Ligand symmetry significantly affect spin crossover behaviour in isomeric $[Fe(pybox)_2]^{2+}$ complexes

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Contents

SI1 Instruments and Materials

SI1.1 Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 or 600 MHz spectrometer. Mass spectrometry was performing using a Water XEVO G2Q-TOF (Waters Corporation). Elemental analysis of carbon, nitrogen and hydrogen was performed using an Elementary Vario EL analyser. Magnetic susceptibility data were collected using a Quantum Design MPMS XL-5 or PPMS-9T (EC-II) SQUID magnetometer. Measurements for all the samples were performed on microcrystalline powder restrained by a parafilm and loaded in a capsule. The magnetic susceptibility data were corrected for the diamagnetism of the samples using Pascal constants and the sample holder and parafilm by corrected measurement. Crystals suitable for single crystal X-ray diffraction were covered in a thin layer of hydrocarbon oil, mounted on a glass fiber attached to a copper pin, and placed under an N_2 cold stream. All data were carried out on a Rigaku Saturn724+ CCD diffractometer with Confocal-monochromator Mo-Kα radiation (λ = 0.71073 Å). Intensities were collected using CrystalClear (Rigaku Inc., 2008) technique and absorption corrections were applied using the 'multi-scan' method. Unit cell dimensions were obtained with least-squares refinements and all structures were solved by direct methods using SHELXS-97. The other nonhydrogen atoms were in successive difference Fourier syntheses. The final refinement was performed using full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F_2. The hydrogen atoms were added theoretically and riding on the concerned atoms. Powder X-ray diffraction (PXRD) data were performed on a Rigaku Dmax 2000 diffractometer with Cu $K\alpha$ radiation (λ = 1.54178 Å) in a flat plate geometry.

SI1.2 Materials

All reagents and solvents were purchased commercially and used as supplied, unless otherwise stated. The crystals of complexes **(*S*)-2(ClO_4)**, **(*R*)-2(ClO_4)**, and **3(ClO_4)** were synthesized according to literature procedure and the crystals were grown in the mixture solution of methanol and dicholoromethane.[1]

Caution! Although not encountered in our experiments, perchlorate salts in the presence of organic ligands are potentially explosive. Only a small amount of the materials should be prepared and handled with care.

SI2 Structural Characterization

SI2.1 NMR spectra

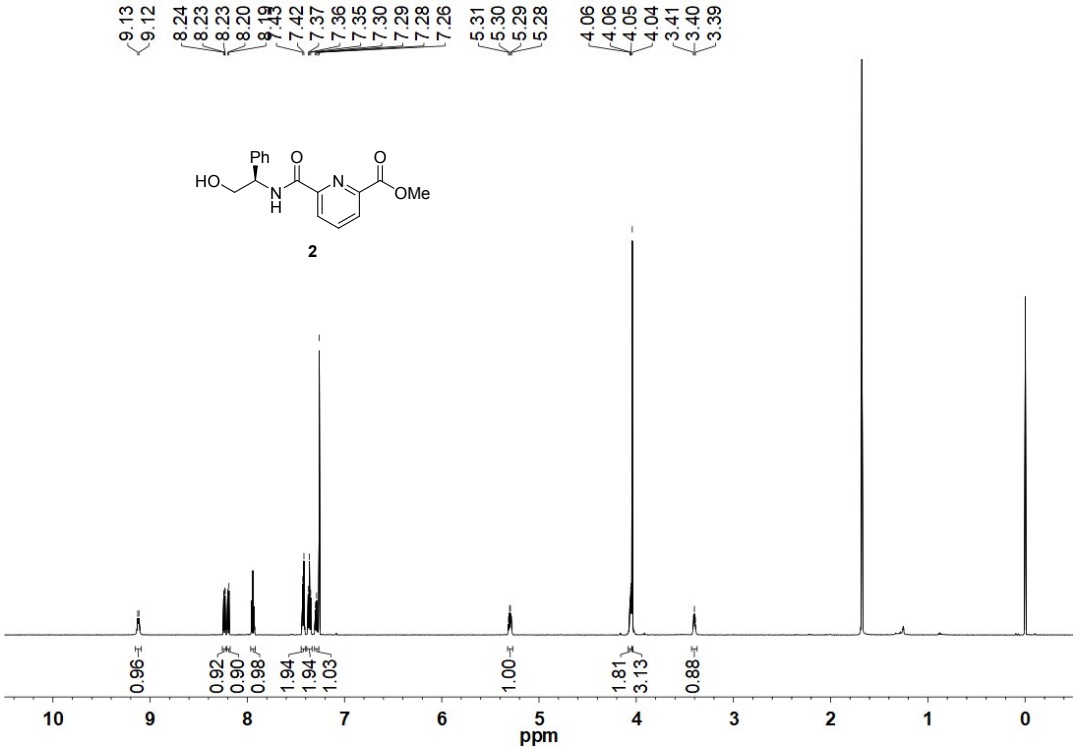

Fig. S1 ^{1}H NMR spectrum of **2** (600 MHz) in $CDCl_3$ at 298 K.

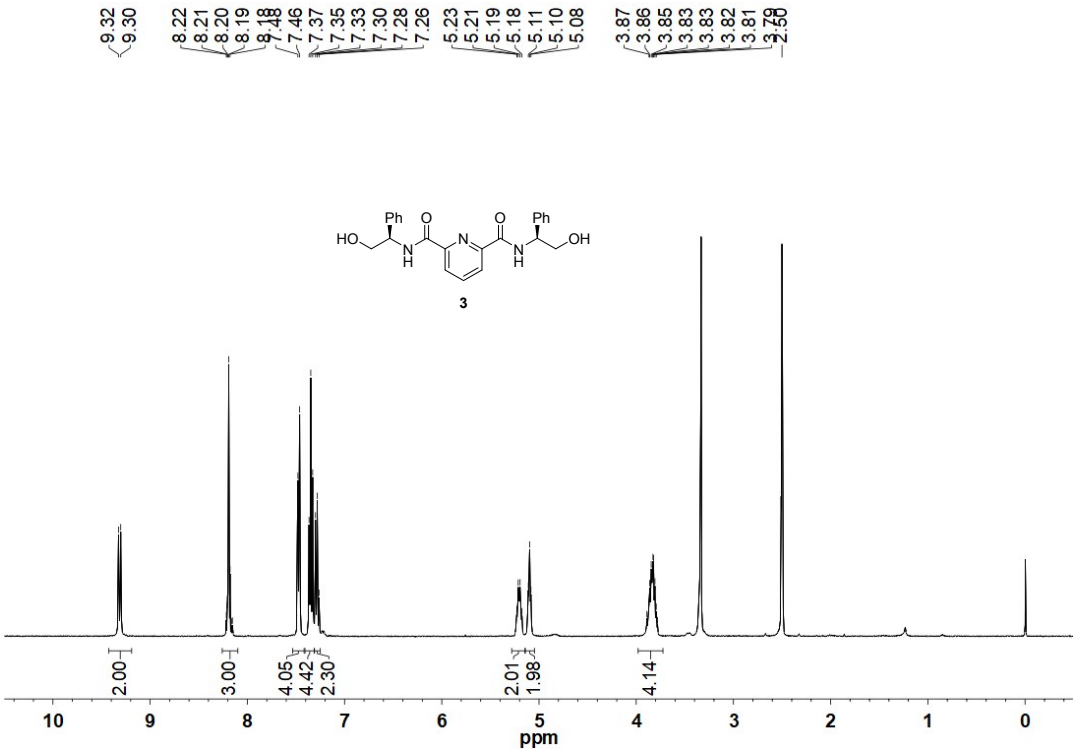

Fig. S2 ^{1}H NMR spectrum of **3** (400 MHz) in DMSO-d_6 at 298 K.

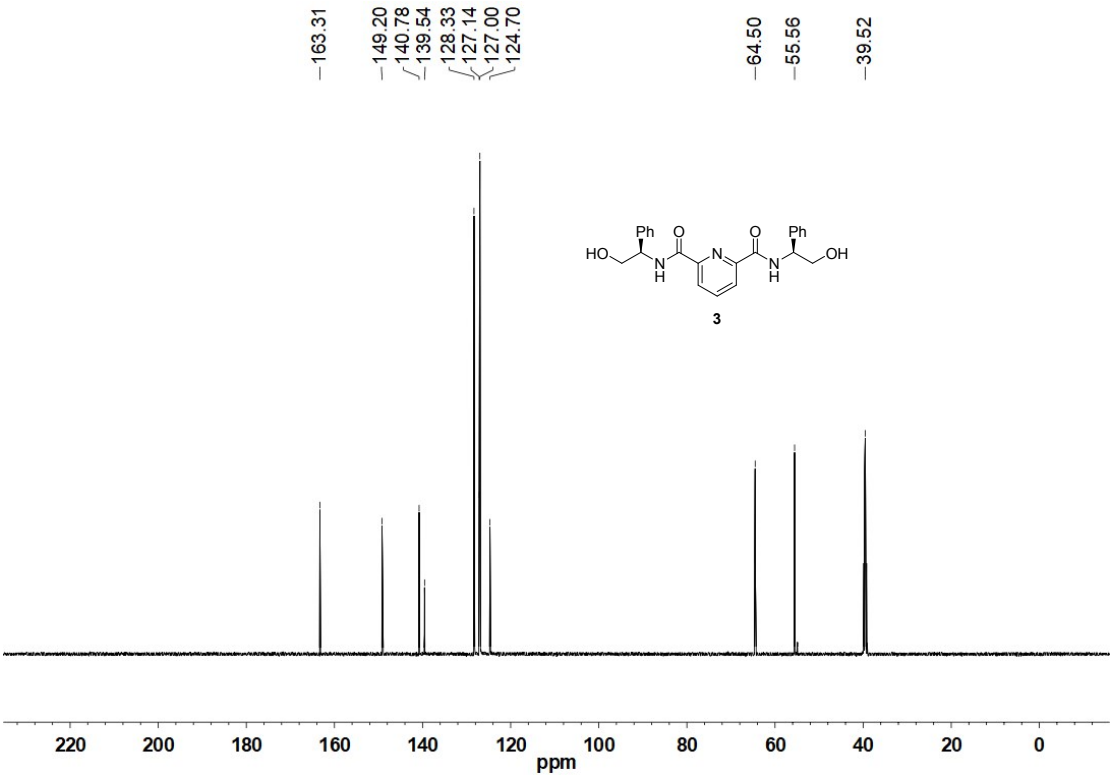

Fig. S3 ^{13}C NMR spectrum of **3** (151 MHz) in DMSO-d_6 at 298 K.

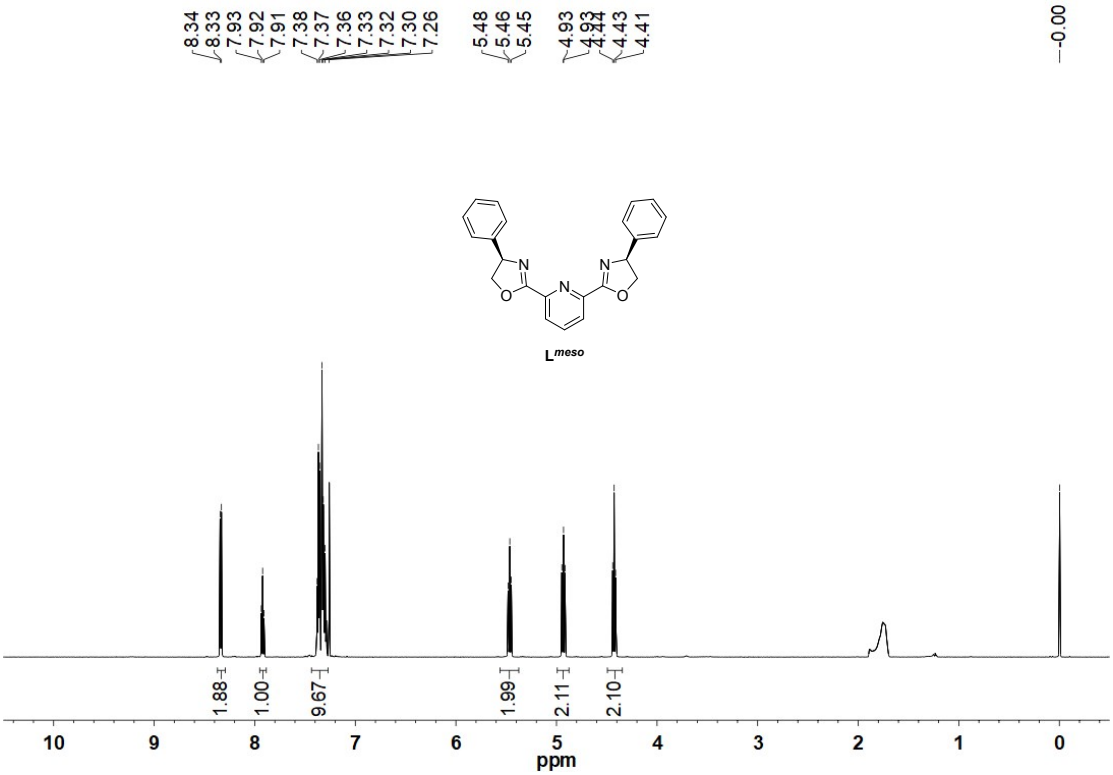

Fig. S4 ^{1}H NMR spectrum of **L**^{meso} (600 MHz) in $CDCl_3$ at 298 K.

