Supporting Informations

Effects of Axial Pyridine Coordination on a Saddle-Distorted Porphyrin Macrocycle: Stabilization of Hexa-coordinated High-Spin Fe(III) and Air-stable Low-Spin Iron(II) Porphyrinates

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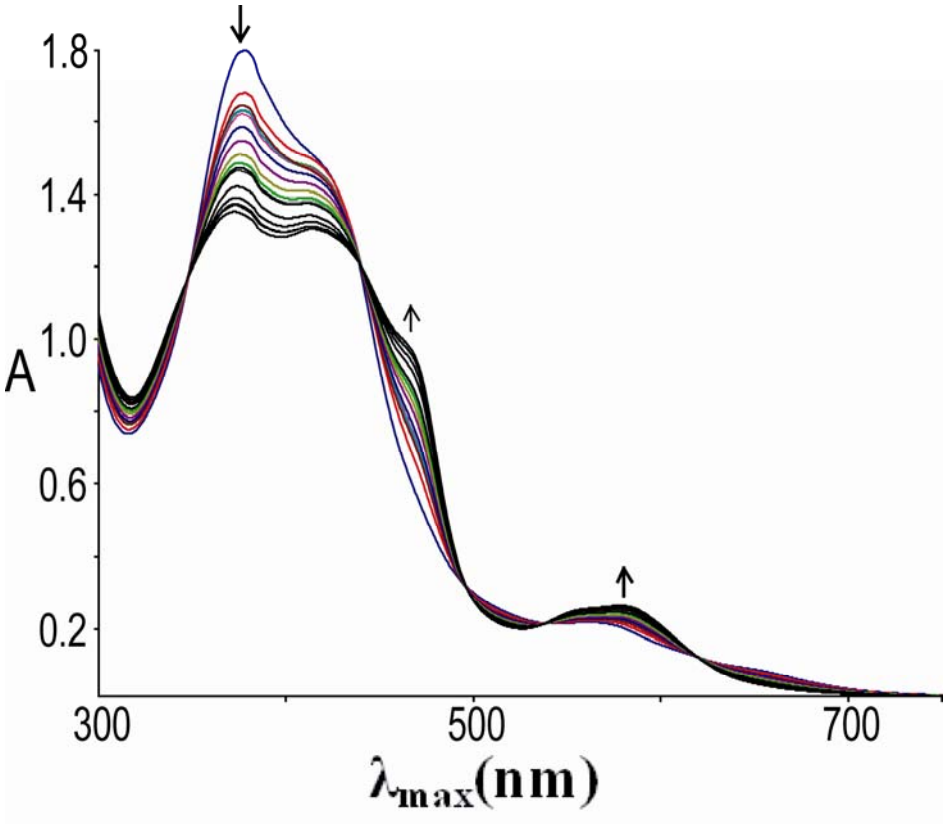

Figure S1. Time-evolution spectral changes (at 298K) of Fe^{III}(*tn*-OEP)ClO_4 in chloroform in presence of excess pyridine in air showing first the appearance of six-coordinated Fe^{III}(*tn*-OEP)$(py)_2.ClO_4$ which, on longer exposure, again converts to Fe^{II}(*tn*-OEP)$(py)_2$. Arrows indicate increase or decrease of band intensity.

