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Supporting Information

Spin-crossover system between S=5/2 and S=1/2 states observed in the iron (III) porphyrin complexes axially coordinated two pyridine-N oxide derivatives

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Table S1 Crystallographic data of **1a-e** and **2**.

Compound	**1a** · $2CH_2Cl_2$	**1c**	**1c**	**1e** · 2 toluene	**2** · CH_2Cl_2 + 2.5 toluene
Temperature (K)	100(2)	300(2)	100(2)	100(2)	100(2)
Chemical formula	$C_{60}H_{60}N_6O_2Cl_2FeBF_4 \cdot 2(CH_2Cl_2)$	$C_{68}H_{68}N_6O_2FeBF_4$	$C_{68}H_{68}N_6O_2FeBF_4$	$C_{70}H_{72}N_6O_2FeBF_4 \cdot 2(C_7H_8)$	$C_{58}H_{28}N_6O_2F_{20}FeBF_4 \cdot CH_2Cl_2 \cdot 2.5(C_7H_8)$
Formula weight	1352.61	1141.92	1141.92	1384.28	1706.80
Crystal size (mm)	0.15 x 0.15 x 0.10	0.25 x 0.10 x 0.08	0.50 x 0.40 x 0.40	0.20 x 0.05 x 0.02	0.18 x 0.06 x 0.02
Crystal color	brown	brown	brown	black	black
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	C_2/c	C_2/c	$P\bar{1}$	$P\bar{1}$
Wave length (Å)	0.71075	0.71075	0.71075	0.71075	0.71075
a (Å)	12.983(5)	25.363(5)	25.480(6)	14.352(2)	14.756(2)
b (Å)	13.837(5)	14.931(3)	14.606(3)	15.273(2)	15.299(2)
c (Å)	19.824(6)	17.644(4)	17.569(4)	18.230(3)	18.938(2)
α (°)	109.92(2)	90	90	70.093(8)	92.515(14)
β (°)	95.24(2)	112.617(3)	114.161(3)	76.760(9)	108.315(10)
γ (°)	100.09(2)	90	90	77.769(9)	117.216(8)
Volume (Å^3)	3252(2)	6168(2)	5966(2)	3618(1)	3619.3(8)
Z	2	4	4	2	2
Density (Calculated) (g cm^{-3})	1.381	1.230	1.271	1.271	1.611
Absorption coefficient (mm^{-1})	0.540	0.305	0.316	0.273	0.410
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Max. and Min. transmission	0.948 and 0.863	0.976 and 0.928	0.987 and 0.984	0.995 and 0.947	0.992 and 0.930
F (000)	1398	2396	2396	1462	1724
θ Range for data collection (°)	2.01 to 28.00	1.62 to 28.00	2.29 to 28.00	1.90 to 26.5	2.12 to 26.5
Index ranges	-17<=h<=17, -18<=k<=18, -26<=l<=26	-33<=h<=33, -19<=k<=19, -23<=l<=23	-33<=h<=33, -19<=k<=19, -23<=l<=23	-18<=h<=18, -19<=k<=19, -22<=l<=22	-18<=h<=18, -19<=k<=19, -23<=l<=23
Reflections collected	15661	7452	7218	14974	14590
Independent reflections	12684 [R_{int} = 0.0683]	5678 [R_{int} = 0.0690]	6683 [R_{int} = 0.0985]	10409 [R_{int} = 0.0977]	10094 [R_{int} = 0.0977]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	15661 / 6 / 836	7452 / 81 / 401	7218 / 60 / 401	14974 / 0 / 922	14590 / 375 / 1163
Goodness-of-fit on F^2	1.053	1.142	1.142	1.141	1.046
Final *R* indices ($I>2\sigma(I)$)	R_1 = 0.0683, wR_2 = 0.1439	R_1 = 0.0690, wR_2 = 0.1802	R_1 = 0.0985, wR_2 = 0.1941	R_1 = 0.0977, wR_2 = 0.1846	R_1 = 0.0988, wR_2 = 0.2119
R indices (all data)	R_1 = 0.0843, wR_2 = 0.1552	R_1 = 0.0897, wR_2 = 0.1975	R_1 = 0.1067, wR_2 = 0.1986	R_1 = 0.1382, wR_2 = 0.2062	R_1 = 0.1373, wR_2 = 0.2368
Largest peak and hole (e Å^{-3})	+0.81 and -0.91	+0.29 and -0.54	+0.57 and -0.50	+0.56 and -0.46	+0.90 and -0.51

