Supporting Information

Deprotonation/Protonation-Driven Tuning of the σ-Donor Ability of a Sulfur Atom in Iron(II) Complexes with a Thioamide SNS Pincer Type Ligand

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Table S1 Crystallographic and structure refinement data for compounds $\mathbf{H_2L^{DPM}}$, $[FeBr_2(\boldsymbol{\kappa^3}\text{-}\mathbf{H_2L^{DPM}})]$, $[Fe(THF)_2(\boldsymbol{\kappa^3}\text{-}\mathbf{L^{DPM}})]$, $[Fe(CO)_3(\boldsymbol{\kappa^3}\text{-}\mathbf{L^{DPM}})]$ and $[Fe(CN\text{-}xylyl)_3(\boldsymbol{\kappa^3}\text{-}\mathbf{L^{DPM}})]$

Compound	$\mathbf{H_2L^{DPM}}$	$[FeBr_2(\boldsymbol{\kappa^3}\text{-}\mathbf{H_2L^{DPM}})]$	$[Fe(THF)_2(\boldsymbol{\kappa^3}\text{-}\mathbf{L^{DPM}})]$	$[Fe(CO)_3(\boldsymbol{\kappa^3}\text{-}\mathbf{L^{DPM}})]$	$[Fe(CN\text{-}xylyl)_3(\boldsymbol{\kappa^3}\text{-}\mathbf{L^{DPM}})]$
Chemical formula	$C_{77}H_{67}N_3S_2$	$C_{77}H_{67}Br_2FeN_3S_2$, $2(C_4H_{10}O_2)$	$C_{85}H_{81}FeN_3O_2S_2$, $3.5(C_4H_8O)$	$C_{80}H_{65}FeN_3O_3S_2$, $2(C_7H_8)$	$C_{104}H_{92}FeN_6S_2$, $2.5(C_6H_6)$, C_5H_{12}
Formula weight	1098.52	1494.42	1537.85	1420.66	1858.33
Temp (°C)	–100	–100	–150	–150	–100
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1 (#2)	P-1 (#2)	$P2_1/n$ (#14)	P-1 (#2)	P-1 (#2)
a / Å	10.888(2)	9.872(3)	19.615(3)	13.514(3)	15.521(4)
b / Å	11.185(2)	19.911(7)	22.908(3)	16.520(3)	19.590(5)
c / Å	24.856(4)	21.027(7)	20.265(3)	19.046(4)	20.683(5)
α / °	97.198(3)	110.172(5)		65.733(7)	107.334(3)
β / °	90.800(2)	98.244(4)	108.4184(12)	79.394(9)	108.6612(3)
γ / °	91.953(3)	94.284(3)		78.280(10)	105.3219(14)
V / Å^3	3001.0(8)	3805(2)	8639(2)	3771.5(13)	5219(2)
Z	2	2	4	2	2
D_{calc}/g cm^{-3}	1.216	1.304	1.187	1.251	1.154
μ(Mo-Kα) / cm^{-1}	1.365	13.577	2.770	3.095	2.363
F(000)	1164	1556	3276	1496	1926
Reflections collected	24032	30489	67790	30043	52730
Independent reflections	13144	16706	19252	16577	23560
R(int)	0.0331	0.0696	0.0312	0.0341	0.0396
R1 ($I > 2\sigma(I)$)[a]	0.0536	0.0769	0.0730	0.0603	0.0702
R1 (all)	0.0854	0.1573	0.0872	0.0849	0.0995
w*R*2 (all)	0.1385	0.1811	0.2187	0.1706	0.1969
GOF	1.045	1.027	1.060	1.064	1.074
CCDC number	984342	984346	984347	984348	984349

[a] $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$, $wR2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$