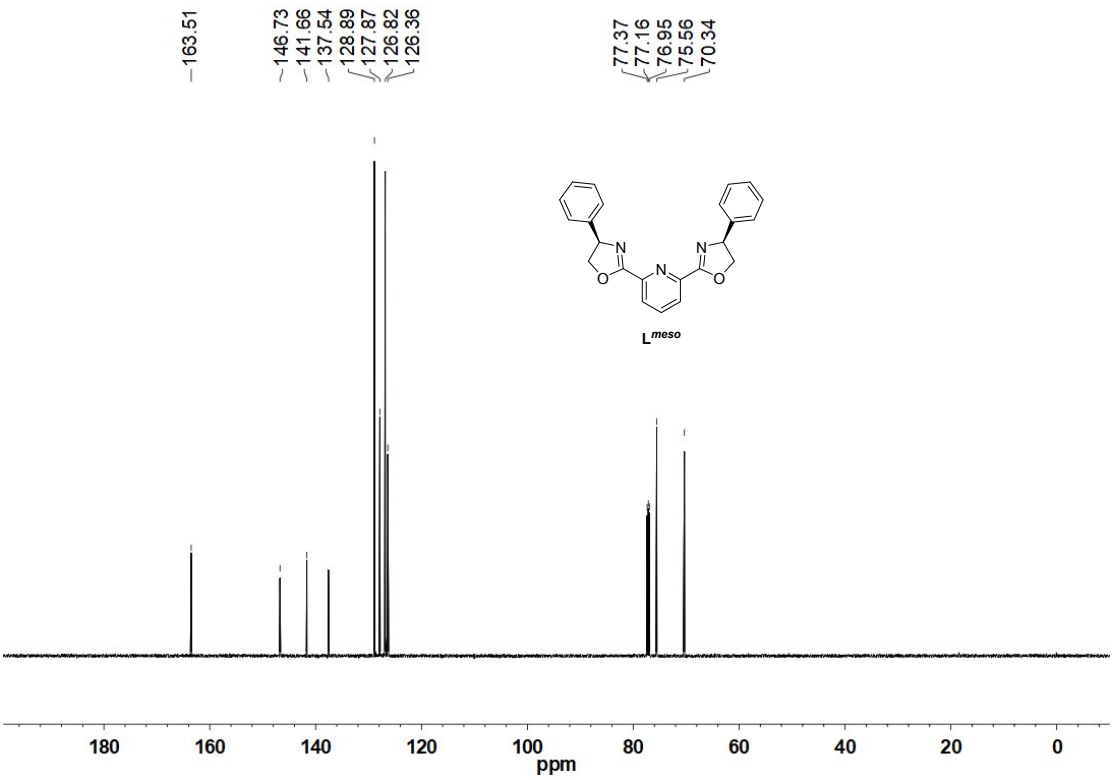

Fig. S5 ^{13}C NMR spectrum of **L*meso*** (151 MHz) in $CDCl_3$ at 298 K.

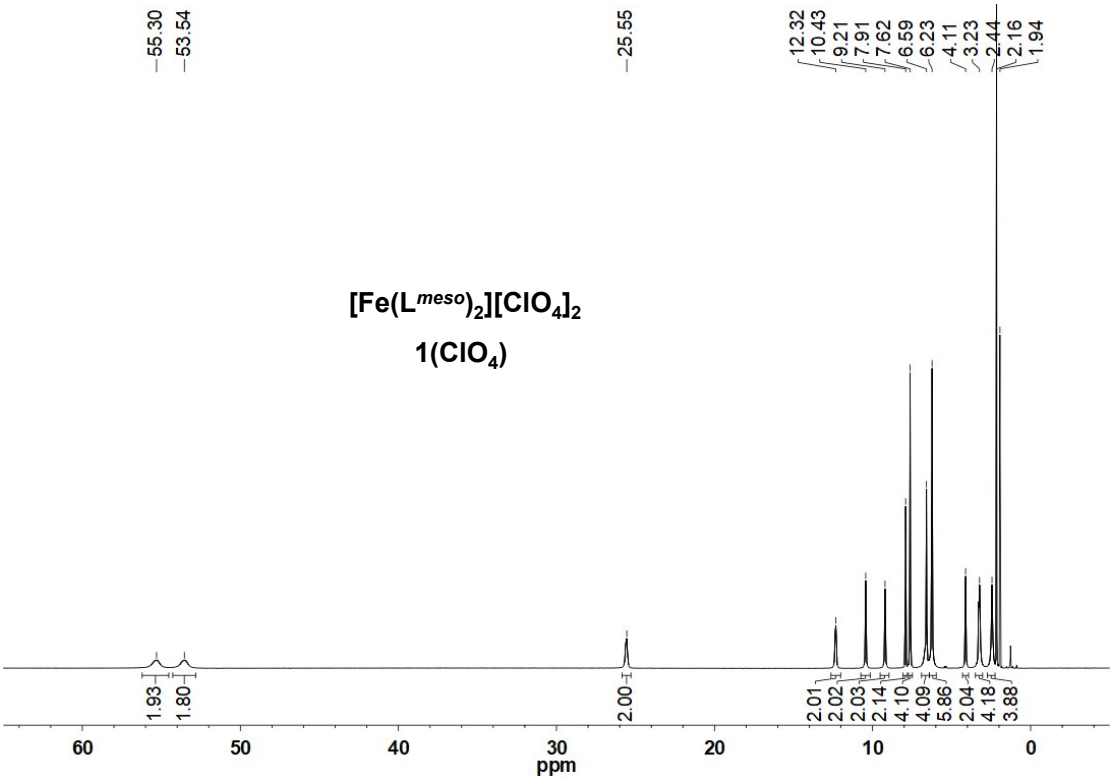

Fig. S6 Paramagnetic ^{1}H NMR spectrum of **1(ClO$_4$)** (600 MHz) in CD_3CN at 298 K.

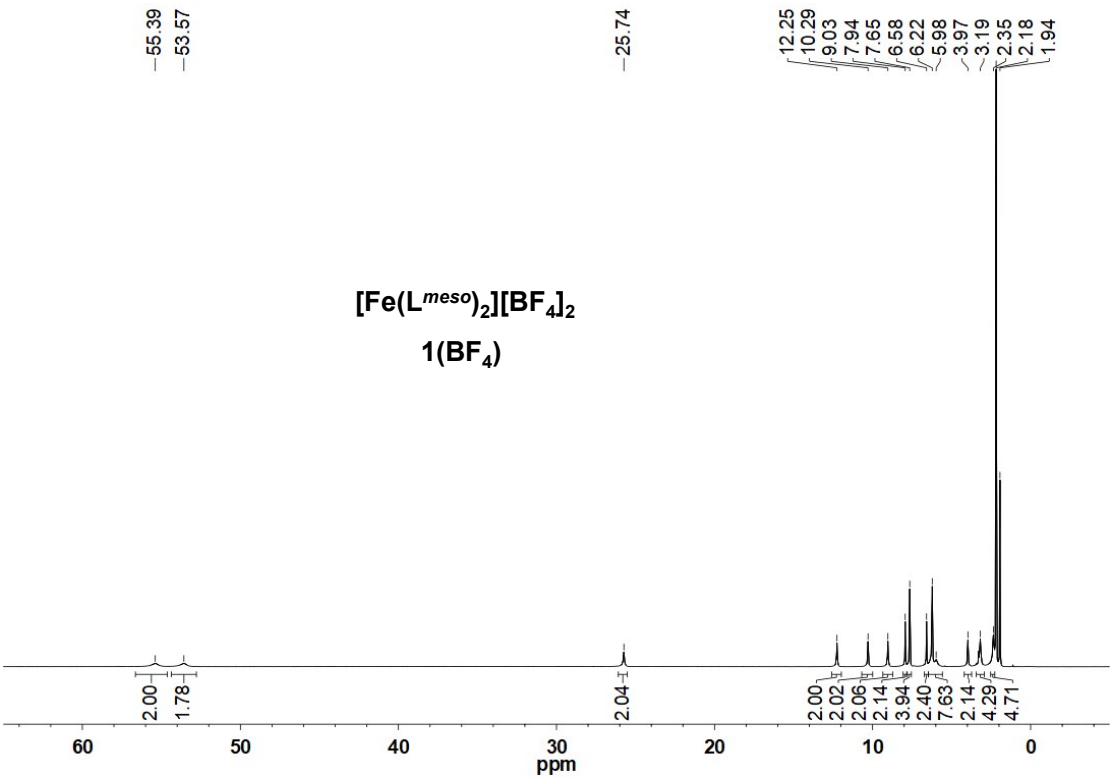

Fig. S7 Paramagnetic ^{1}H NMR spectrum of **1(BF$_4$)** (600 MHz) in CD_3CN at 298 K.

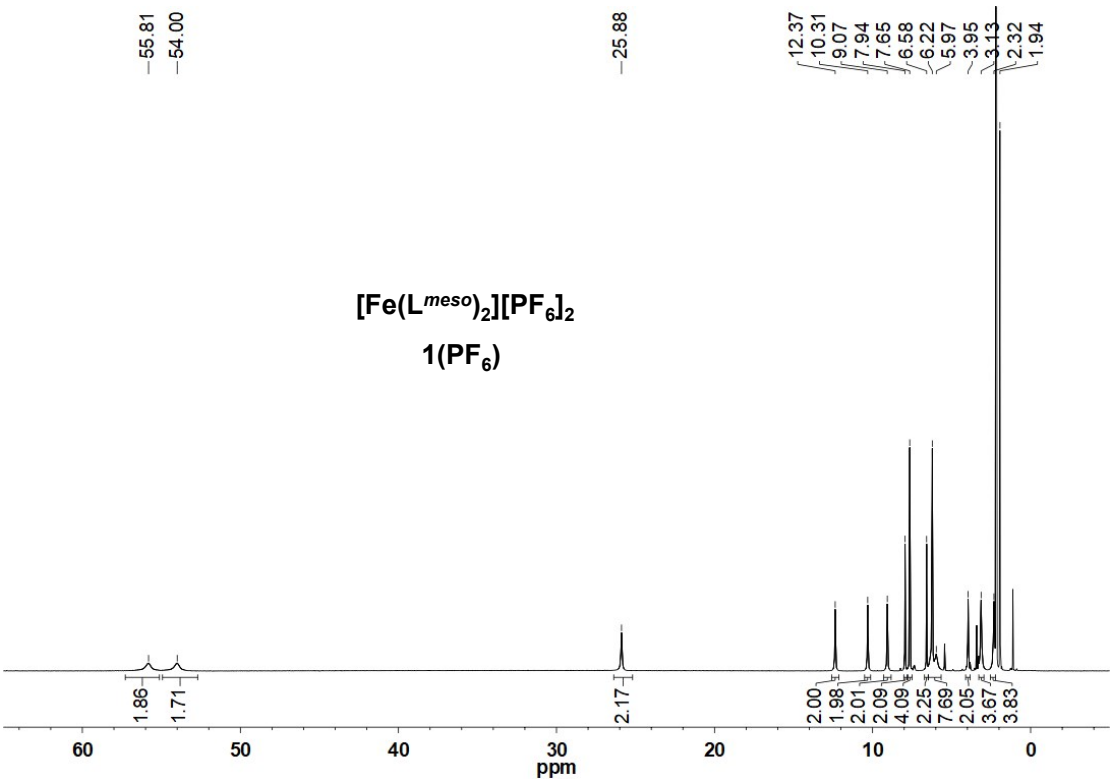

Fig. S8 Paramagnetic ^{1}H NMR spectrum of **1(PF$_6$)** (600 MHz) in CD_3CN at 298 K.