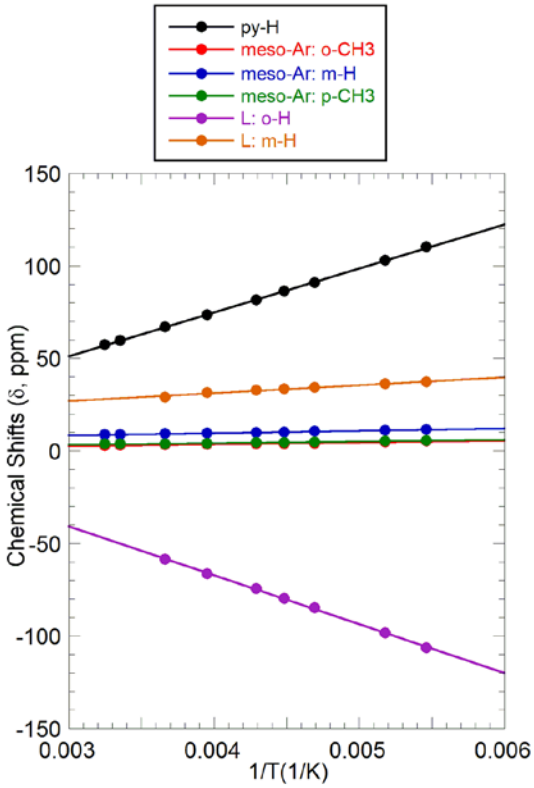


Fig. S1 Curie plots of proton signals of **1a** taken in CD_2Cl_2 solution.

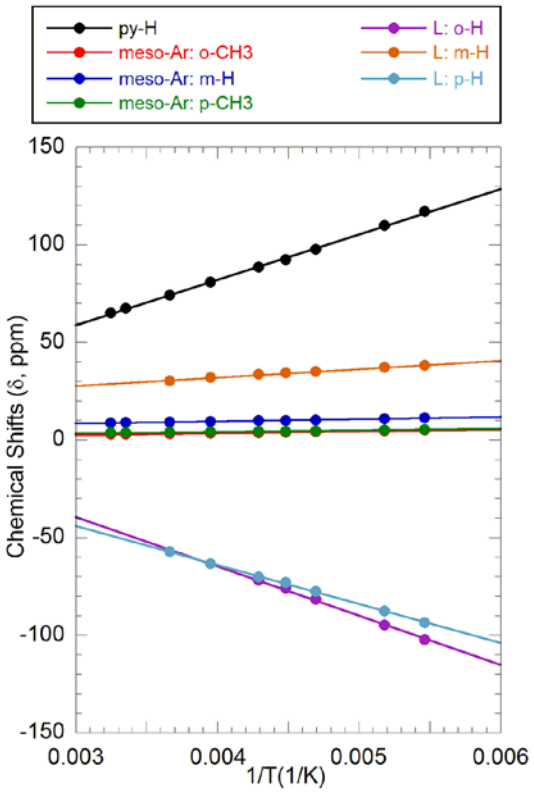


Fig. S2 Curie plots of proton signals of **1b** taken in CD_2Cl_2 solution.

