Electronic Supplementary Information

Iron(II) coordination pyrazole complexes with aromatic sulfonate ligands: the role of ether

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Figure S1: Representation of pairing scheme and intramolecular aromatic interaction between **DMPP** and anionic ***ps*** molecules in **1**. The same pairing scheme is also applicable to other complexes, **2** – **4.**

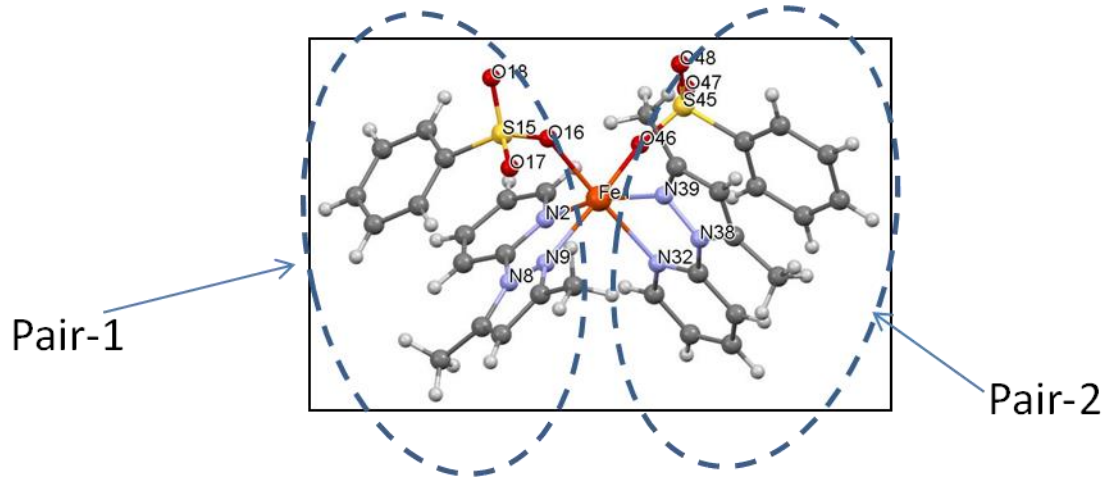

Figure S2: Comparison of Powder XRD patterns of precipitate form of **4** (black) with simulated pattern (red) obtained from single crystal XRD.

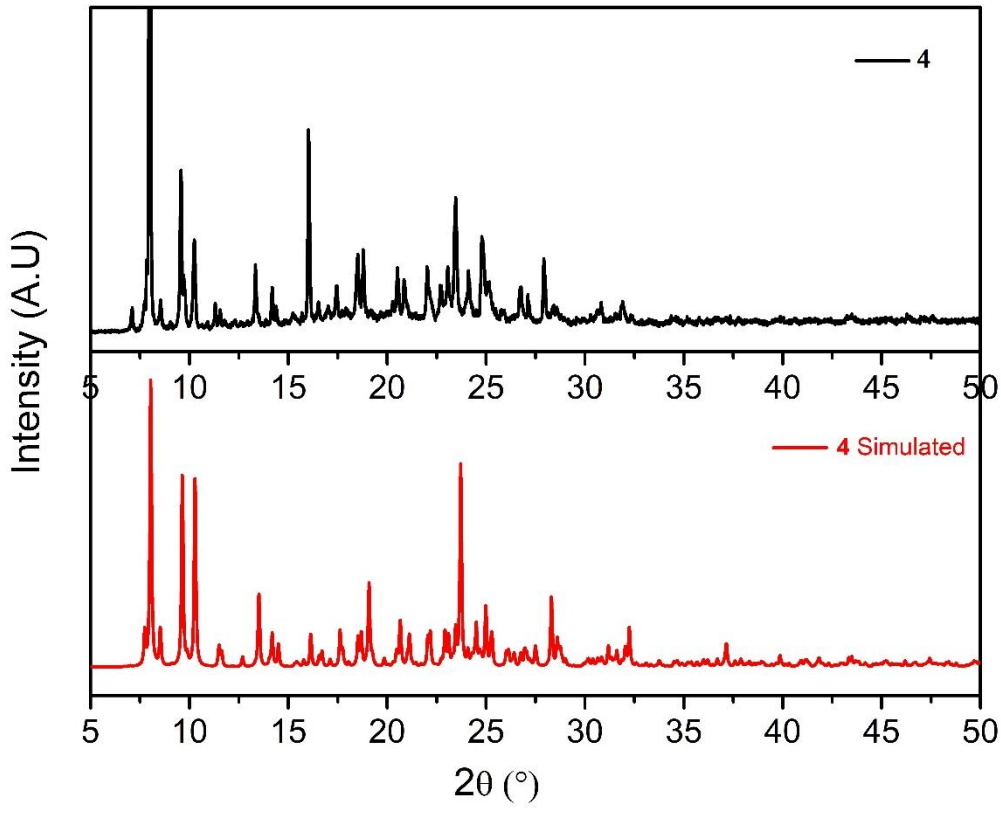

Table S1: Crystallographic and refinement data of **1** - **4**.