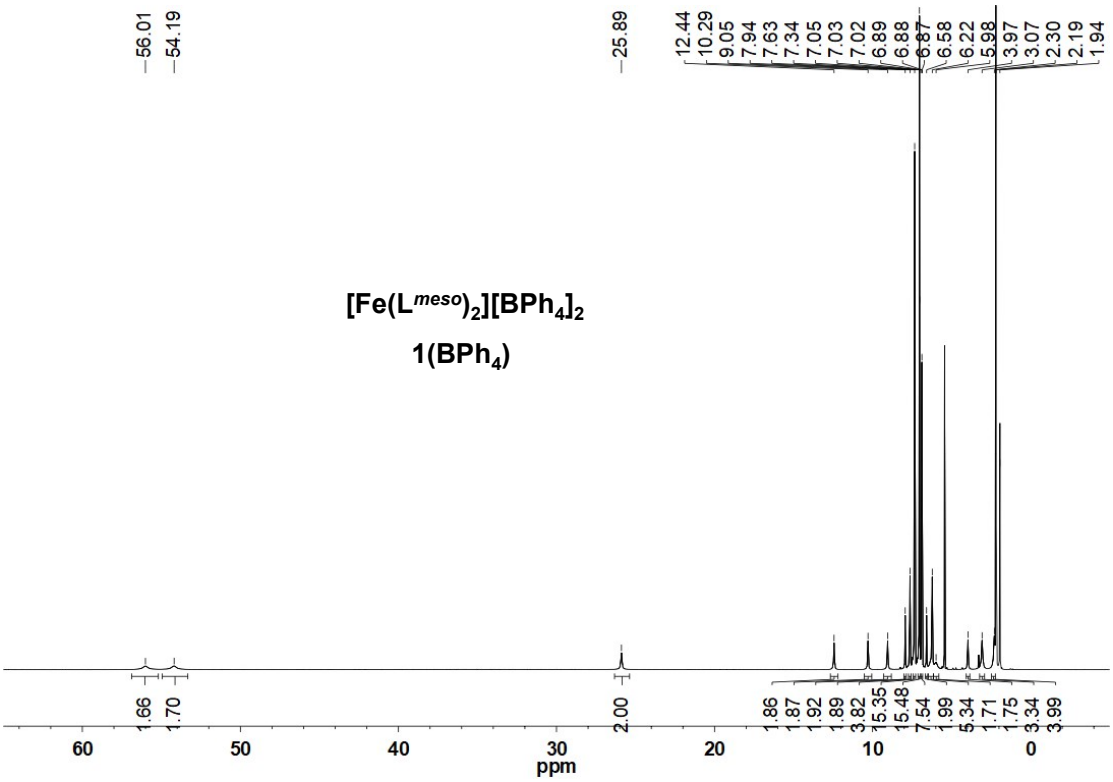

Fig. S9 Paramagnetic ^{1}H NMR spectrum of **1(BPh$_4$)** (600 MHz) in CD_3CN at 298 K.

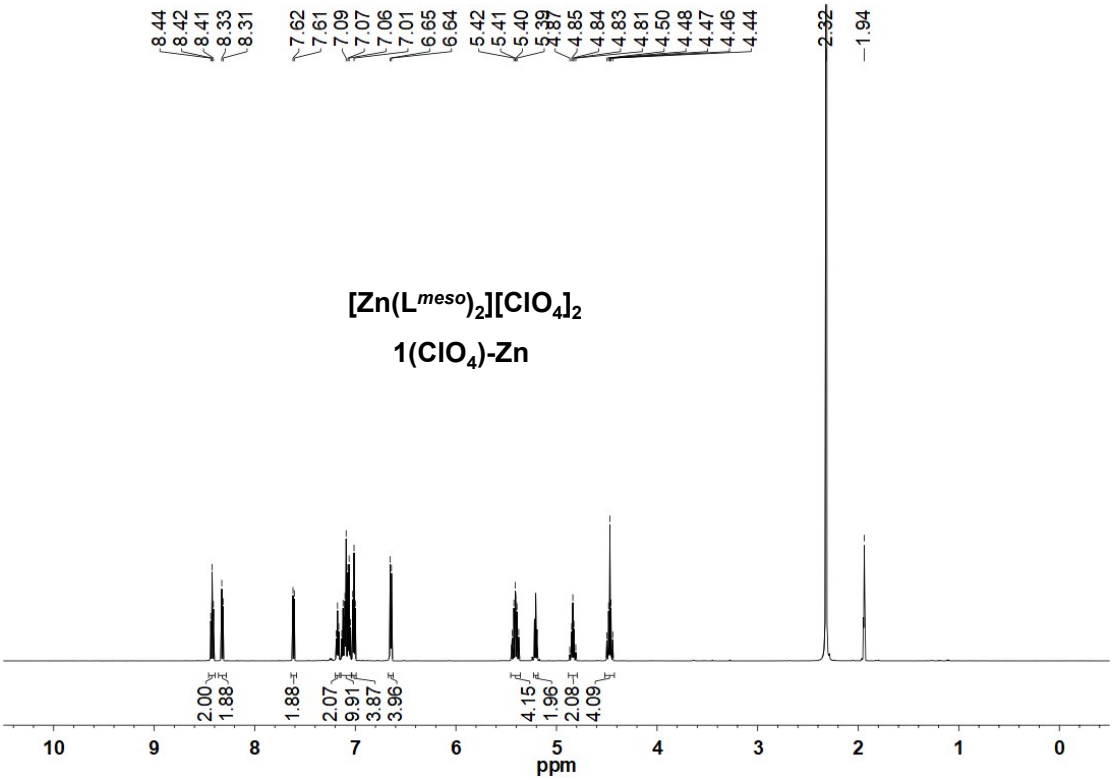

Fig. S10 ^{1}H NMR spectrum of **1(ClO$_4$)-Zn** (600 MHz) in CD_3CN at 298 K.

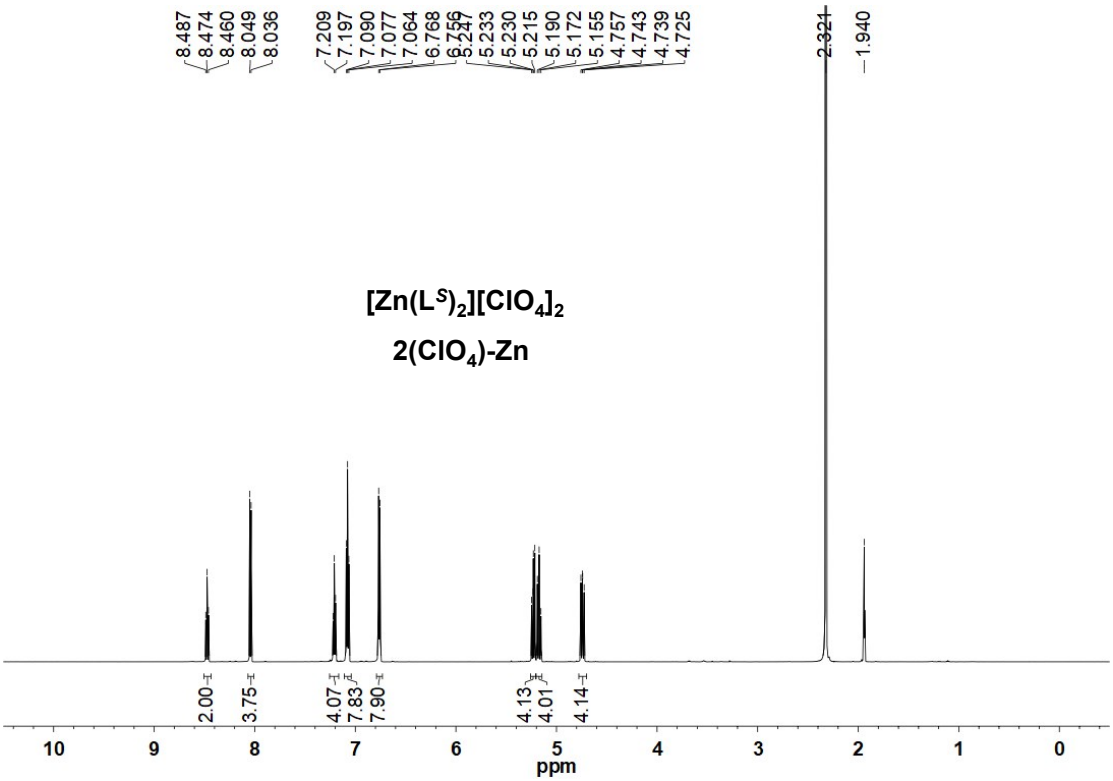

Fig. S11 ^{1}H NMR spectrum of **2(ClO$_4$)-Zn** (600 MHz) in CD_3CN at 298 K.

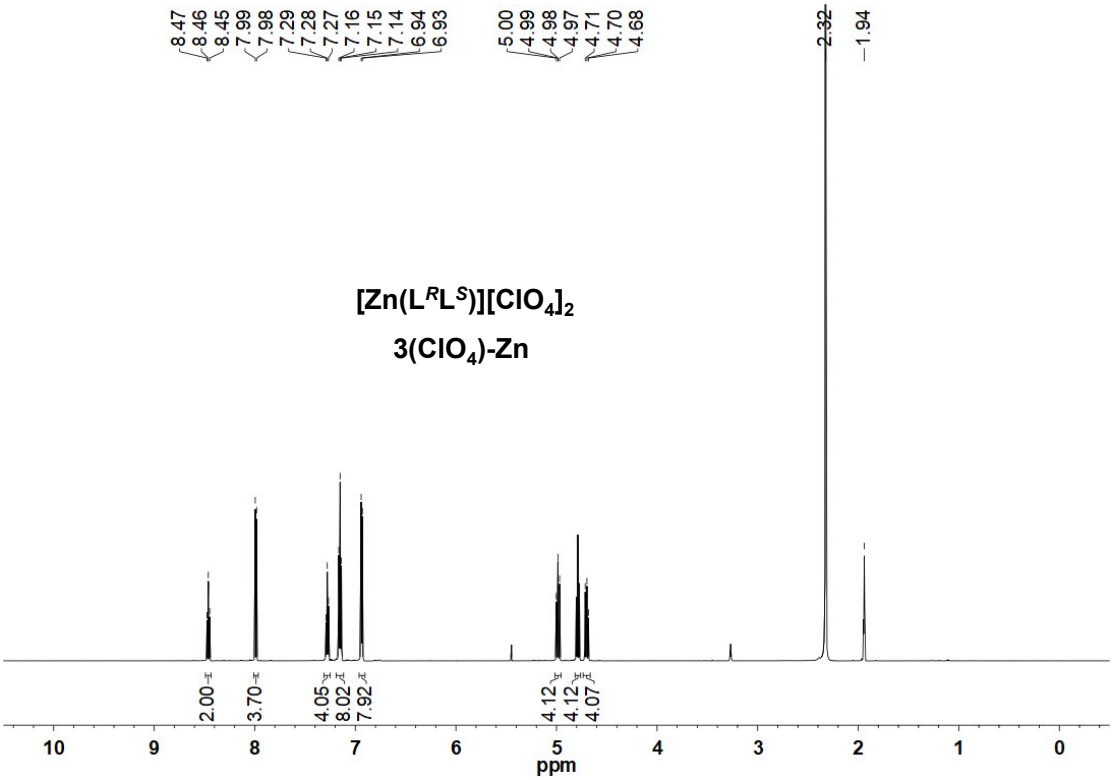

Fig. S12 ^{1}H NMR spectrum of **3(ClO$_4$)-Zn** (600 MHz) in CD_3CN at 298 K.