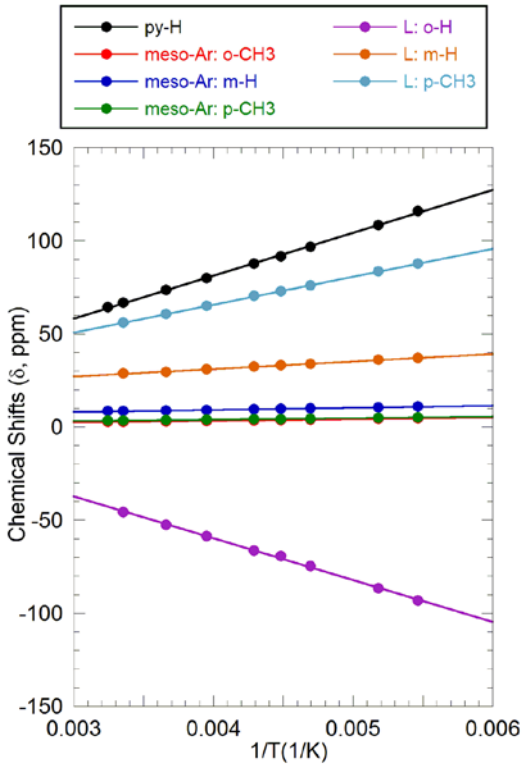


Fig. S3 Curie plots of proton signals of **1c** taken in CD_2Cl_2 solution.

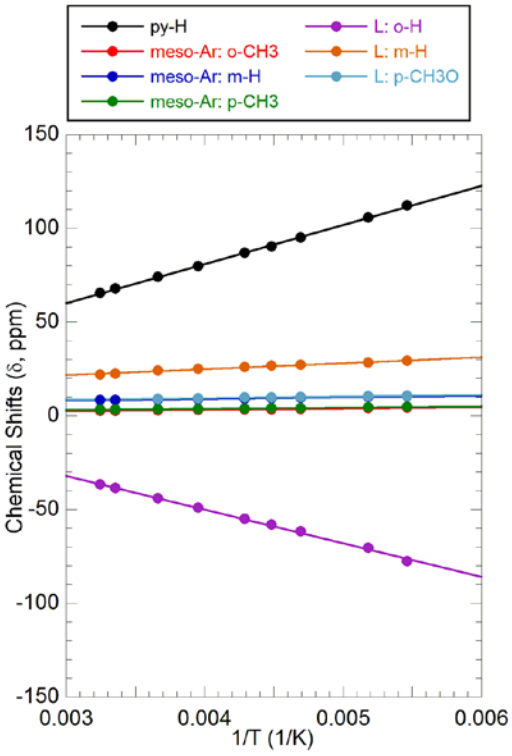


Fig. S4 Curie plots of proton signals of **1d** taken in CD_2Cl_2 solution.

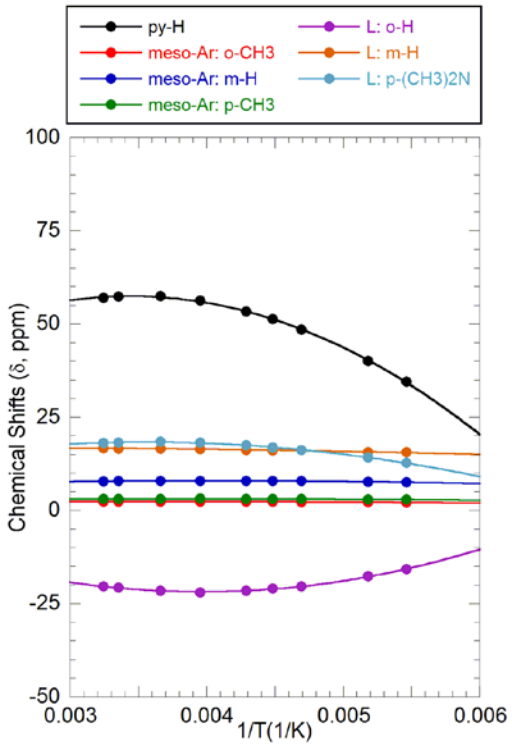


Fig. S5 Curie plots of proton signals of **1e** taken in CD_2Cl_2 solution.