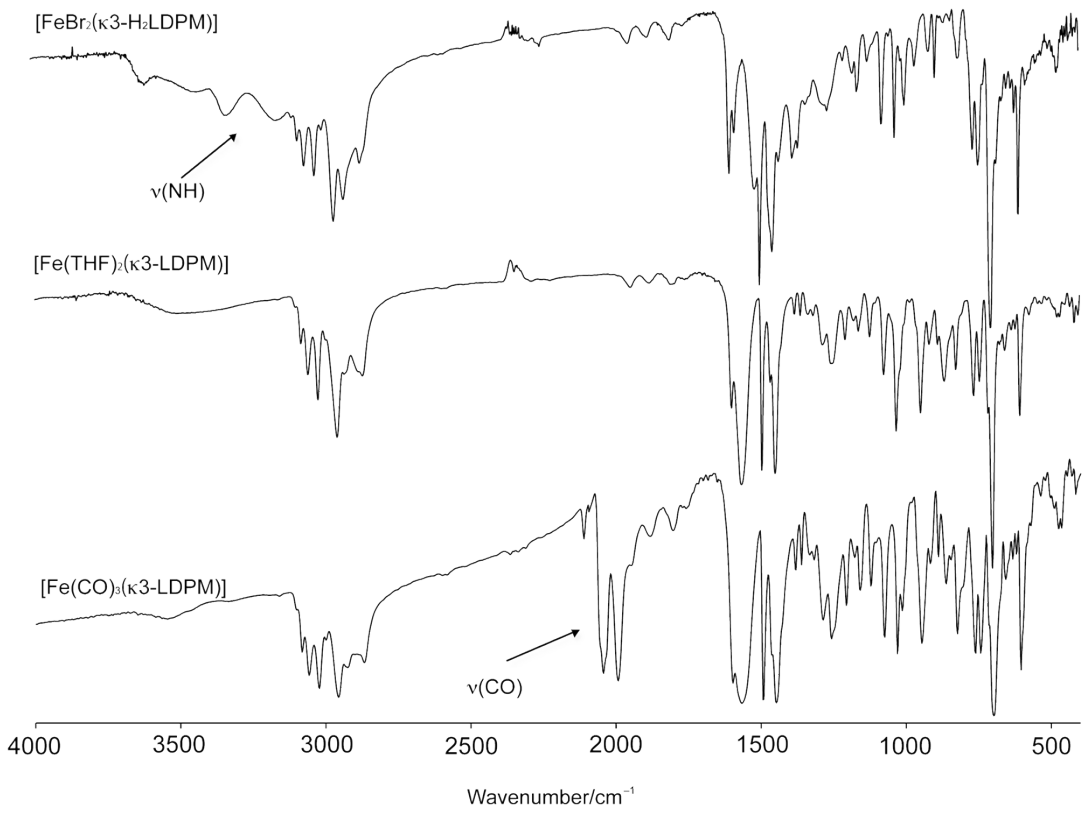

Figure S1 Solid state IR spectra of [$FeBr_2$(κ^3-H_2L^{DPM})], [Fe(THF)(κ^3-L^{DPM})] and [$Fe(CO)_3$(κ^3-L^{DPM})]