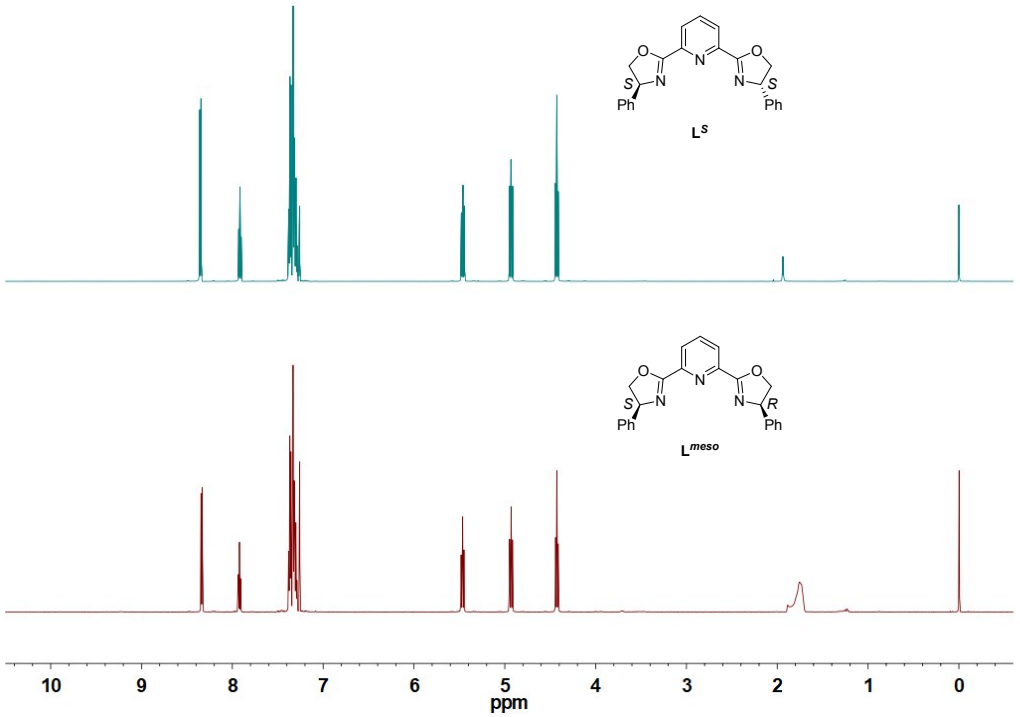

Fig. S13 The stacking ^{1}H NMR spectra of $\mathbf{L}^{meso}$ and $\mathbf{L}^{S}$ (600 MHz) in $CDCl_3$ at 298 K.

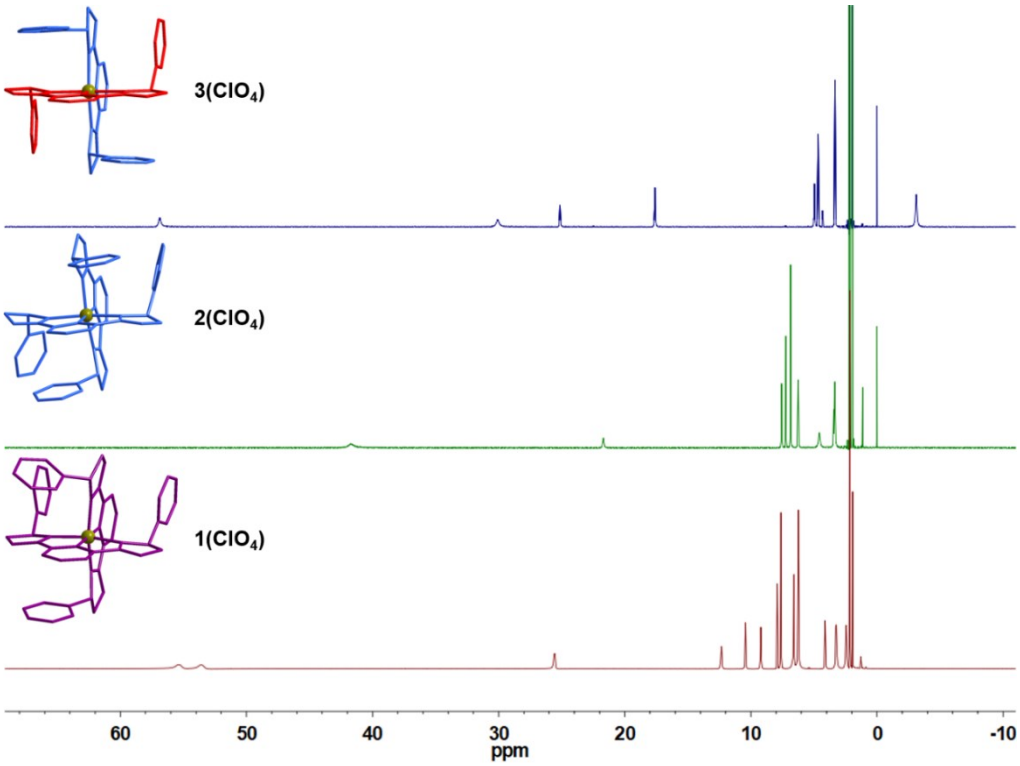

Fig. S14 The merged paramagnetic ^{1}H NMR spectra of **1(ClO$_4$)**, **2(ClO$_4$)**, and **3(ClO$_4$)** in CD_3CN at 298 K.

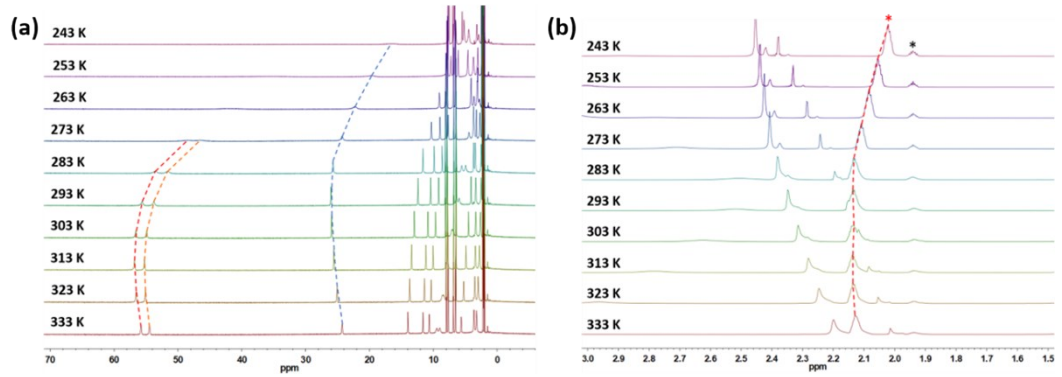

Fig. S15 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 333 to 243 K for **1(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* and * represent the solvent residual signals in solution and in the inner tube, respectively).

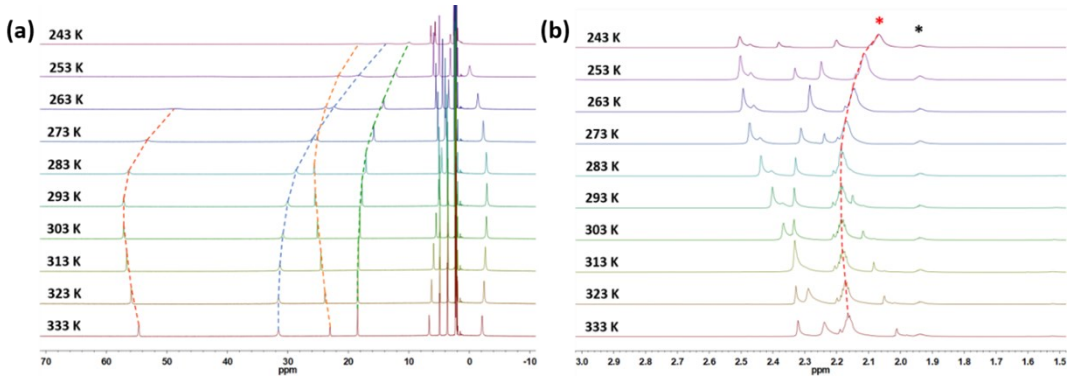

Fig. S16 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 333 to 243 K for **2(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* and * represent the solvent residual signals in solution and in the inner tube, respectively).

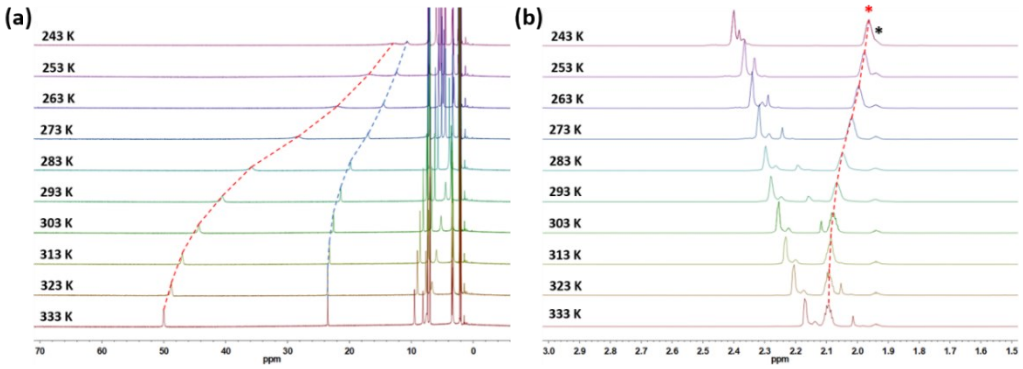

Fig. S17 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 333 to 243 K for **3(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* and * represent the solvent residual signals in solution and in the inner tube, respectively).

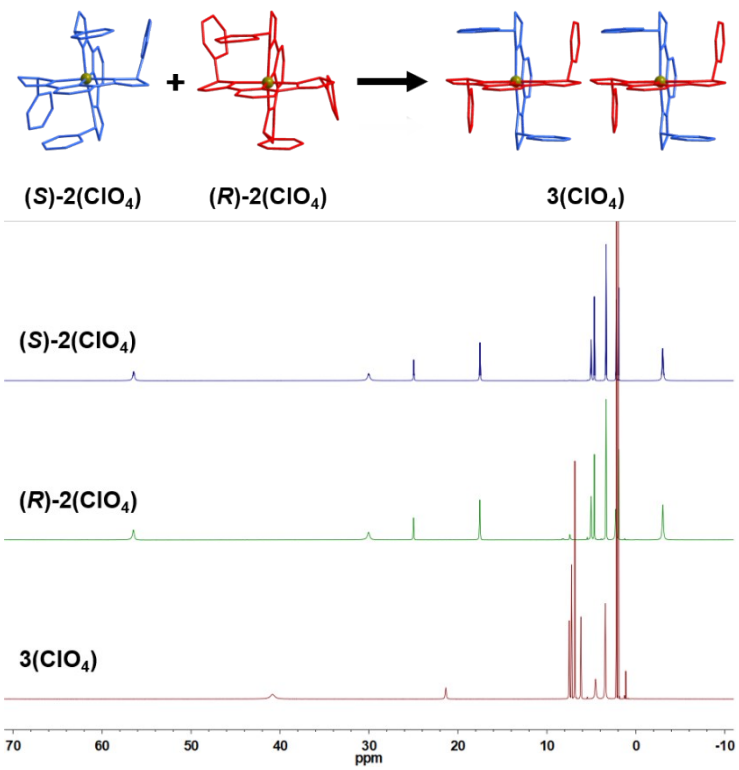

Fig. S18 The paramagnetic ^{1}H NMR spectra of crystalline sample **(*S*)-2(ClO_4)**, **(*R*)-2(ClO_4),** and the crystal sample **3(ClO_4)** obtained from the re-assembly of equivalent **(*S*)-2(ClO_4)** and **(*R*)-2(ClO_4)** in solution. All samples are measured in CD_3CN at 298 K.