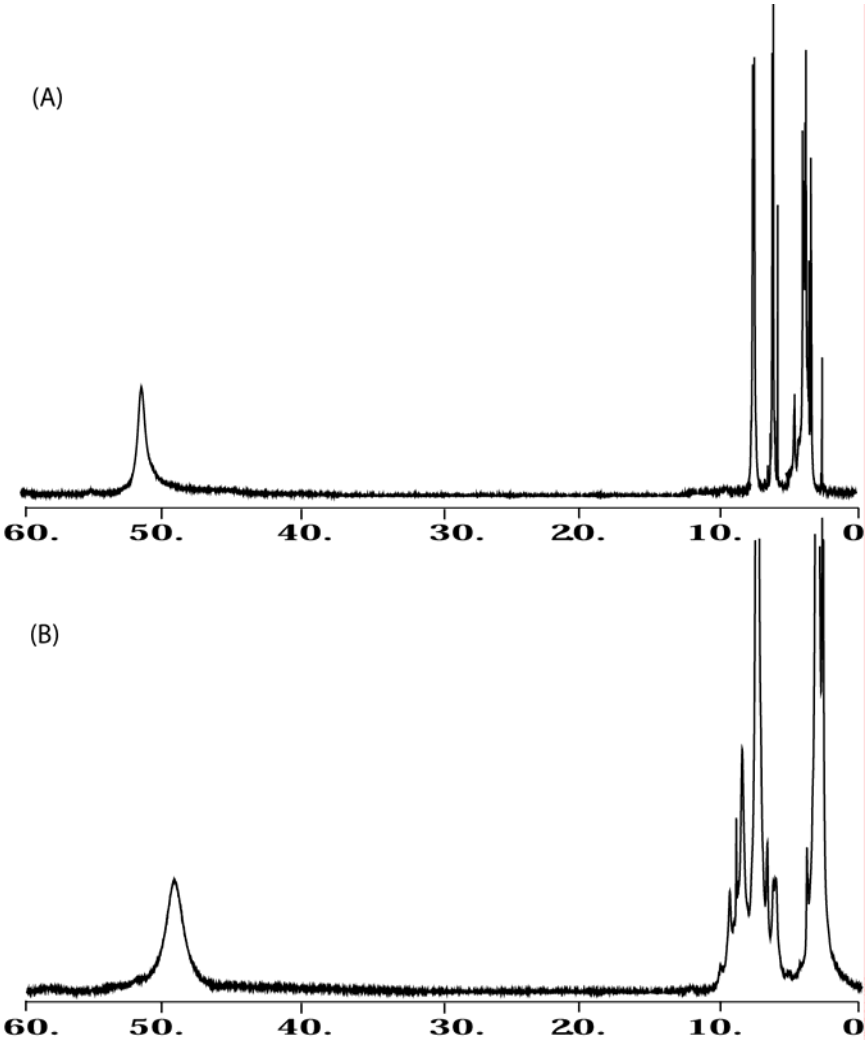

Figure S2: ^{1}H NMR spectra in $CDCl_3$ at 295K for (A) for Fe^{III}(*tn*-OEP)(4-CNpy)$_2$.ClO_4 (B) for Fe^{III}(*tn*-OEP)(3-Clpy)$_2$.ClO_4.

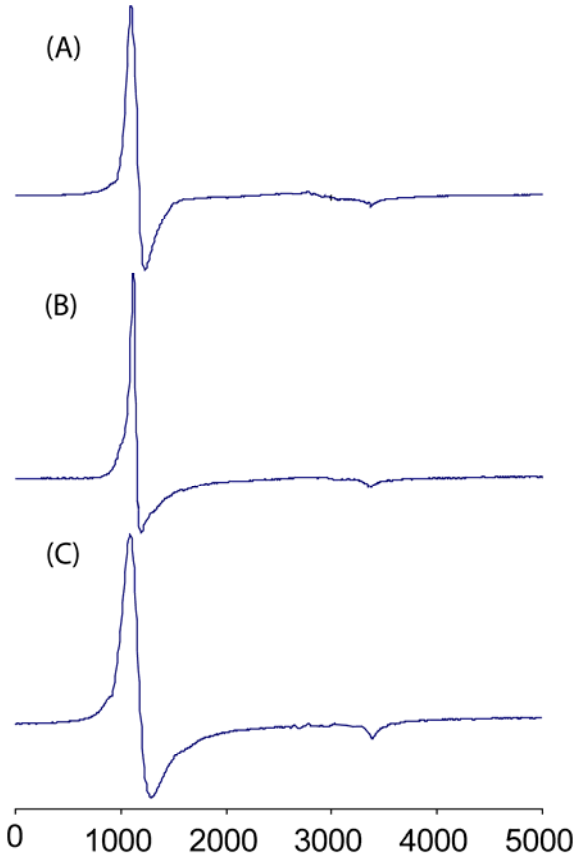

Figure S3. X-band EPR spectra of the isolated solid (at 120K) of (A) Fe^{III}(*tn*-OEP)(4-CNpy)$_2$.ClO_4 ; (B) Fe^{III}(*tn*-OEP)(3-Clpy)$_2$.ClO_4 and (C) Fe^{III}(*tn*-OEP)(py)$_2$.ClO_4.