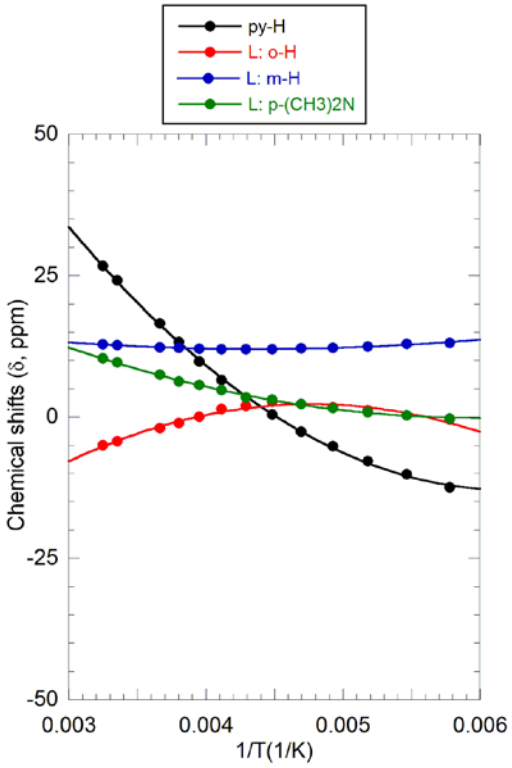


Fig. S6 Curie plots of proton signals of **2** taken in CD_2Cl_2 solution.

Table S2 EPR g values of **1a-e** and **2**.

Complex	EPR (CH_2Cl_2 / toluene, 15 K)			EPR (solid, 4 K)		
	g_1	g_2	g_3	g_1	g_2	g_3
1a	5.94	5.94	1.99	5.62	5.62	1.98
1b	5.88	5.88	1.99	5.68	5.68	1.95
1c	5.89	5.89	1.99	2.41	2.23	1.92
1d	5.68	5.68	1.99	2.41	2.23	1.99
	2.41	2.22	1.92			
1e	2.39	2.21	1.93	2.41	2.22	1.93
2e	2.42	2.22	1.92	2.37	2.19	1.95

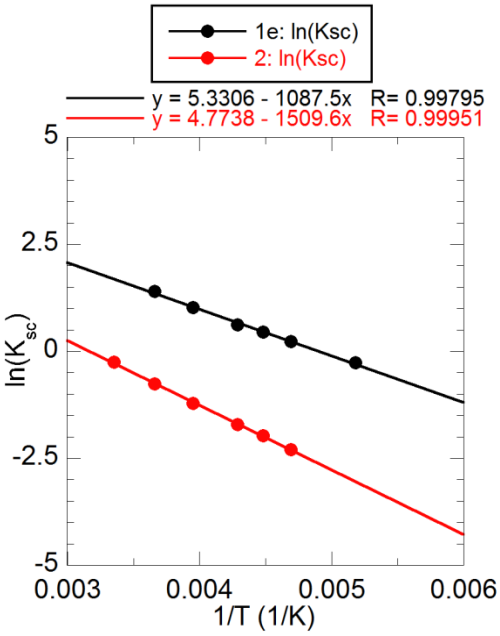


Fig. S7 Van't Hoff plots for **1e**(black) and **2**(red).