SI2.2 Structural characterization of Fe(II) complexes

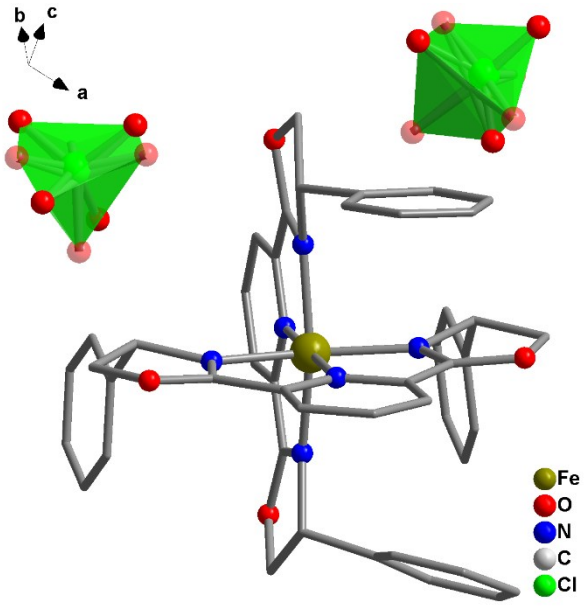

Fig. S19 Molecular structure of **1(ClO_4)** at 296 K.

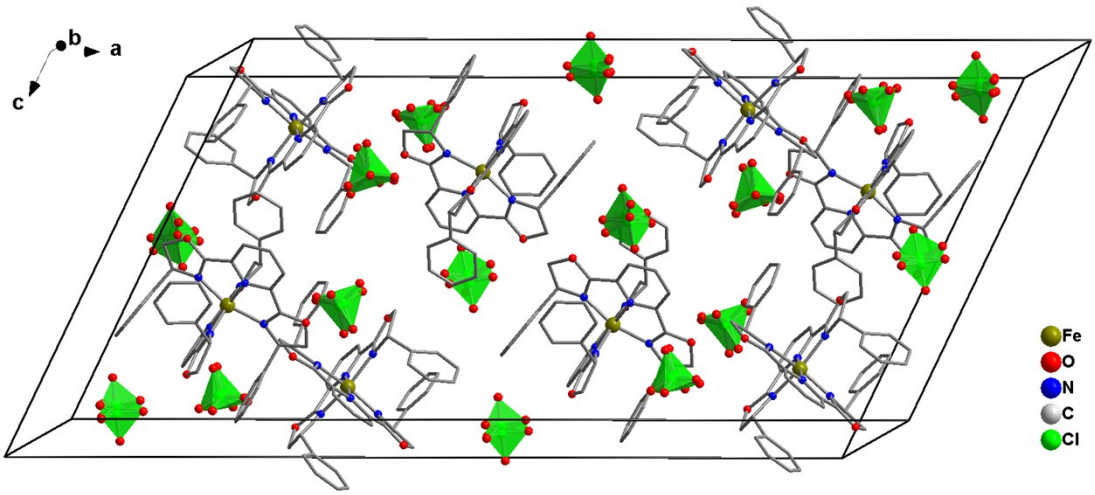

Fig. S20 The packing of **1(ClO_4)** in one unit cell.

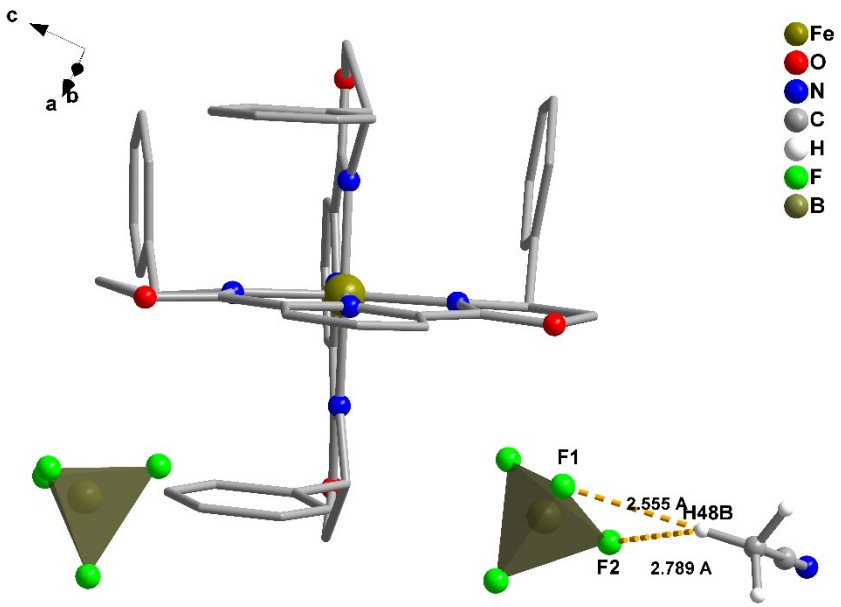

Fig. S21 Molecular structure of **1(BF$_4$)·MeCN** at 163 K, the F···H hydrogen bondings between lattice acetonitrile and tetrafluoroborate anion are illustrated.

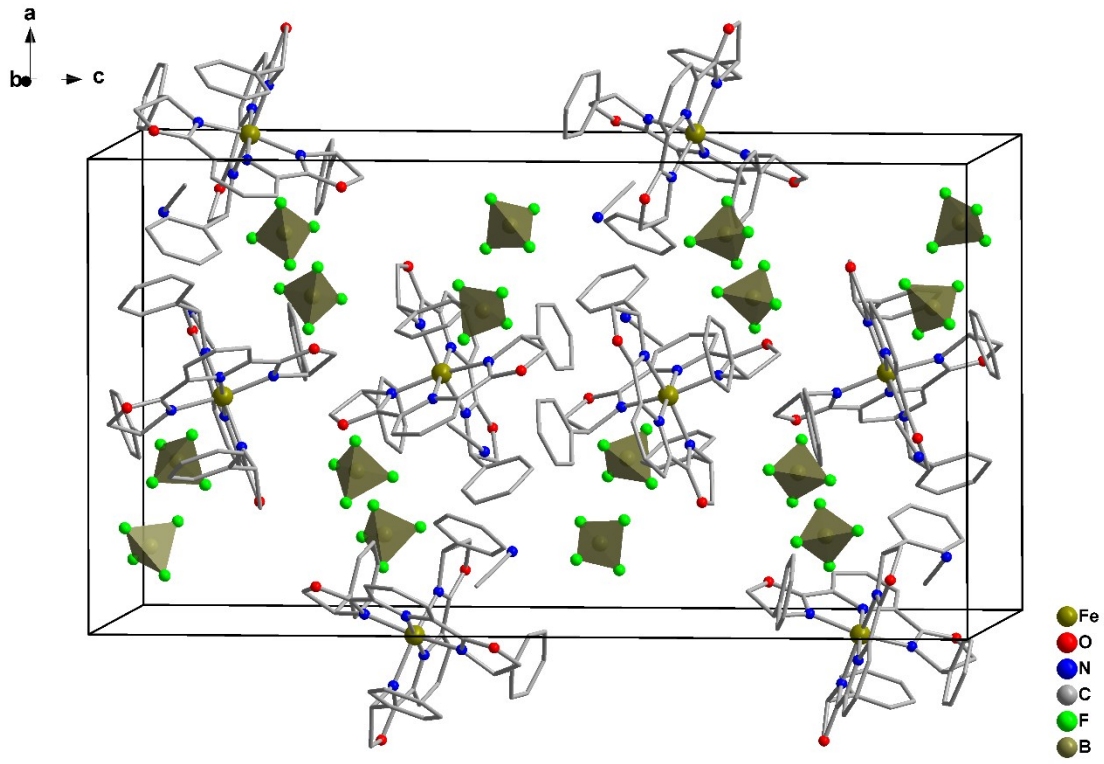

Fig. S22 The packing of **1(BF$_4$)·MeCN** in one unit cell.

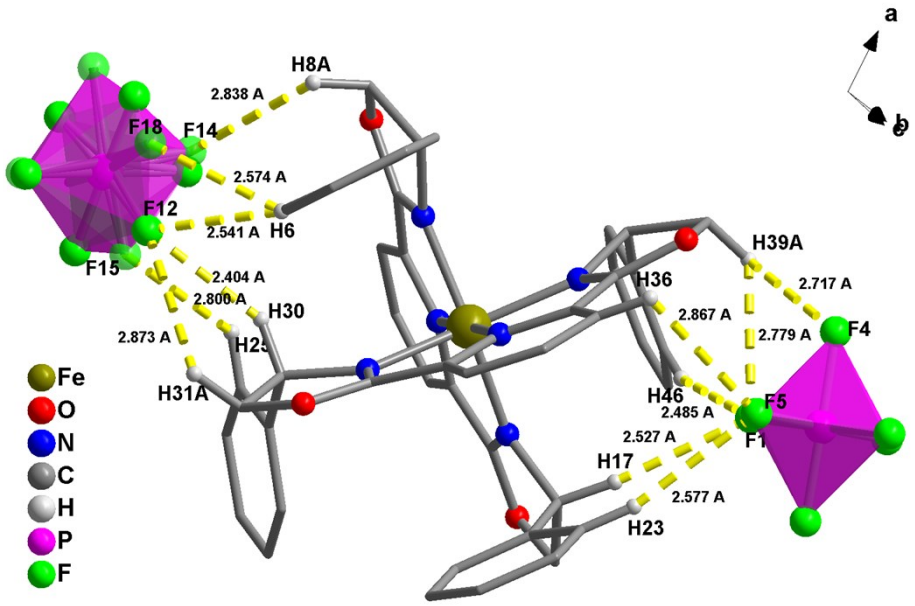

Fig. S23 Molecular structure of **1(PF$_6$)·MeCN** at 163 K.

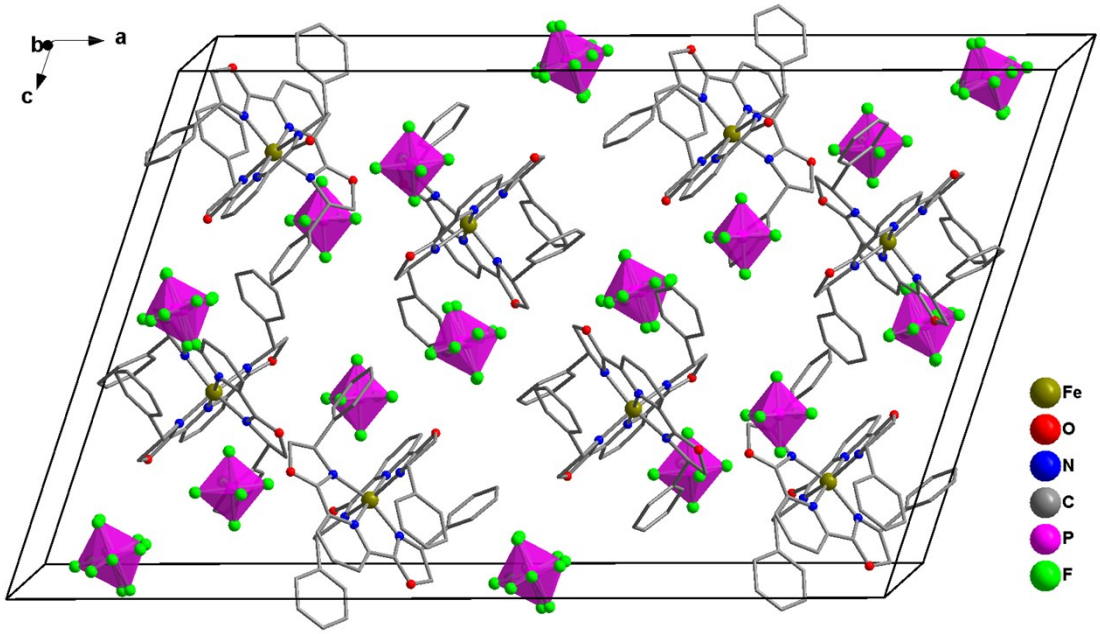

Fig. S24 The packing of **1(PF$_6$)·MeCN** in one unit cell.