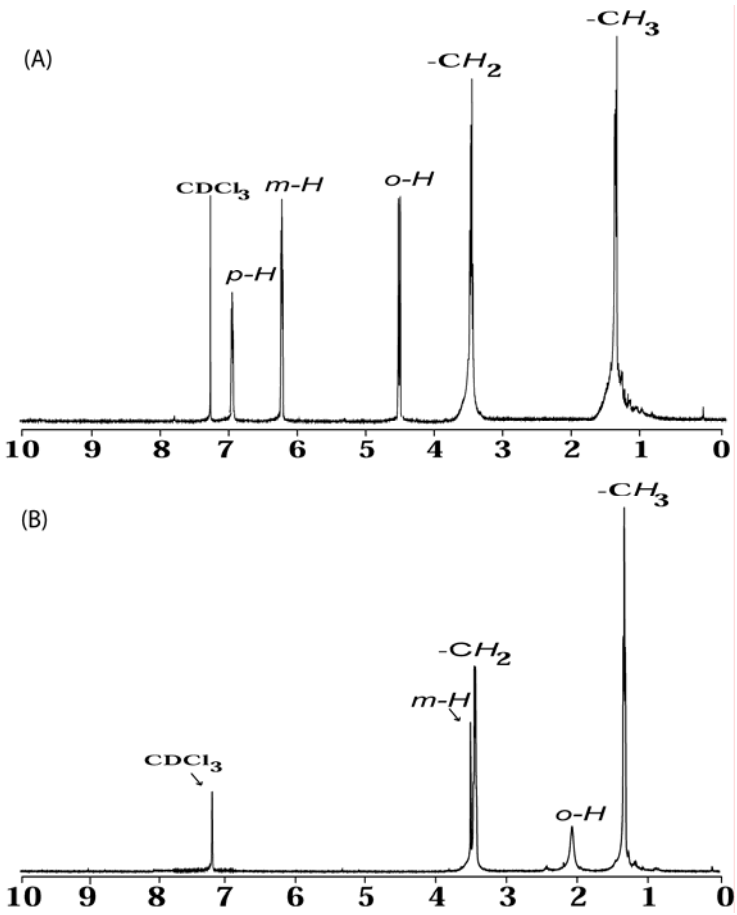

Figure S4: ^{1}H NMR spectra in $CDCl_3$ at 295K (A) for Fe^{II}(*tn*-OEP)$(py)_2$ and (B) for Fe^{II}(*tn*-OEP)$(4\text{-CNpy})_2$