	1	**2**	**3**	**4**
Formula	$C_{32}H_{32}FeN_6O_6S_2$	$C_{34}H_{36}FeN_6O_6S_2$	$C_{32}H_{30}FeN_8O_{10}S_2$	$C_{42}H_{46}FeN_6O_{11}S_2$
M_r	716.60	744.66	806.61	930.82
T [K]	150(2)	150(2)	150(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P\ 2_1/n$	C 2/c	$P\ 2_1/n$
a [Å]	8.70221(16)	12.4313(5)	27.047(2)	12.5554(4)
b [Å]	16.0669(2)	8.8652(3)	13.0561(7)	15.3850(4)
c [Å]	11.6137(2)	31.2595(15)	21.6228(12)	22.1022(7)
α [°]	90	90	90	90
β [°]	95.3729(18)	98.123(4)	103.535(7)	96.438(3)
γ [°]	90	90	90	90
V [Å^3]	1616.66(5)	3410.4(2)	7423.5(8)	4242.4(2)
Z	2	4	8	4
ρ_c [g cm^{-3}]	1.472	1.450	1.443	1.457
μ [mm^{-1}]	0.650	0.619	0.584	0.522
F(000)	744.0	1552	3328	1944
θ range	3.067 - 25.521	3.023-25.265	3.079- 25.616	2.648 - 29.609
Independent reflns	5551	6121	6772	10644
Abs. correction	Multi-scan	Multi-scan	Multi-scan	Gaussian
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
GoF on F^2	1.052	1.065	1.043	1.038
Final R indices [$I > 2\ \sigma(I)$]	$R_1 = 0.0330$ $wR_2 = 0.0865$	$R_1 = 0.0471$ $wR_2 = 0.0945$	R1 = 0.0521 wR2 = 0.1509	$R_1 = 0.0638$ $wR_2 = 0.1308$
R indices (all data)	$R_1 = 0.0369$ $wR_2 = 0.0897$	$R_1 = 0.0766$ $wR_2 = 0.1062$	R1 = 0.0577 wR2 = 0.1565	$R_1 = 0.1334$ $wR_2 = 0.1643$

Table S2: Hydrogen bonding parameters in **1** – **4**.

D-H---A	Interaction	D-H (Å)	H---A(Å)	D----A(Å)	∠D-H-A (˚)
1					
C3-H3---O46	Intramolecular	0.95	2.42	3.023 (6)	121
C4-H4---O45	Intermolecular	0.95	2.33	3.213 (8)	154
C5-H5---O17	Intermolecular	0.95	2.60	3.199 (7)	121
C6-H6---O17	Intermolecular	0.95	2.54	3.166 (6)	123
C13-H13A---O17	Intramolecular	0.98	2.52	3.312 (7)	138
C13-H13B---O18	Intermolecular	0.98	2.58	3.427 (6)	144
C20-H20---O17	Intramolecular	0.95	2.54	2.915 (5)	104
C21-H21---O47	Intermolecular	0.95	2.53	3.399 (6)	153
C35-H35---O46	Intermolecular	0.95	2.57	3.433 (6)	151
C44-H44C---O18	Intermolecular	0.98	2.44	3.329 (8)	150
C54-H54---O48	Intramolecular	0.95	2.53	2.902 (7)	103
2					
C14-H14B---O47	Intermolecular	0.98	2.48	3.254 (5)	136
C24-H24---O17B	Intramolecular	0.95	2.41	2.844 (15)	108
C25-H25A---O18B	Intermolecular	0.98	2.42	3.366 (13)	161
C33-H33---O17B	Intramolecular	0.95	2.48	3.404 (14)	165
C34-H34---O17B	Intermolecular	0.95	2.32	3.253 (14)	165
C43-H43C---O47	Intermolecular	0.98	2.45	3.361 (4)	155
C50-H50---O48	Intramolecular	0.95	2.57	2.924 (4)	102
3					
C3-H3---O47	Intramolecular	0.95	2.35	3.191 (5)	148
C5-H5---O48	Intermolecular	0.95	2.55	3.046 (5)	113
C6-H6---O56	Intermolecular	0.95	2.57	3.328 (5)	137
C24-H24---O17	Intramolecular	0.95	2.47	2.867 (4)	105
C33-H33---O17	Intramolecular	0.95	2.36	3.238 (4)	153
C35-H35---O18	Intermolecular	0.95	2.55	3.090 (5)	116
C54-H54---O47	Intramolecular	0.95	2.46	2.852 (4)	105
4					
O15-H15---O12	Intermolecular	0.92	1.81	2.729 (3)	174
O20-H20---O17	Intermolecular	0.93	1.80	2.714 (3)	169
C2-H2---O11	Intramolecular	0.95	2.54	3.131 (4)	120
C5-H5---O13	Intermolecular	0.95	2.49	3.077 (4)	120
C12-H12---O16	Intramolecular	0.95	2.47	3.052 (4)	119
C17-H17---019	Intermolecular	0.95	2.54	3.334 (4)	141
C23-H23---O19	Intermolecular	0.95	2.50	3.179 (4)	129
C25-H25---O18	Intermolecular	0.95	2.38	3.249 (4)	152
C27-H27---O14	Intramolecular	0.95	2.57	2.879 (5)	100
C28-H28---O18	Intermolecular	0.95	2.42	3.355 (4)	169
C32-H32---O14	Intermolecular	0.95	2.41	3.279 (4)	152
C35-H35---O18	Intramolecular	0.95	2.50	2.890 (5)	105
C36-H36---O19	Intramolecular	0.95	2.51	2.851(5)	101