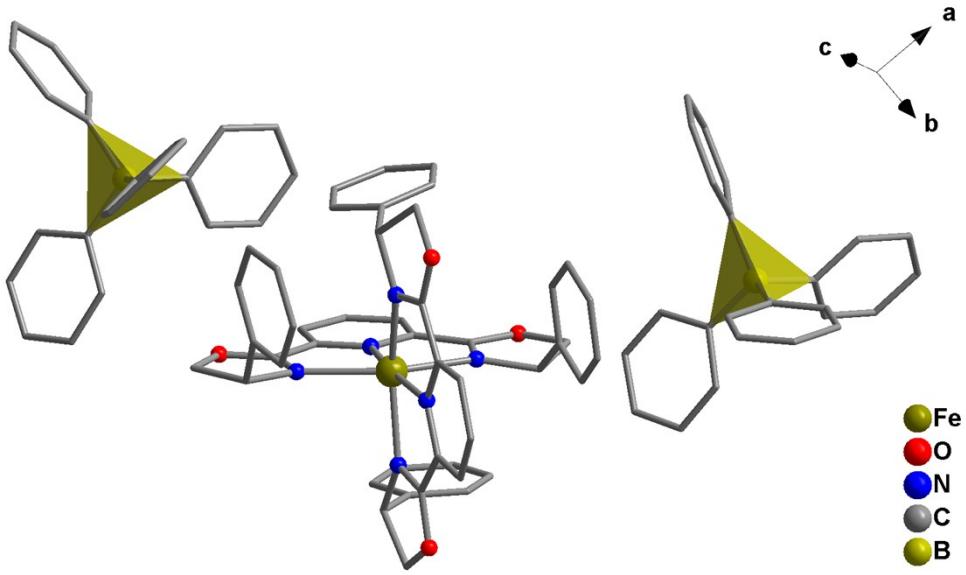

Fig. S25 Molecular structure of **1(BPh$_4$)·MeCN·Et$_2$O** at 163 K.

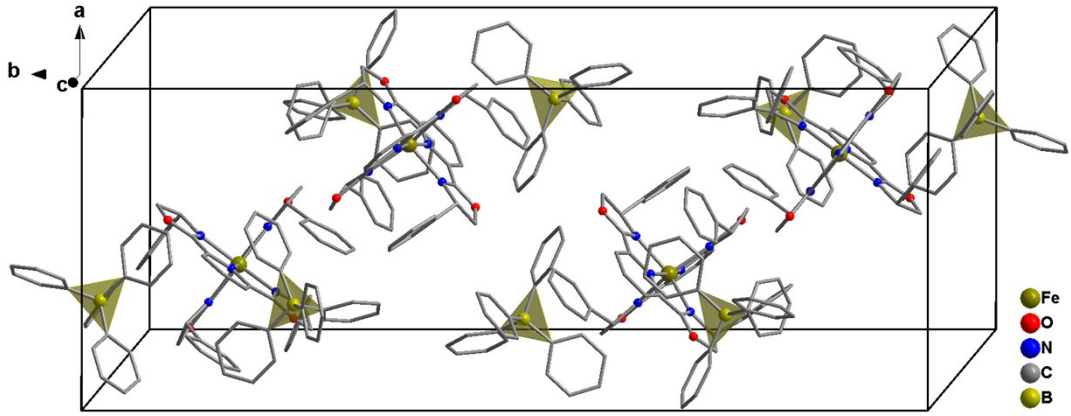

Fig. S26 The packing of **1(BPh$_4$)·MeCN·Et$_2$O** in one unit cell.

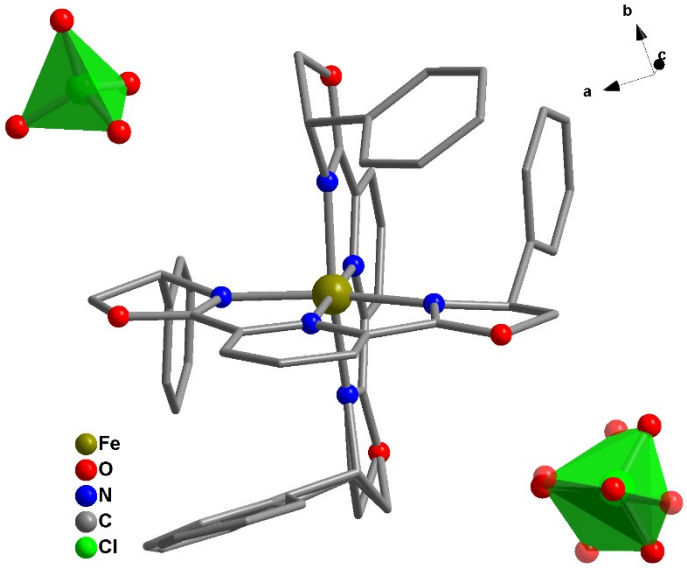

Fig. S27 Molecular structure of **2(ClO$_4$)·MeOH** at 153 K.

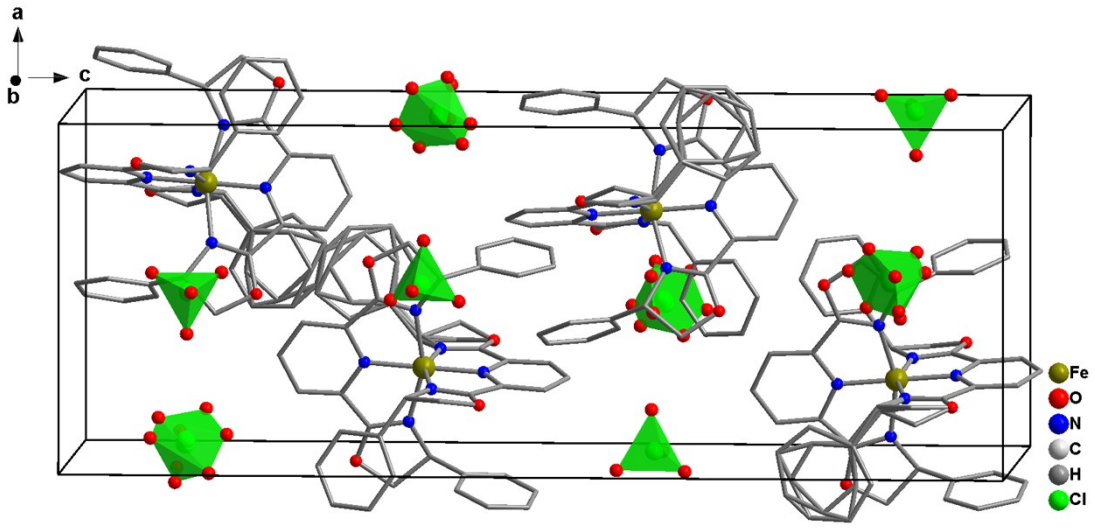

Fig. S28 The packing of **2(ClO$_4$)·MeOH** in one unit cell.

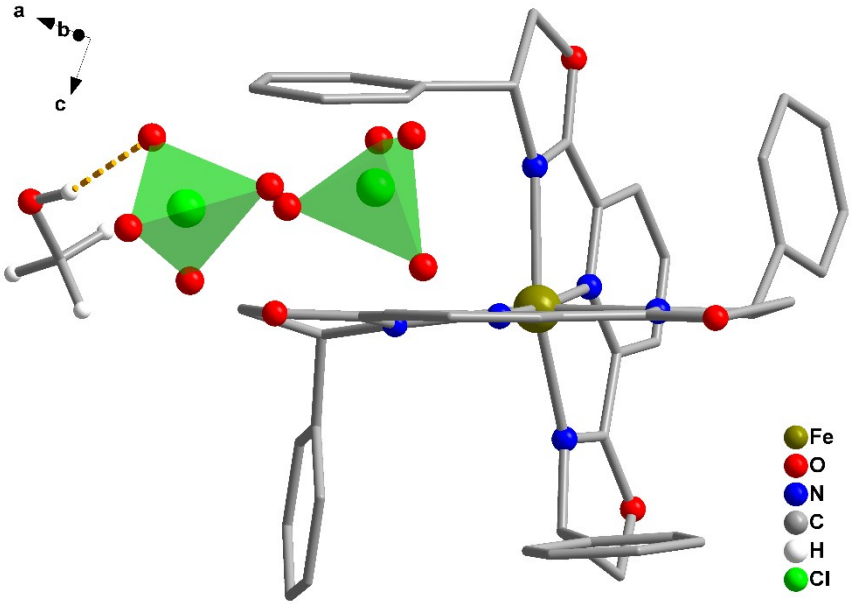

Fig. S29 Molecular structure of **3(ClO$_4$)·MeOH** at 153 K, the O···H hydrogen bondings between lattice methanol and perchlorate anion are illustrated.

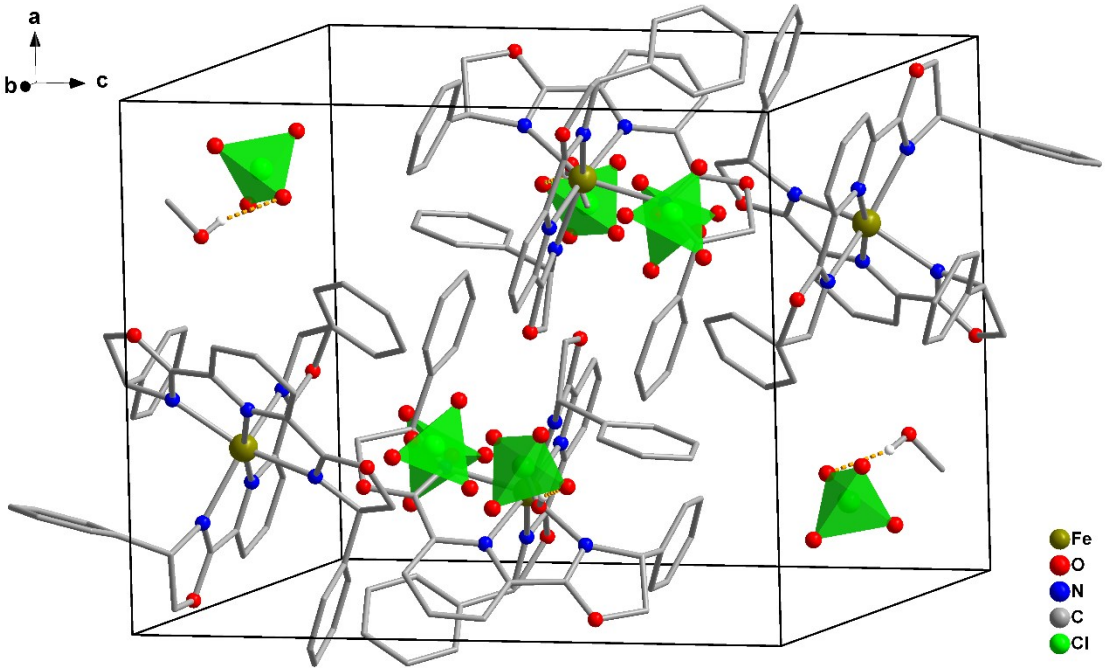

Fig. S30 The packing of **3(ClO$_4$)·MeOH** in one unit cell.

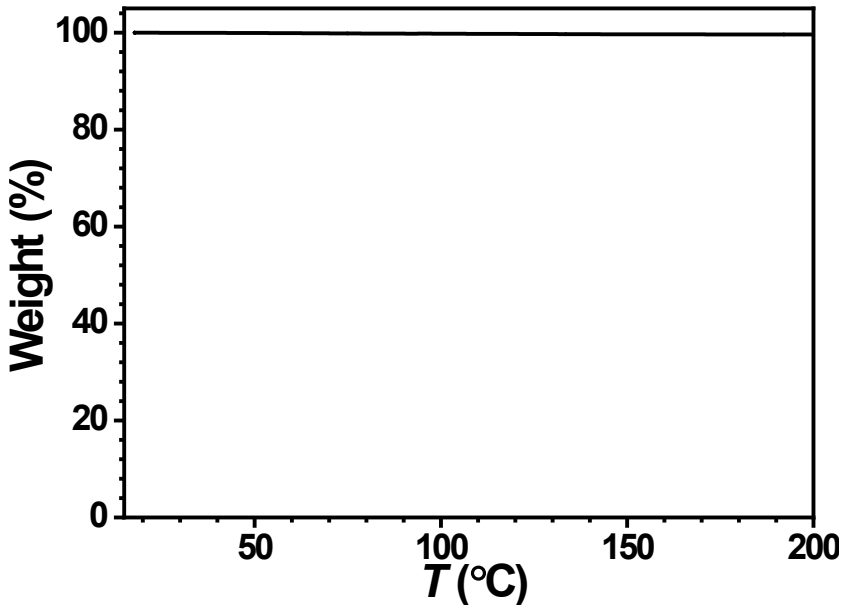

Fig. S31 The TGA trace of **1(ClO$_4$)**, revealing no solvent loss and decomposition take place below 200 ºC. Due to the probably explosion at ~215 °C,[2] measurement towards higher temperature was not performed.