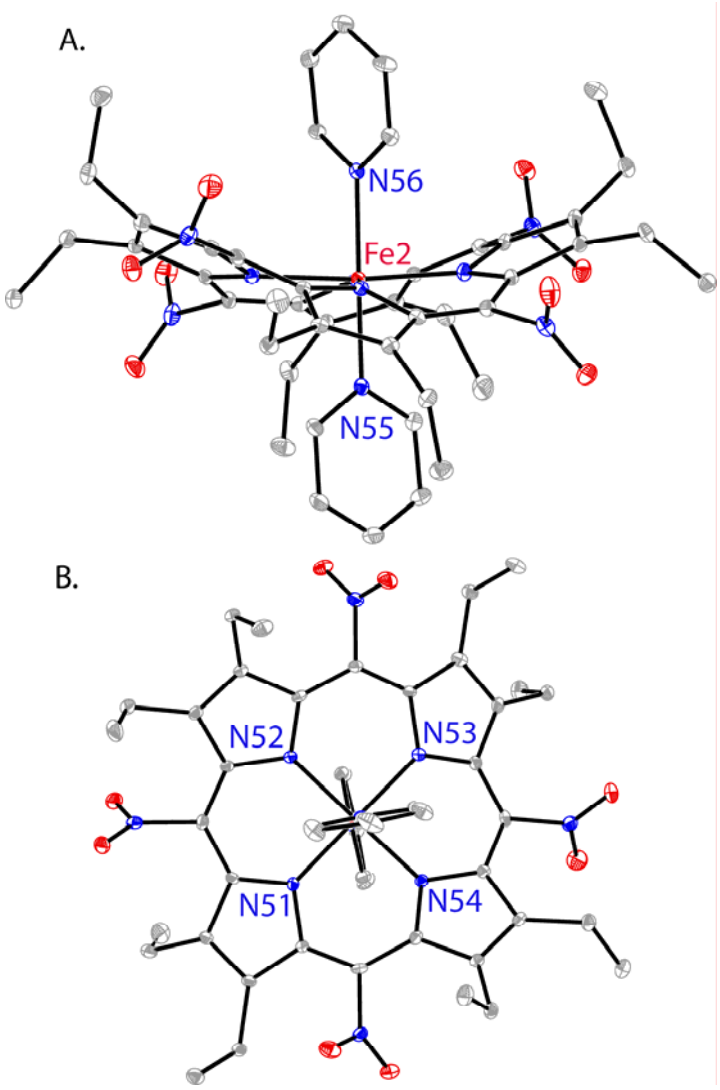

Figure S5. Two perspective views [A, side view; B, top view] for molecule 2 of Fe^{II}(*tn*-OEP)$(py)_2$ showing 50% thermal contours for all non-hydrogen atoms at 100K (H-atoms have been omitted for clarity).