Table S3: Aromatic interaction parameters of **1 - 4**.

Complex	Interaction	Pair	Centroid-Centroid distance (Å)	Closest ring contact (Å)	Plane–Plane angle (˚)	Displacement Angle (˚)
1	Intra-molecular	1	C49C50C51C52C53C54 - N32C33C34C35C36C37 = 4.066(3)	C50 - N32 = 3.379(5)	11.6(2)	-
			C49C50C51C52C53C54 - N38N39C40C41C42 = 3.987(3)	C54 - C40 = 3.819(6)	11.9(2)	-
		2	C19C20C21C22C23C24 - N2C3C4C5C6C7 = 3.928(2)	C6 - C22 = 3.552(7)	15.9(2)	-
			C19C20C21C22C23C24 - N8N9C10C11C12 = 4.206(3)	C20 - N8 = 3.249(5)	14.0(2)	-
2	Intra-molecular	1	C1920C21C22C23C24 - N2C3C4C5C6C7 = 3.903(2)	C19 - N2 = 3.629(4)	5.32(17)	20.7
			C1920C21C22C23C24 - N8N9C1011C12 = 4.286(2)	C20 - N8 = 3.485(5)	12.90(19)	-
3	Intra-molecular	1	C19C20C21C22C23C24 - N8N9C10C11C12 = 3.767(2)	C19 - N9 = 3.481(4)	7.54(19)	18.8
			C19C20C21C22C23C24 - N2C3C4C5C6C7 = 4.497(2)	C20 - C7 = 3.479(4)	1.35(17)	39.5
		2	C49C50C51C52C53C54 - N38N39C40C41C42 = 3.807(2)	N38 - C49 = 3.493(4)	5.12(18)	21.2
			C49C50C51C52C53C54 - N32C33C34C35C36C37 = 4.602(2)	C37 - C50 = 3.457(5)	3.96(17)	40.0
	Inter-molecular		C49C50C51C52C53C54 - C49C50C51C52C53C54 = 3.871(2)	C51 - C51 = 3.410(6)	15.59(16)	-
4	Intra-molecular	1	C30C31C32C33C34C35 - N1C1C2C3C4C5 = 3.539(19)	C34 - C4 = 3.394(5)	6.03(16)	12.7
		2	C21C22C23C24C25C26 - N4C11C12C13C14C15 = 3.791(2)	C24 - C13 = 3.347(5)	14.24(16)	-

Table S4: Fitting parameters of χ^{-1} vs temperature plot of **1** - **4**.

Compound	C ($cm^3 mol^{-1} K$)	θ (K)	Magnetic interaction
1	3.44 (1)	-2.62 (1)	Negligible
2	3.42 (1)	-3.76 (1)	Negligible
3	3.50 (1)	-2.45 (1)	Negligible
4	3.08 (1)	0.68 (1)	Negligible