(5)–Fe(1)–N(4)	95.79(5)	F(10)–C(14)–C(13)	118.79(13)
N(1)–Fe(1)–N(4)	90.12(4)	C(15)–C(14)–C(13)	122.72(12)
N(2)–Fe(1)–N(4)	177.27(4)	C(14)–C(15)–C(16)	118.34(14)
N(3)–Fe(1)–N(4)	89.08(4)	C(14)–C(15)–H(15)	120.8
N(5)–Fe(1)–N(6)	175.08(4)	C(16)–C(15)–H(15)	120.8
N(1)–Fe(1)–N(6)	88.20(4)	C(11)–C(16)–C(15)	120.89(13)
N(2)–Fe(1)–N(6)	88.98(4)	C(11)–C(16)–H(16)	119.6
N(3)–Fe(1)–N(6)	87.07(4)	C(15)–C(16)–H(16)	119.6
N(4)–Fe(1)–N(6)	88.30(4)	C(22)–C(21)–C(26)	118.74(11)
C(a1)–N(1)–C(a2)	105.88(9)	C(22)–C(21)–C(m2)	119.39(11)
C(a1)–N(1)–Fe(1)	127.05(8)	C(26)–C(21)–C(m2)	121.83(11)
C(a2)–N(1)–Fe(1)	127.07(8)	C(23)–C(22)–C(21)	121.19(11)
C(a4)–N(2)–C(a3)	105.91(10)	C(23)–C(22)–H(22)	119.4
C(a4)–N(2)–Fe(1)	126.43(8)	C(21)–C(22)–H(22)	119.4
C(a3)–N(2)–Fe(1)	126.83(8)	C(24)–C(23)–C(22)	117.86(12)
C(a5)–N(3)–C(a6)	105.81(10)	C(24)–C(23)–H(23)	121.1
C(a5)–N(3)–Fe(1)	126.40(8)	C(22)–C(23)–H(23)	121.1
C(a6)–N(3)–Fe(1)	127.56(8)	F(20)–C(24)–C(25)	119.04(11)
C(a8)–N(4)–C(a7)	105.68(10)	F(20)–C(24)–C(23)	117.76(12)
C(a8)–N(4)–Fe(1)	126.64(8)	C(25)–C(24)–C(23)	123.20(12)
C(a7)–N(4)–Fe(1)	127.68(8)	C(24)–C(25)–C(26)	117.92(12)
C(a3)–C(m1)–C(a2)	123.63(11)	C(24)–C(25)–H(25)	121.0
C(a3)–C(m1)–C(11)	118.66(11)	C(26)–C(25)–H(25)	121.0
C(a2)–C(m1)–C(11)	117.66(10)	C(25)–C(26)–C(21)	121.02(12)
C(a5)–C(m2)–C(a4)	123.89(11)	C(25)–C(26)–H(26)	119.5
C(a5)–C(m2)–C(21)	117.74(10)	C(21)–C(26)–H(26)	119.5
C(a4)–C(m2)–C(21)	118.34(10)	C(32)–C(31)–C(36)	118.56(12)
C(a7)–C(m3)–C(a6)	123.45(11)	C(32)–C(31)–C(m3)	122.01(11)