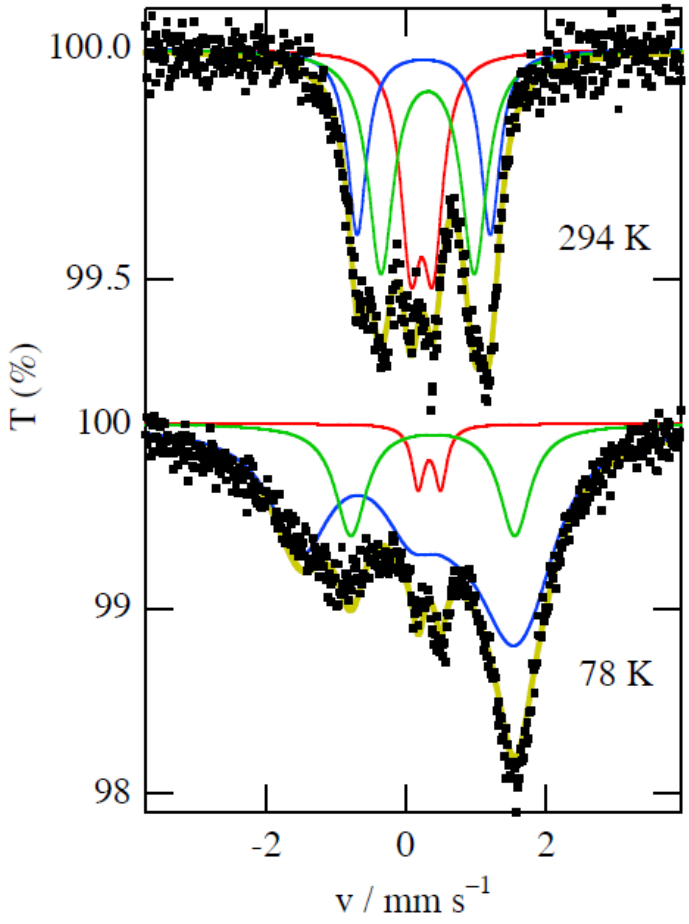


Fig. S8 ^{57}Fe Mössbauer spectra of **1e** taken for a microcrystalline sample at 294 (upper) and 78 K (lower).

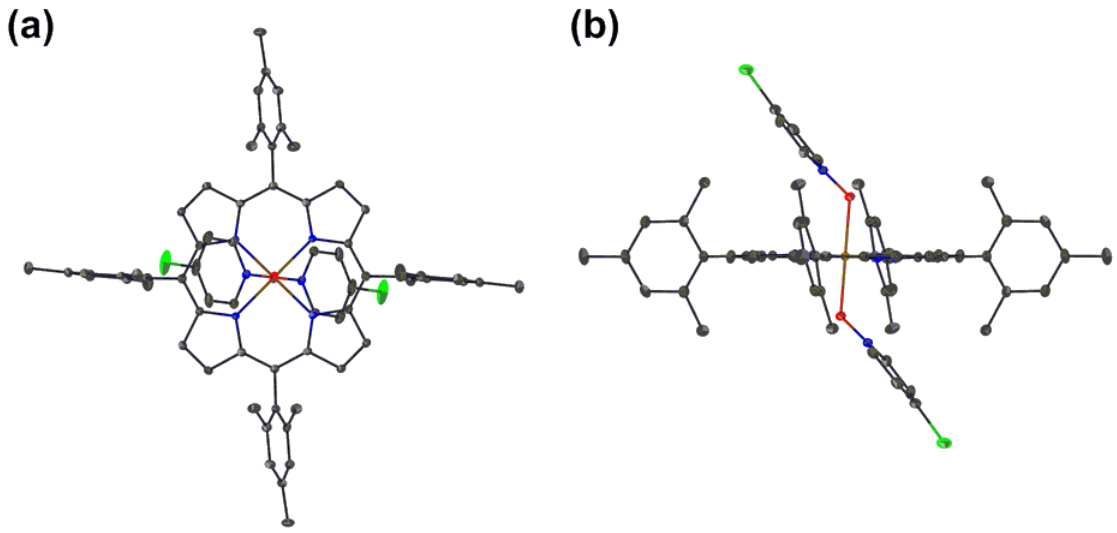


Fig. S9 ORTEP drawing of **1a**·$2CH_2Cl_2$ (100 K) seen along the: (a) O-Fe-O and (b) N-Fe-N axis, showing the thermal ellipsoids at 30% probability level. Hydrogen, solvent, and counter anion atoms are omitted for clarity.