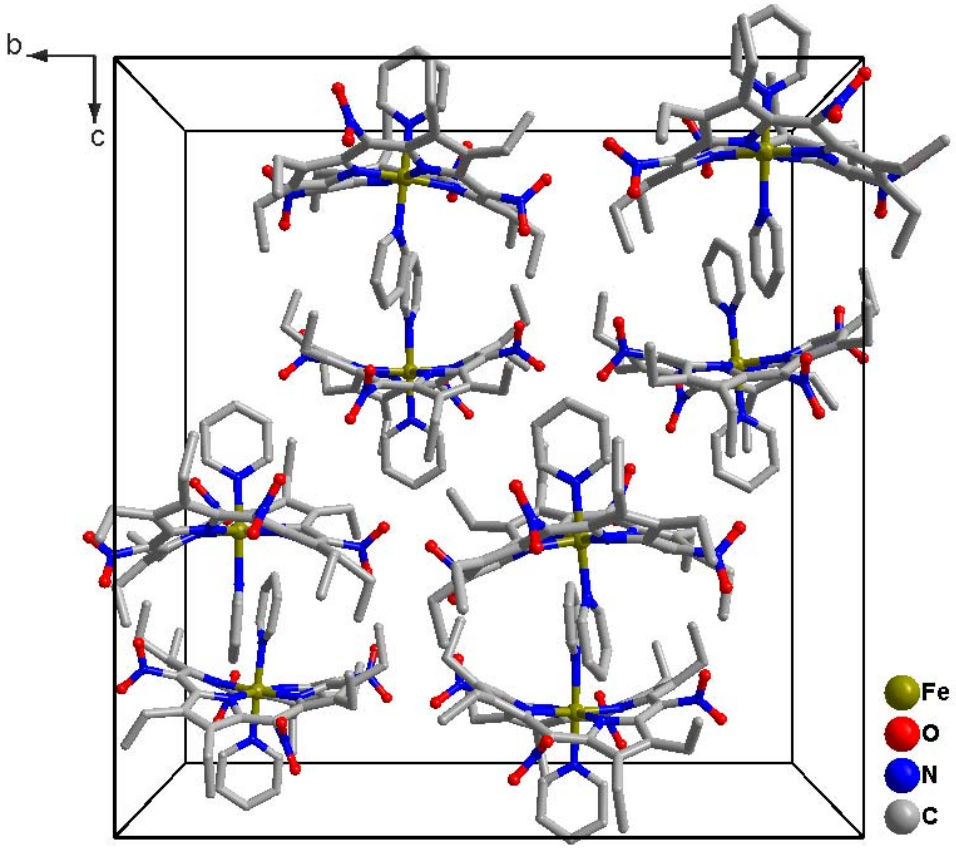

Figure S6. Diagram illustrating the packing of the Fe^{II}(*tn*-OEP)$(py)_2$ molecules in the unit cell.

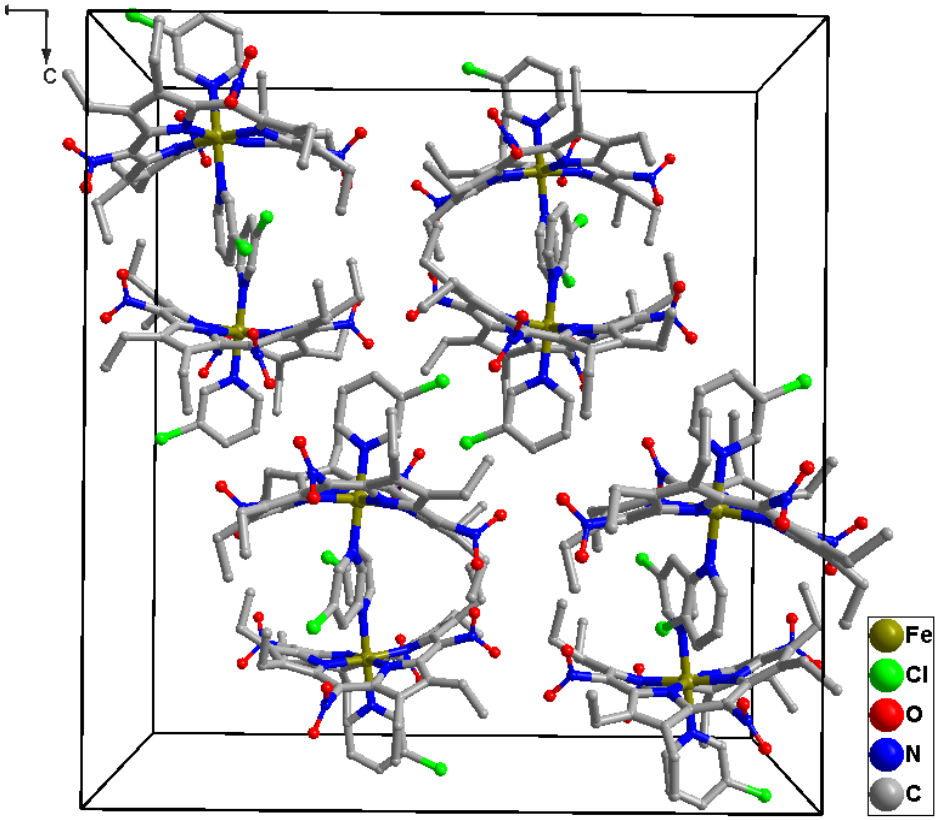

Figure S7. Diagram illustrating the packing of the Fe^{II}(*tn*-OEP)(3-Clpy)$_2$ molecules in the unit cell.