Table S10. Continued

angle	degree	angle	degree
C(a7)–C(m3)–C(31)	118.55(11)	C(36)–C(31)–C(m3)	119.42(11)
C(a6)–C(m3)–C(31)	117.80(11)	C(31)–C(32)–C(33)	120.96(13)
C(a8)–C(m4)–C(a1)	124.05(11)	C(31)–C(32)–H(32)	119.5
C(a8)–C(m4)–C(41)	118.62(11)	C(33)–C(32)–H(32)	119.5
C(a1)–C(m4)–C(41)	117.32(10)	C(34)–C(33)–C(32)	118.41(13)
N(1)–C(a1)–C(m4)	126.27(11)	C(34)–C(33)–H(33)	120.8
N(1)–C(a1)–C(b1)	110.16(10)	C(32)–C(33)–H(33)	120.8
C(m4)–C(a1)–C(b1)	123.55(11)	F(30)–C(34)–C(33)	118.53(13)
N(1)–C(a2)–C(m1)	125.94(11)	F(30)–C(34)–C(35)	118.73(13)
N(1)–C(a2)–C(b2)	110.13(10)	C(33)–C(34)–C(35)	122.73(12)
C(m1)–C(a2)–C(b2)	123.91(11)	C(34)–C(35)–C(36)	118.12(13)
N(2)–C(a3)–C(m1)	125.53(11)	C(34)–C(35)–H(35)	120.9
N(2)–C(a3)–C(b3)	110.06(10)	C(36)–C(35)–H(35)	120.9
C(m1)–C(a3)–C(b3)	124.40(11)	C(35)–C(36)–C(31)	121.19(13)
N(2)–C(a4)–C(m2)	125.92(11)	C(35)–C(36)–H(36)	119.4
N(2)–C(a4)–C(b4)	110.27(10)	C(31)–C(36)–H(36)	119.4
C(m2)–C(a4)–C(b4)	123.81(11)	C(42)–C(41)–C(46)	118.73(12)
N(3)–C(a5)–C(m2)	126.01(11)	C(42)–C(41)–C(m4)	119.55(11)
N(3)–C(a5)–C(b5)	110.29(10)	C(46)–C(41)–C(m4)	121.68(12)
C(m2)–C(a5)–C(b5)	123.70(11)	C(41)–C(42)–C(43)	121.16(13)
N(3)–C(a6)–C(m3)	126.26(11)	C(41)–C(42)–H(42)	119.4
N(3)–C(a6)–C(b6)	110.24(10)	C(43)–C(42)–H(42)	119.4
C(m3)–C(a6)–C(b6)	123.50(11)	C(44)–C(43)–C(42)	117.95(13)
N(4)–C(a7)–C(m3)	125.46(11)	C(44)–C(43)–H(43)	121.0
N(4)–C(a7)–C(b7)	110.32(10)	C(42)–C(43)–H(43)	121.0
C(m3)–C(a7)–C(b7)	123.98(11)	F(40)–C(44)–C(45)	118.89(13)
N(4)–C(a8)–C(m4)	125.69(11)	F(40)–C(44)–C(43)	117.98(13)
N(4)–C(a8)–C(b8)	110.46(10)	C(45)–C(44)–C(43)	123.13(13)
C(m4)–C(a8)–C(b8)	123.84(11)	C(44)–C(45)–C(46)	118.11(14)
C(b2)–C(b1)–C(a1)	106.92(11)	C(44)–C(45)–H(45)	120.9
C(b2)–C(b1)–H(b1)	126.5	C(46)–C(45)–H(45)	120.9
C(a1)–C(b1)–H(b1)	126.5	C(41)–C(46)–C(45)	120.92(14)
C(b1)–C(b2)–C(a2)	106.90(11)	C(41)–C(46)–H(46)	119.5
C(b1)–C(b2)–H(b2)	126.5	C(45)–C(46)–H(46)	119.5