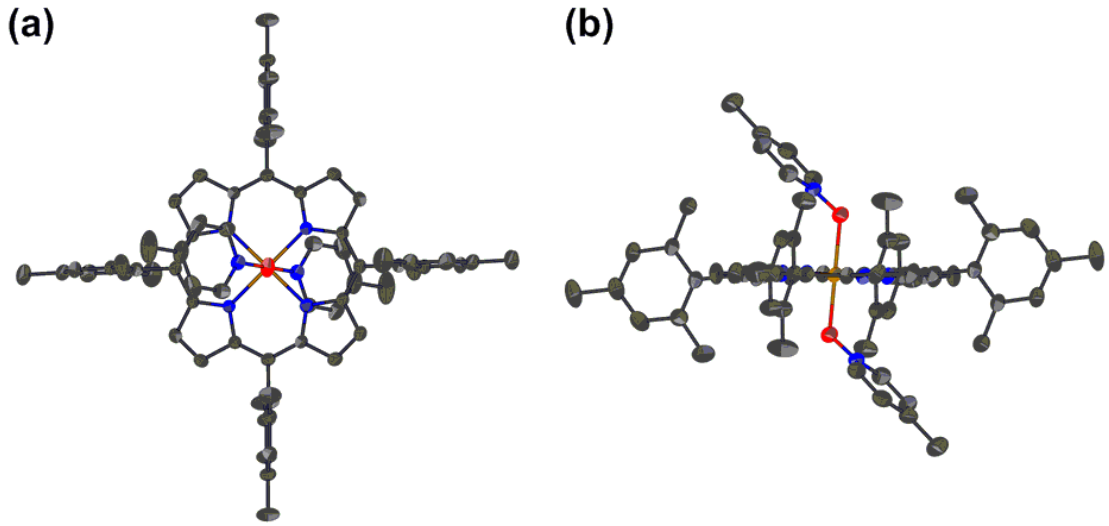


Fig. S10 ORTEP drawing of **1c** (300 K) seen along the: (a) O-Fe-O and (b) N-Fe-N axis, showing the thermal ellipsoids at 30% probability level. Hydrogen, solvent, and counter anion atoms are omitted for clarity.

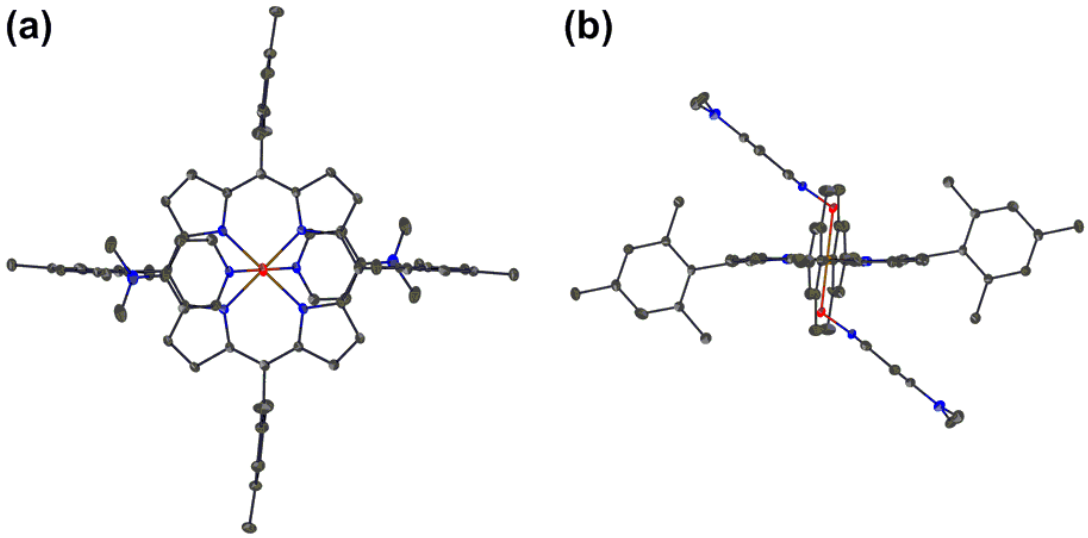


Fig. S11 ORTEP drawing of **1e**·2toluene (100 K) seen along the: (a) O-Fe-O and (b) N-Fe-N axis, showing the thermal ellipsoids at 30% probability level. Hydrogen, solvent, and counter anion atoms are omitted for clarity.