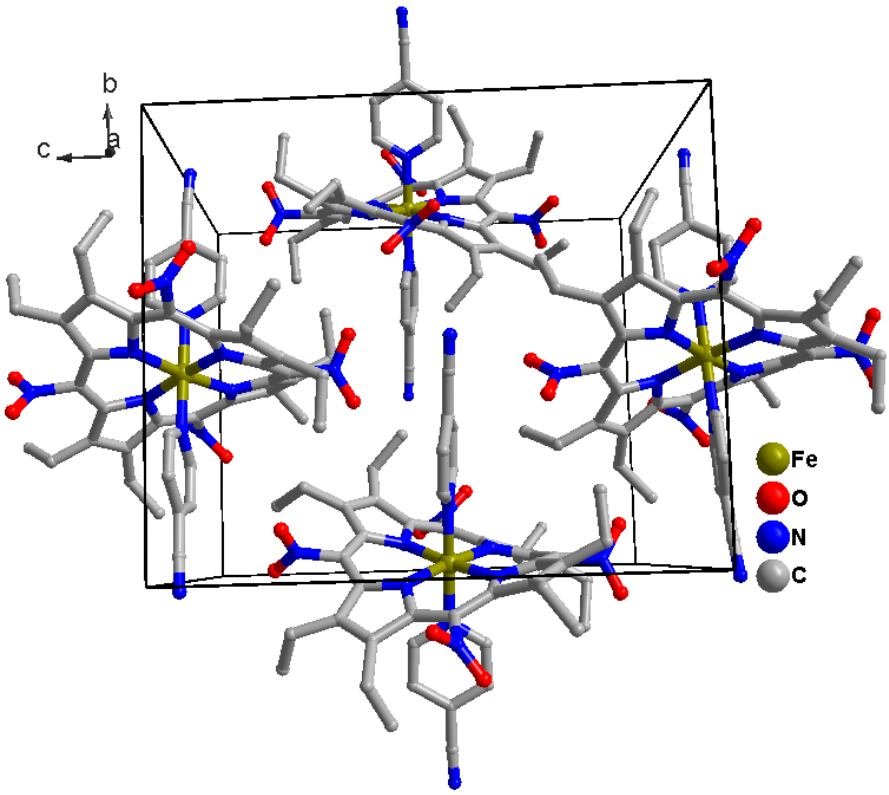

Figure S8. Diagram illustrating the packing of the Fe^{II}(tn-OEP)(4-CNpy)$_2$ molecules in the unit cell.

Table S1. Crystal Data and Data Collection Parameters

	Fe^{II}(*tn*-OEP)$(Py)_2$	Fe^{II}(*tn*-OEP)$(4\text{-CNpy})_2$	Fe^{II}(*tn*-OEP)$(3\text{-Clpy})_2$
T, K	100(2)	100(2)	100(2)
Formula	$C_{46}\ H_{50}\ Fe\ N_{10}\ O_8$	$C_{48}\ H_{48}\ Fe\ N_{12}\ O_8$	$C_{46}\ H_{48}\ Cl_2\ Fe\ N_{10}\ O_8$
Formula weight	926.81	976.83	995.69
Color and Habit	Dark green	Dark green	Dark green
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	P2(1)2(1)2(1)	P2(1)/c	Pbca
a, Å	13.4183(11)	19.4563(17)	13.3561(10)
b, Å	25.469(2)	14.1225(12)	25.439(2)
c, Å	26.501(2)	16.7267(14)	27.699(2)
α , deg	90	90	90
β, deg	90	93.694(2)	90
γ, deg	90	90	90
V, $Å^3$	9056.9(13)	4586.5(7)	9411.1(13)
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Z	8	4	8
d_{calcd}, g•cm^{-3}	1.359	1.415	1.405
μ, mm^{-1}	0.398	0.398	0.498
F(000)	3888	2040	4144
No. of unique data	15904	8767	9247
No. of restraints	0	0	0
No. of params. Refined	1188	630	622
GOF on F^2	1.045	1.021	1.032
R1[a] $[I > 2\sigma(I)]$	0.0544	0.0468	0.0558
R1[a] (all data)	0.0726	0.0730	0.0905
wR2[b] (all data)	0.1288	0.1219	0.1381

$$^{a}\ R1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|};\ ^{b}\ wR2 = \sqrt{\frac{\sum \left[w\left(Fo^2 - Fc^2\right)^2\right]}{\sum \left[w\left(Fo^2\right)^2\right]}}$$