Table S10. Continued

angle	degree	angle	degree
C(a2)–C(b2)–H(b2)	126.5	O(1)–N(5)–Fe(1)	137.27(9)
C(b4)–C(b3)–C(a3)	106.93(11)	C(1)–N(6)–C(3)	105.46(11)
C(b4)–C(b3)–H(b3)	126.5	C(1)–N(6)–Fe(1)	130.05(8)
C(a3)–C(b3)–H(b3)	126.5	C(3)–N(6)–Fe(1)	124.48(8)
C(b3)–C(b4)–C(a4)	106.82(11)	C(1)–N(7)–C(2)	107.13(11)
C(b3)–C(b4)–H(b4)	126.6	C(1)–N(7)–C(4)	127.85(12)
C(a4)–C(b4)–H(b4)	126.6	C(2)–N(7)–C(4)	125.01(11)
C(b6)–C(b5)–C(a5)	106.60(11)	N(6)–C(1)–N(7)	111.39(11)
C(b6)–C(b5)–H(b5)	126.7	N(6)–C(1)–H(1)	124.3
C(a5)–C(b5)–H(b5)	126.7	N(7)–C(1)–H(1)	124.3
C(b5)–C(b6)–C(a6)	107.04(11)	C(3)–C(2)–N(7)	106.24(11)
C(b5)–C(b6)–H(b6)	126.5	C(3)–C(2)–H(2)	126.9
C(a6)–C(b6)–H(b6)	126.5	N(7)–C(2)–H(2)	126.9
C(b8)–C(b7)–C(a7)	106.83(11)	C(2)–C(3)–N(6)	109.78(12)
C(b8)–C(b7)–H(b7)	126.6	C(2)–C(3)–H(3)	125.1
C(a7)–C(b7)–H(b7)	126.6	N(6)–C(3)–H(3)	125.1
C(b7)–C(b8)–C(a8)	106.66(11)	N(7)–C(4)–H(4a)	109.5
C(b7)–C(b8)–H(b8)	126.7	N(7)–C(4)–H(4b)	109.5
C(a8)–C(b8)–H(b8)	126.7	H(4a)–C(4)–H(4b)	109.5
C(16)–C(11)–C(12)	118.89(12)	N(7)–C(4)–H(4C)	109.5
C(16)–C(11)–C(m1)	119.80(11)	H(4a)–C(4)–H(4C)	109.5
C(12)–C(11)–C(m1)	121.27(11)	H(4b)–C(4)–H(4C)	109.5
C(13)–C(12)–C(11)	121.01(12)		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S11. Anisotropic Displacement Parameters (Å^2) for *mono*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0112(1)	0.0102(1)	0.0100(1)	−0.0004(1)	0.0016(1)	0.0001(1)
N(1)	0.0136(4)	0.0123(4)	0.0112(4)	−0.0003(3)	0.0017(3)	0.0003(3)
N(2)	0.0126(4)	0.0132(4)	0.0109(4)	0.0001(3)	0.0017(3)	0.0000(3)
N(3)	0.0123(4)	0.0138(4)	0.0116(4)	0.0000(3)	0.0021(3)	0.0003(3)
N(4)	0.0130(4)	0.0133(4)	0.0117(4)	−0.0009(3)	0.0019(3)	0.0003(3)
C(M1)	0.0135(5)	0.0121(5)	0.0132(5)	−0.0013(4)	0.0008(4)	0.0002(4)
C(M2)	0.0142(5)	0.0145(5)	0.0116(5)	0.0003(4)	0.0034(4)	0.0007(4)
C(M3)	0.0122(5)	0.0132(5)	0.0149(5)	−0.0002(4)	0.0003(4)	0.0009(4)
C(M4)	0.0163(5)	0.0137(5)	0.0122(5)	−0.0010(4)	0.0033(4)	−0.0005(4)
C(A1)	0.0159(5)	0.0130(5)	0.0116(5)	−0.0004(4)	0.0022(4)	−0.0004(4)
C(A2)	0.0146(5)	0.0124(5)	0.0121(5)	−0.0005(4)	0.0008(4)	−0.0002(4)
C(A3)	0.0122(5)	0.0138(5)	0.0139(5)	−0.0013(4)	0.0014(4)	−0.0001(4)
C(A4)	0.0131(5)	0.0137(5)	0.0129(5)	−0.0001(4)	0.0031(4)	−0.0001(4)
C(A5)	0.0142(5)	0.0144(5)	0.0112(5)	0.0004(4)	0.0017(4)	0.0007(4)
C(A6)	0.0130(5)	0.0143(5)	0.0128(5)	0.0005(4)	0.0006(4)	0.0005(4)
C(A7)	0.0125(5)	0.0129(5)	0.0139(5)	−0.0002(4)	0.0024(4)	0.0009(4)
C(A8)	0.0146(5)	0.0138(5)	0.0132(5)	−0.0010(4)	0.0038(4)	0.0005(4)
C(B1)	0.0187(5)	0.0187(6)	0.0115(5)	0.0008(4)	0.0015(4)	−0.0013(4)
C(B2)	0.0162(5)	0.0184(6)	0.0126(5)	0.0006(4)	−0.0003(4)	−0.0010(4)
C(B3)	0.0125(5)	0.0197(6)	0.0163(5)	−0.0022(4)	0.0025(4)	−0.0009(4)
C(B4)	0.0141(5)	0.0189(6)	0.0154(5)	−0.0005(4)	0.0044(4)	−0.0008(4)
C(B5)	0.0161(5)	0.0209(6)	0.0121(5)	−0.0004(4)	0.0014(4)	0.0010(4)
C(B6)	0.0153(5)	0.0210(6)	0.0126(5)	−0.0001(4)	−0.0003(4)	0.0011(4)
C(B7)	0.0135(5)	0.0206(6)	0.0162(5)	0.0002(4)	0.0035(4)	0.0019(4)
C(B8)	0.0150(5)	0.0199(6)	0.0153(5)	−0.0005(4)	0.0049(4)	0.0018(4)
F(10)	0.0173(4)	0.0433(6)	0.0353(5)	−0.0046(4)	−0.0093(4)	0.0052(4)
C(11)	0.0143(5)	0.0155(5)	0.0136(5)	−0.0007(4)	0.0004(4)	0.0002(4)
C(12)	0.0164(5)	0.0144(5)	0.0193(5)	−0.0013(4)	0.0006(4)	0.0002(4)
C(13)	0.0185(6)	0.0188(6)	0.0193(6)	−0.0014(4)	−0.0009(4)	−0.0034(4)
C(14)	0.0147(5)	0.0278(7)	0.0225(6)	−0.0013(5)	−0.0032(4)	0.0021(5)
C(15)	0.0236(7)	0.0316(8)	0.0439(9)	−0.0150(7)	−0.0105(6)	0.0133(6)
C(16)	0.0231(7)	0.0241(7)	0.0350(8)	−0.0136(6)	−0.0086(6)	0.0078(5)
F(20)	0.0228(4)	0.0334(5)	0.0126(3)	0.0003(3)	0.0057(3)	0.0031(3)
C(21)	0.0137(5)	0.0164(5)	0.0119(5)	0.0000(4)	0.0031(4)	−0.0003(4)