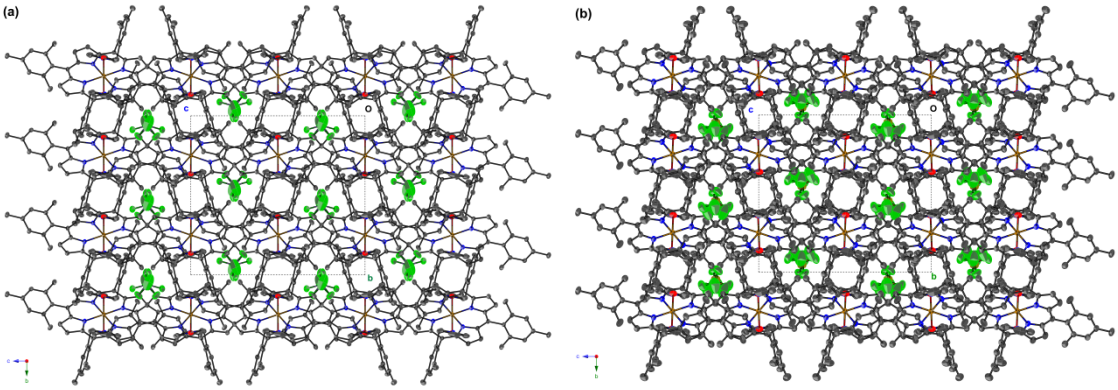


Fig. S12 Crystal packing diagrams of **1c** viewed along with the a axis at 100K(a) and 300K(b).

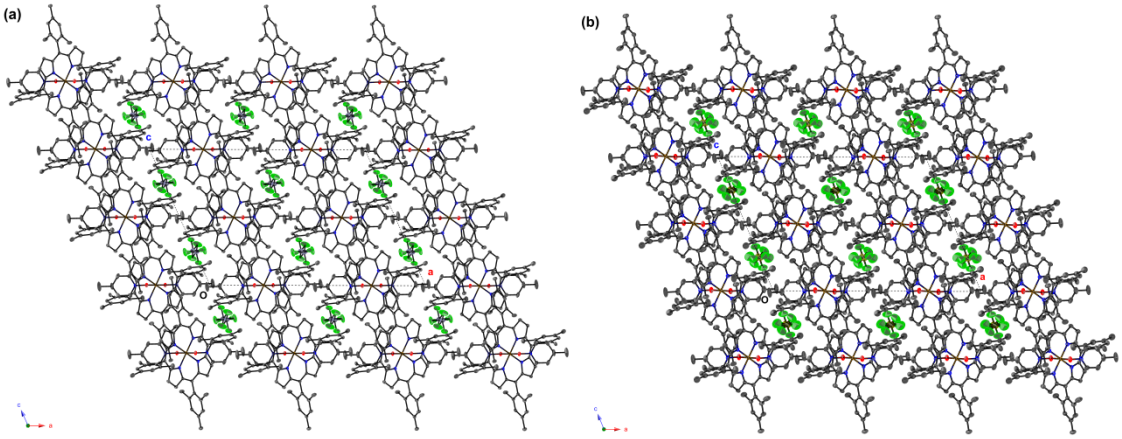


Fig. S13 Crystal packing diagrams of **1c** viewed along with the b axis at 100K(a) and 300K(b).

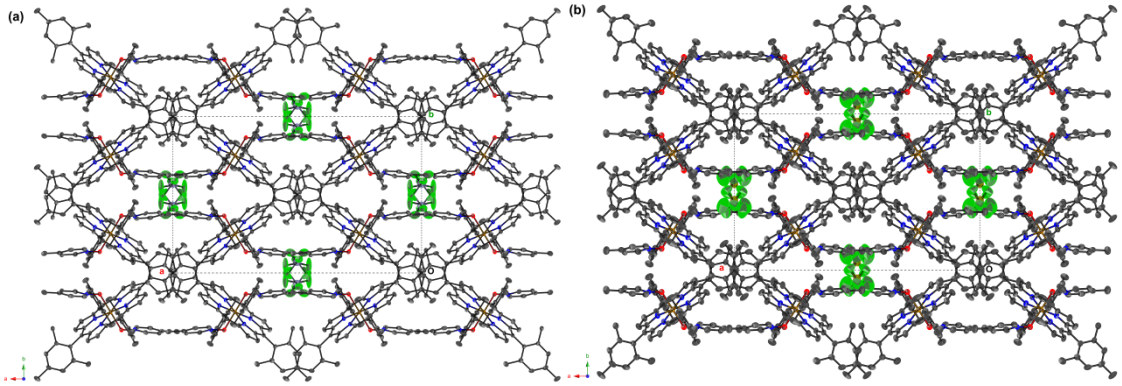


Fig. S14 Crystal packing diagrams of **1c** viewed along with the c axis at 100K(a) and 300K(b).