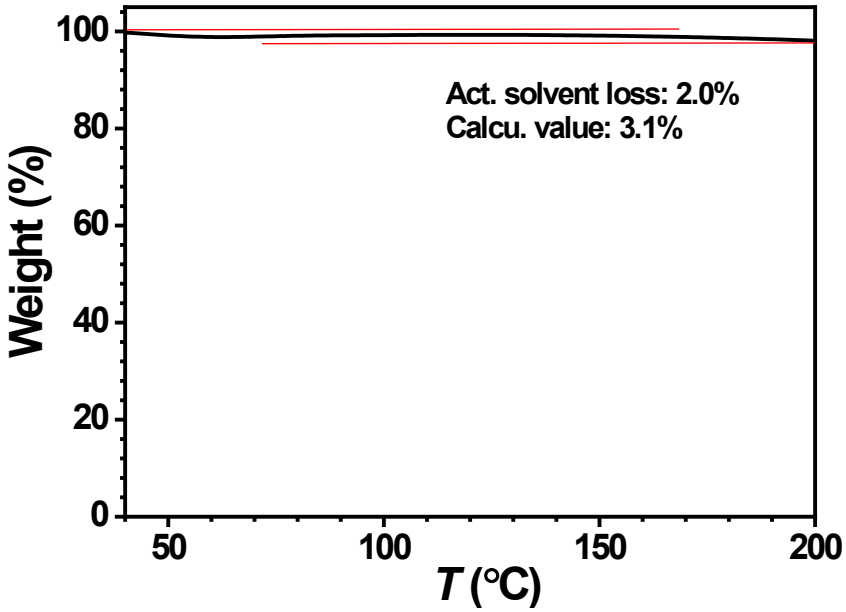

Fig. S32 The TGA trace of **2(ClO_4)·MeOH**, indicating the complete solvent loss of acetonitrile below 200 ºC.

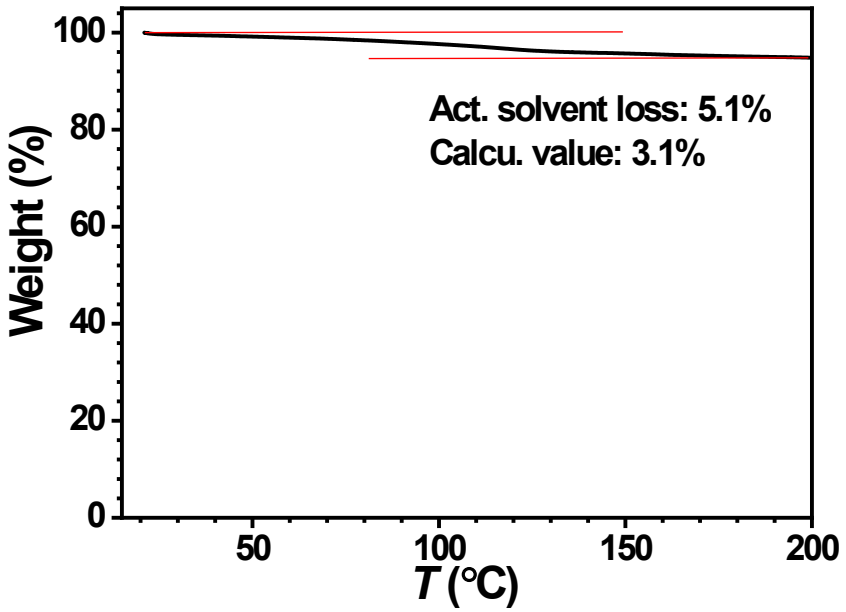

Fig. S33 The TGA trace of **3(ClO_4)·MeOH**, indicating the complete solvent loss of acetonitrile below 200 ºC.

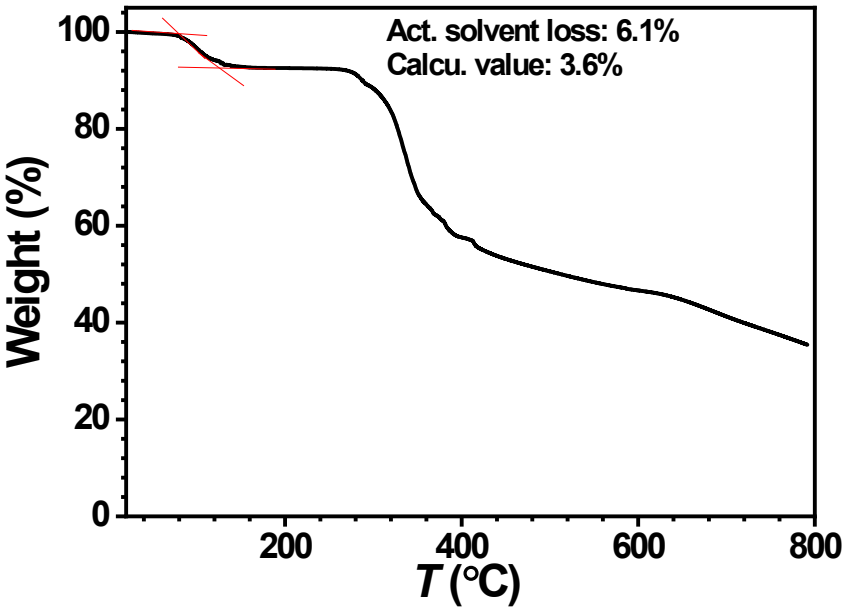

Fig. S34 The TGA trace of **1**(BF_4)·**MeCN**, indicating the loss of acetonitrile completes below 160 ºC.

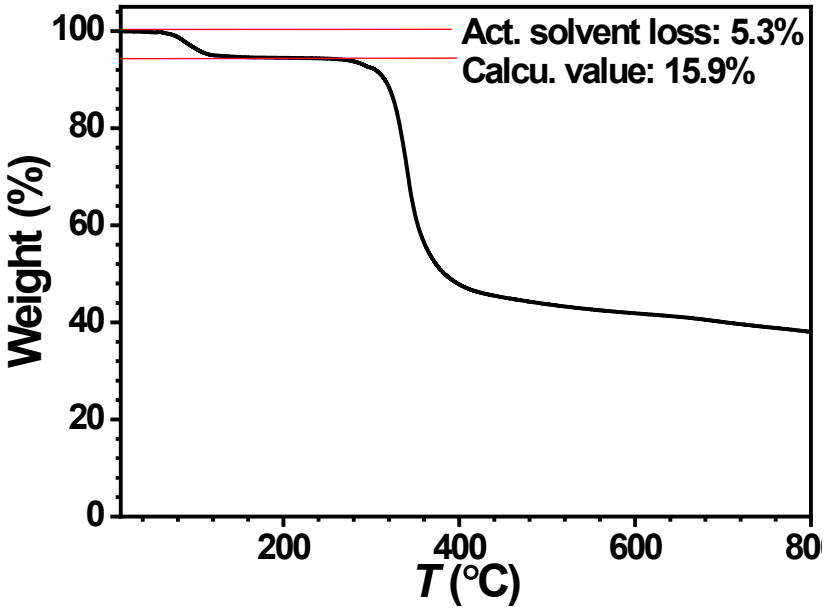

Fig. S35 The TGA trace of **1**(PF_6)·**5MeCN**, indicating the loss of acetonitrile completes below 160 ºC. Two disordered acetonitrile are included in the weight calculation.

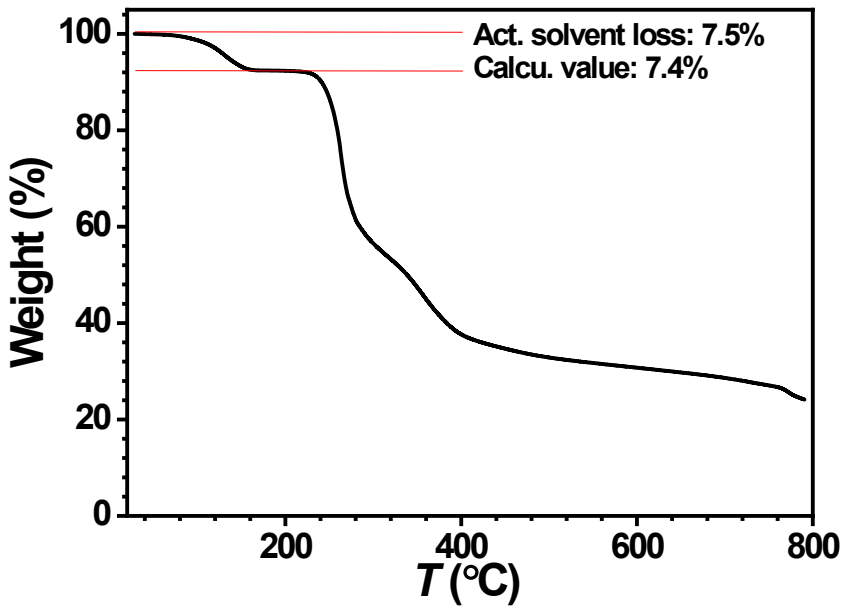

Fig. S36 The TGA trace of **1(BPh$_4$)·MeCN·Et$_2$O**, indicating the loss of solvent completes below 160 ºC.

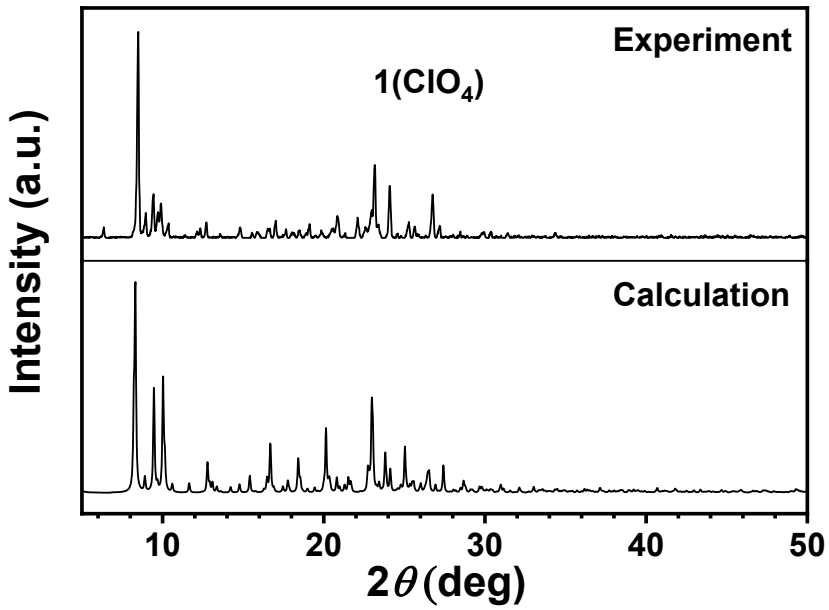

Fig. S37 The powder XRD pattern of **1(ClO$_4$)** and the simulated pattern from the single-crystal X-ray structure.