Table S11. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(22)	0.0172(5)	0.0165(5)	0.0141(5)	0.0018(4)	0.0037(4)	0.0010(4)
C(23)	0.0187(5)	0.0189(6)	0.0158(5)	−0.0016(4)	0.0046(4)	0.0019(4)
C(24)	0.0151(5)	0.0250(6)	0.0112(5)	−0.0008(4)	0.0030(4)	−0.0006(4)
C(25)	0.0248(6)	0.0230(6)	0.0165(5)	0.0062(5)	0.0061(5)	0.0047(5)
C(26)	0.0252(6)	0.0184(6)	0.0172(5)	0.0031(4)	0.0075(5)	0.0046(5)
F(30)	0.0146(4)	0.0432(6)	0.0334(5)	−0.0051(4)	−0.0049(3)	−0.0027(4)
C(31)	0.0118(5)	0.0157(5)	0.0141(5)	0.0002(4)	0.0016(4)	−0.0002(4)
C(32)	0.0173(6)	0.0164(6)	0.0272(6)	−0.0020(5)	−0.0012(5)	0.0010(4)
C(33)	0.0165(6)	0.0227(7)	0.0322(7)	−0.0004(5)	−0.0028(5)	0.0042(5)
C(34)	0.0126(5)	0.0292(7)	0.0204(6)	−0.0015(5)	0.0000(4)	−0.0018(5)
C(35)	0.0207(6)	0.0214(7)	0.0362(8)	−0.0050(6)	−0.0021(5)	−0.0054(5)
C(36)	0.0189(6)	0.0170(6)	0.0345(7)	−0.0016(5)	−0.0022(5)	0.0002(5)
F(40)	0.0277(4)	0.0495(6)	0.0130(4)	0.0018(4)	0.0077(3)	−0.0034(4)
C(41)	0.0156(5)	0.0190(6)	0.0122(5)	−0.0001(4)	0.0032(4)	0.0001(4)
C(42)	0.0258(6)	0.0205(6)	0.0183(6)	−0.0017(5)	0.0067(5)	−0.0042(5)
C(43)	0.0295(7)	0.0256(7)	0.0197(6)	0.0036(5)	0.0083(5)	−0.0054(5)
C(44)	0.0180(6)	0.0339(7)	0.0122(5)	0.0023(5)	0.0038(4)	0.0001(5)
C(45)	0.0559(11)	0.0292(8)	0.0232(7)	−0.0081(6)	0.0213(7)	−0.0042(7)
C(46)	0.0571(11)	0.0206(7)	0.0242(7)	−0.0044(5)	0.0216(7)	−0.0051(7)
N(5)	0.0174(5)	0.0130(4)	0.0146(4)	0.0001(3)	0.0032(4)	0.0017(4)
O(1)	0.0213(5)	0.0141(4)	0.0319(5)	−0.0021(4)	0.0021(4)	−0.0023(3)
N(6)	0.0141(4)	0.0132(4)	0.0136(4)	−0.0009(3)	0.0024(3)	−0.0006(3)
N(7)	0.0176(5)	0.0121(5)	0.0225(5)	0.0000(4)	0.0020(4)	0.0010(4)
C(1)	0.0159(5)	0.0135(5)	0.0226(6)	−0.0001(4)	0.0002(4)	−0.0005(4)
C(2)	0.0168(6)	0.0140(5)	0.0304(7)	−0.0013(5)	−0.0005(5)	−0.0018(4)
C(3)	0.0156(5)	0.0149(6)	0.0282(6)	−0.0009(5)	−0.0008(5)	−0.0009(4)
C(4)	0.0235(6)	0.0137(6)	0.0388(8)	0.0018(5)	0.0008(6)	0.0042(5)

[a]The estimated standard deviations of the least significant digits are given in parentheses. The anisotropic displacement factor exponent takes the form: $-2\,\pi\,[h^2\,U_{11}\,+...+\,2\,h\,k\,a^*\,b^*\,U_{12}]$.