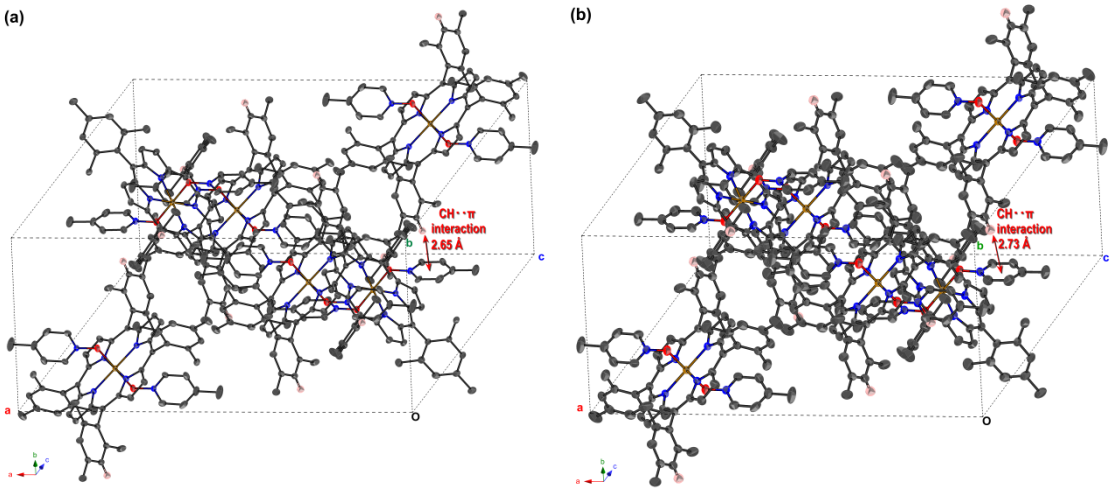
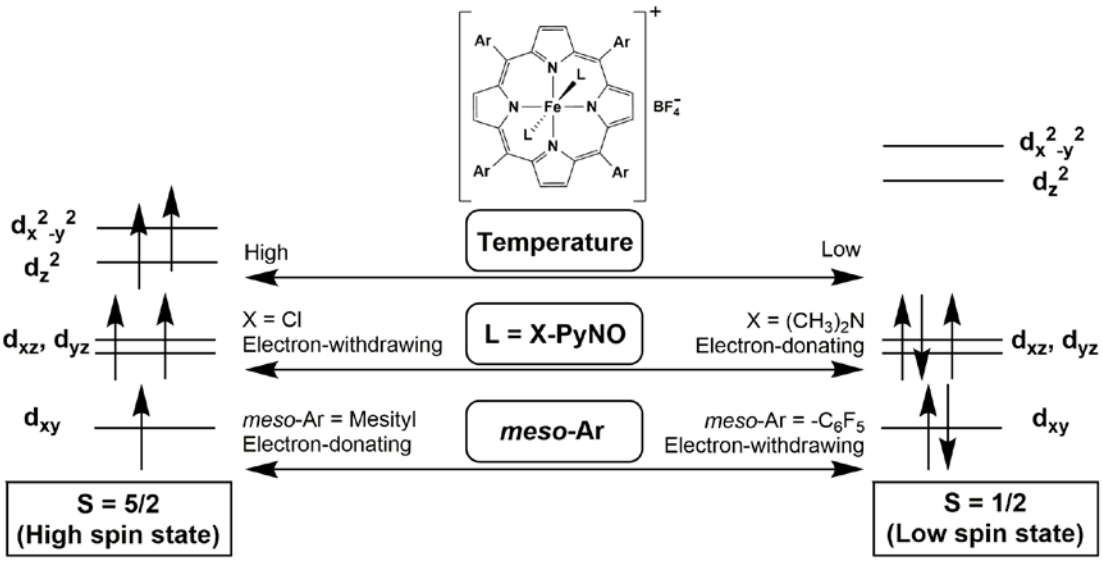


Fig. S15 Crystal packing diagrams of **1c** for one unit cell at 100K(a) and 300K(b).



Scheme S1 Spin crossover between S=5/2(high spin state) and S=1/2(low spin state) for these Fe(III) porphyrin complexes.