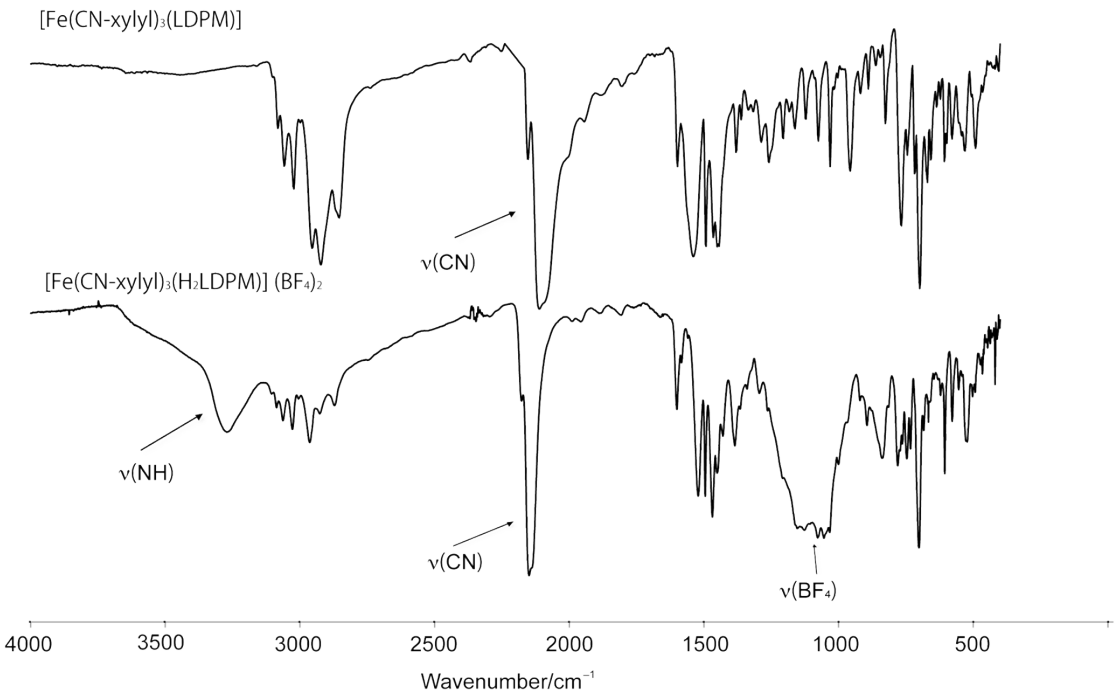

Figure S2 Solid state IR spectra of [$Fe(CN\text{-}xylyl)_3$(κ^3-L^{DPM})] and [$Fe(CN\text{-}xylyl)_3$(κ^3-H_2L^{DPM})]$(BF_4)_2$