Table S12. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for *mono*-[Fe(T*p*FPP)(NO)(1-MeIm)][a]

atom	x	y	z	U(eq)
H(B1	0.6299	0.1314	0.3773	0.020
H(B2	0.4670	0.1285	0.4225	0.019
H(B3	0.3300	0.1055	0.7360	0.019
H(B4	0.4025	0.1103	0.8981	0.019
H(B5	0.7537	0.1354	1.0694	0.020
H(B6	0.9159	0.1272	1.0228	0.020
H(B7	1.0512	0.0948	0.7110	0.020
H(B8	0.9791	0.1019	0.5487	0.020
H(12)	0.3654	0.0238	0.4964	0.020
H(13)	0.2117	0.0311	0.4142	0.023
H(15)	0.1762	0.2250	0.5255	0.041
H(16)	0.3301	0.2173	0.6072	0.034
H(22)	0.5129	0.2299	0.9905	0.019
H(23)	0.4625	0.2479	1.1328	0.021
H(25)	0.5511	0.0479	1.2084	0.025
H(26)	0.6022	0.0309	1.0660	0.024
H(32)	1.0500	0.0061	0.8859	0.025
H(33)	1.2059	0.0153	0.9630	0.029
H(35)	1.1736	0.2291	0.9822	0.032
H(36)	1.0187	0.2198	0.9031	0.029
H(42)	0.8478	0.2309	0.4458	0.025
H(43)	0.9030	0.2455	0.3051	0.029
H(45)	0.8513	0.0367	0.2491	0.042
H(46)	0.7968	0.0224	0.3903	0.039
H(1)	0.5685	0.2629	0.6763	0.021
H(2)	0.8079	0.3714	0.7595	0.025
H(3)	0.8412	0.2419	0.7757	0.024
H(4A)	0.5738	0.4029	0.6347	0.038
H(4B)	0.6654	0.4452	0.6829	0.038
H(4C)	0.5842	0.4197	0.7412	0.038

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor the estimated standard deviations of the least significant digits are given in parentheses.

Supporting Information

Figure 1. Comparison of the measured VDOS for powder samples of *mono*- and *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)].

Figure 2. Illustration of the two crystalline forms of [Fe(T*p*FPP)(1-MeIm)(NO)]. The triclinic form is on the right.

Figure 3. Diagram showing overlap of molecules of the two polymorphs. The two molecules are centered on the four porphyrin nitrogen atoms. The triclinic species is drawn with thermal ellipsoids contoured at the 50% probability level as solid surfaces, whereas atoms of the monoclinic form are drawn with translucent spheres of arbitary radius. Atoms of the NO and the porphyrin core are seen to be close to overlap, whereas the imidiazole and peripheral *p*-fluorophenyl groups are not.

Figure 4. Predicted vibrational modes for *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] with frequencies of 147 $cm^{-1}$and 166 cm^{-1}.

Figure 5. Predicted vibrational mode for the complex in-plane and out-of-plane motion of the FeNO group and the imidazole leading to changes in the Fe–N_{Im} bond at 322 cm^{-1}. The experimentally observed values are 315 cm^{-1} in *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] and 310 cm^{-1} in *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)].

Figure 6. Predicted vibrational modes for the in-plane motion of the FeNO group. The imidazole group is omitted for clarity. The experimentally observed values that correspond to the calculated values in parentheses for *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] are 219 (219), 343 (339) and 456/471 (463/466) cm^{-1} and for *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] are 218 (219), 338 (339) and 457 (463/466) cm^{-1}.

Figure 7. Formal diagram of the porphyrinato core of *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] (top) and *tri*-[Fe(T*p*FPP)(1-MeIm)(NO)] (bottom) both displaying the perpendicular displacements (in units of 0.01 Å) of the core atoms from the 24-atom mean plane. Positive displacements are toward the nitrosyl-coordinated face, while the imidazole ligand is displaced on the negative side of the porphyrin core. The orientation of the imidazole ligand with respect to the porphyrin core is also illustrated. The location of the 1-methyl group is represented by the large circle, while the location nitrosyl projection onto the porphyrin core is indicated by the small circle. Average bond distances (Å) and angles (degrees) are also displayed.

Table S1. Complete Crystallographic Details for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)].

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for *tri*-[Fe(T*p*FPP)(NO)(1-MeIm)].