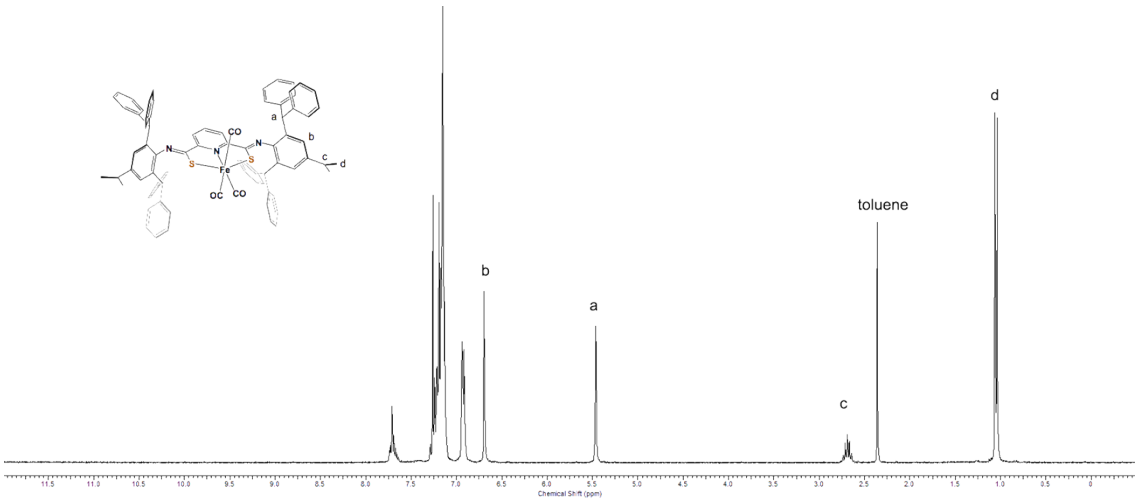

Figure S3 ^{1}H NMR spectrum of [Fe(CO)$_3$(**L^{DPM}**)] in $CDCl_3$

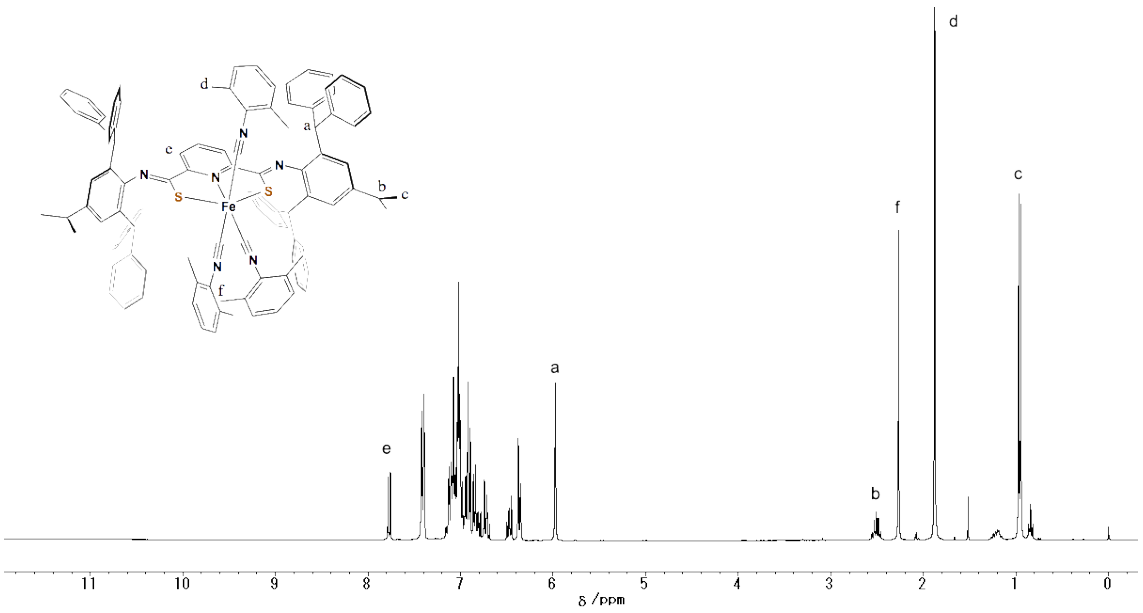

Figure S4 ^{1}H NMR spectrum of [Fe(CN-xylyl)$_3$(**L^{DPM}**)] in $CDCl_3$

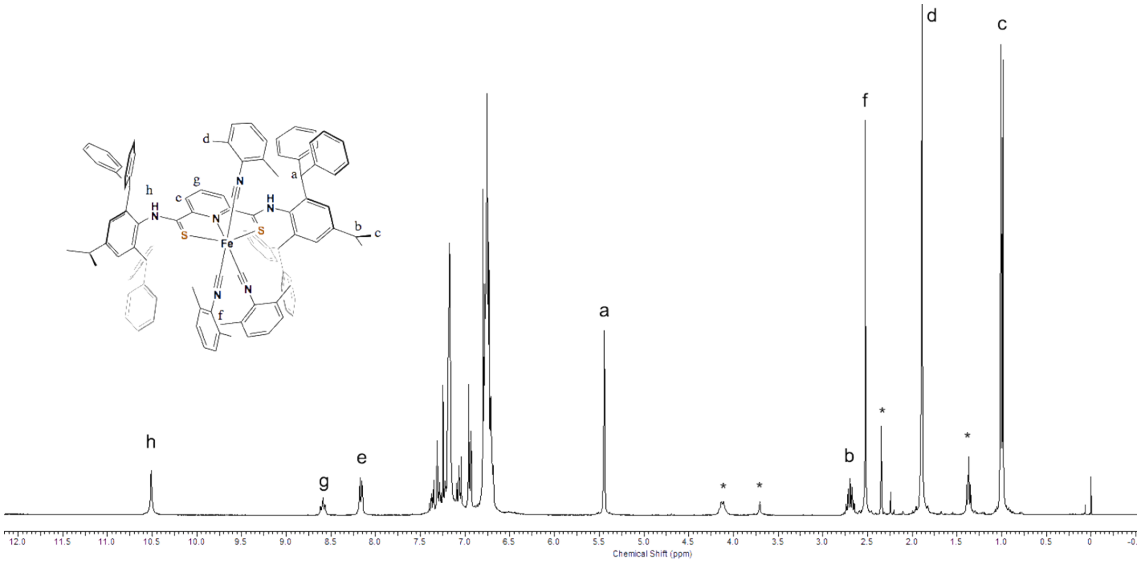

Figure S5 ^{1}H NMR spectrum of [Fe(CN-xylyl)$_3$(**H$_2$L^{DPM}**)](BF$_4$)$_2$ in CDCl$_3$