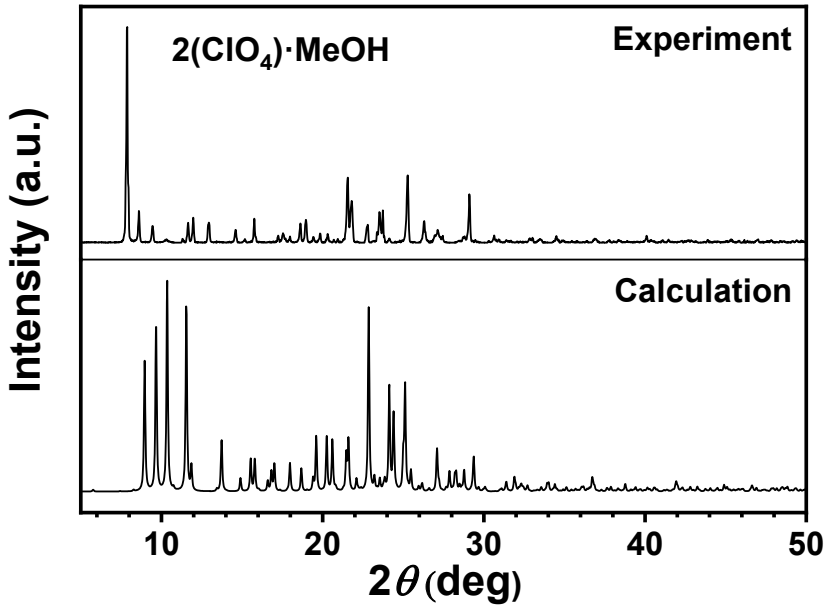

Fig. S38 The powder XRD pattern of **2(ClO_4)·MeOH** and the simulated pattern from the single-crystal X-ray structure, indicating the lattice methanol solvent is tend to remove after grinding.

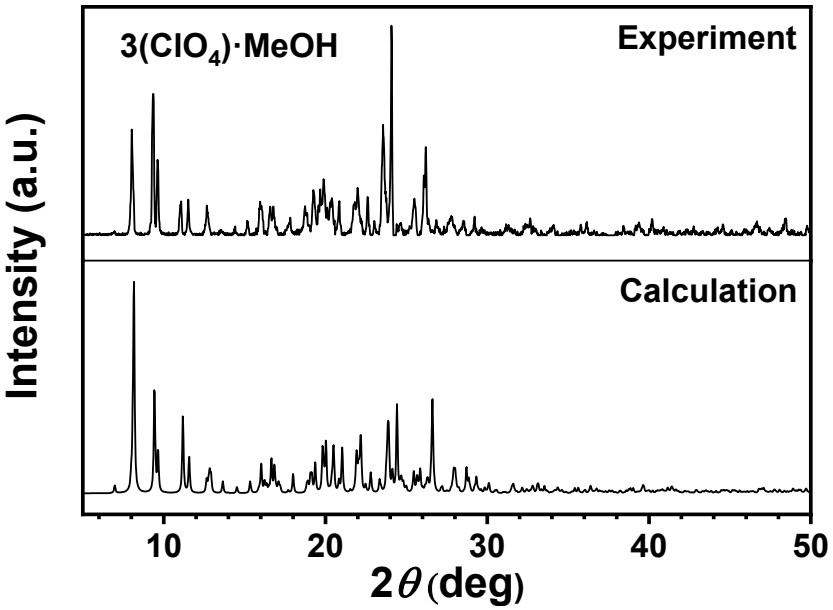

Fig. S39 The powder XRD pattern of **3(ClO_4)·MeOH** and the simulated pattern from the single-crystal X-ray structure.

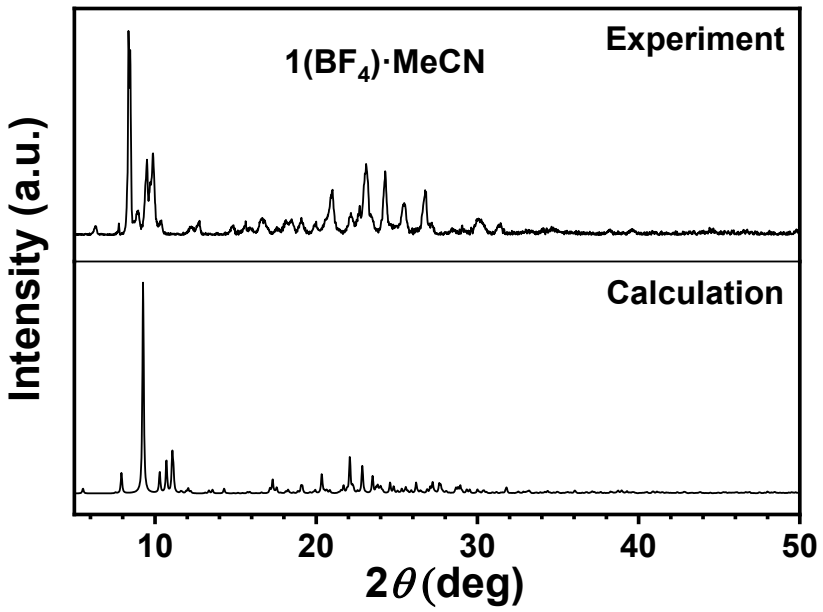

Fig. S40 The powder XRD pattern of **1(BF$_4$)·MeCN** and the simulated pattern from the single-crystal X-ray structure.

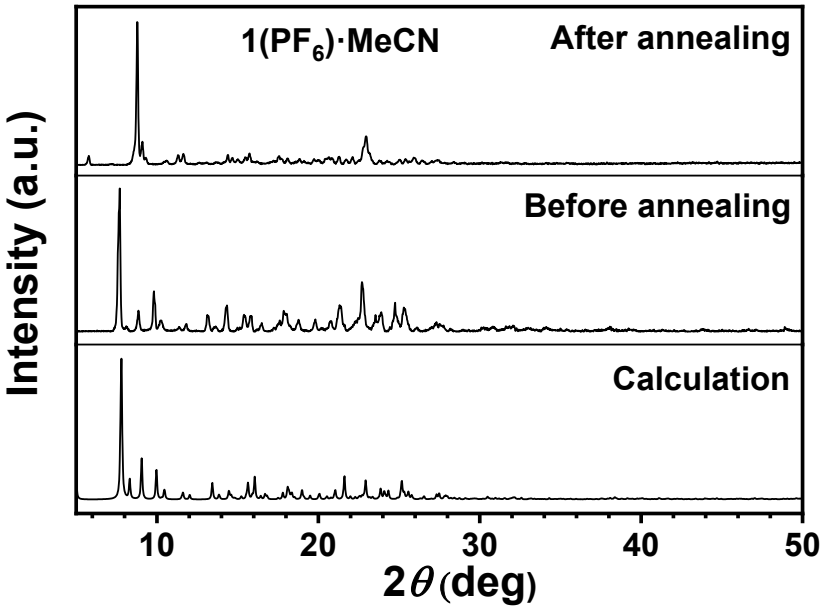

Fig. S41 The powder XRD pattern of **1(PF$_6$)·MeCN** and the simulated pattern from the single-crystal X-ray structure.

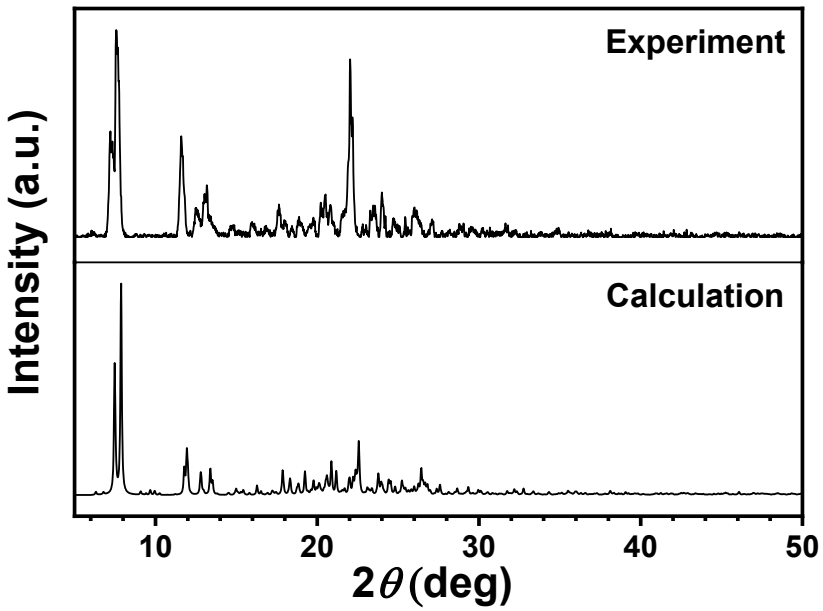

Fig. S42 The powder XRD pattern of **1**(BPh_4)·**MeCN**·Et_2O and the simulated pattern from the single-crystal X-ray structure.

Table S1. Crystal data, data collection, solution, and refinement information of iron(II) compounds.

	1(ClO_4)	**1(BF_4)·MeCN**	**1(PF_6)·5MeCN**	**1(BPh_4)·MeCN·Et_2O**	**2(ClO_4)·MeOH**	**3(ClO_4)·MeOH**
Formula	$C_{46}H_{38}N_6O_{12}Cl_2Fe$	$C_{48}H_{41}B_2N_7O_4F_8Fe$	$C_{54}H_{50}N_{10}O_4F_{12}P_2Fe$	$C_{98}H_{86}B_2N_7O_{4.5}Fe$	$C_{47}H_{42}N_6O_{13}Cl_2Fe$	$C_{47}H_{42}N_6O_{13}Cl_2Fe$
formula weight	993.57	1009.35	1248.83	1511.20	1025.61	1025.62
crystal system	*C*2/c	*P*bca	*C*2/c	$P2_1$/n	$P2_12_12_1$	$P2_1$/n
space group	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
a, Å	42.453(5)	17.173(3)	37.525(8)	14.263(3)	11.389(2)	13.856(3)
b, Å	11.2220(12)	16.506(3)	12.034(2)	38.290(8)	12.886(3)	18.314(4)
c, Å	21.261(2)	31.917(6)	23.788(5)	15.471(3)	30.629(6)	17.523(4)
α, deg	90	90	90	90	90	90.00
β, deg	118.425(2)	90	109.13(3)	104.04(3)	90	90.47(3)
γ, deg	90	90	90	90	90	90.00
V, Å^3	8907.7(17)	9047(3)	10149(4)	8196(3)	4495.3(16)	4446.5(16)
Z	8	8	8	4	4	4
T, K	296.2(2)	163.2(2)	163.2(2)	163.2(2)	153.2(2)	153.2(2)
F(000)	4096	4144	5296	3264	2120	2120
D_C, g cm^{-3}	1.482	1.482	1.688	1.255	1.515	1.532
μ, mm^{-1}	0.530	0.421	0.469	0.244	0.530	0.536
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal size, mm^3	0.25 × 0.20 × 0.16	0.30 × 0.25 × 0.17	0.22 × 0.20 × 0.12	0.30 × 0.24 × 0.15	0.18 × 0.16 × 0.12	0.22 × 0.14 × 0.08
T_{min} and T_{max}	0.6729, 0.7456	0.6624, 1.0000	0.8086, 1.0000	0.8684, 1.0000	0.7736, 1.0000	0.8184, 1.0000
θ_{min}, θ_{max}, deg	2.179, 24.027	0.6380, 27.4430	1.1487, 27.4816	1.0636, 28.7134	1.3297, 27.4816	1.4698, 27.4855
no. total reflns.	67060	36594	34044	55792	26929	29967
no. uniq. reflns, R_{int}	8752, 0.0452	8565, 0.0650	11585, 0.0484	18208, 0.0504	10196, 0.0366	10124, 0.0452
no. obs. [$I\geq2\sigma(I)$]	6749	8037	10170	15906	9655	9309
no. params	696	632	704	964	710	624
*R*1 [$I\geq2\sigma(I)$]	0.0601	0.0839	0.0805	0.0773	0.0538	0.0568
*wR*2 (all data)	0.1364	0.1407	0.2190	0.1666	0.1377	0.1263
S	1.194	1.292	1.177	1.168	1.076	1.125
$\Delta\rho^a$, e/ Å^3	0.474, −0.278	0.454, −0.387	0.386, −0.455	0.283, −0.413	0.403, −0.430	0.447, −0.508
max. and mean Δ/σ^b	0.000, 0.000	0.001, 0.000	0.002, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000
Flack parameter	/	/	/	/	0.051(8)	/
CCDC	2045167	2045168	2045169	2045170	2045171	2045172

[a] Max and min residual density. [b] Max and mean shift/σ. [c] The refinement showed there are 42 electrons per one complex, belonging to the seriously disordered solvent molecules, could not be modeled. These undetermined Q peaks were treated by SQUEEZE, PLATON. These electrons might come from two acetonitrile molecules and were excluded in the formula.

Table S2. Selected bond lengths (Å) for the single crystal structures of **1(ClO_4),** **1(BF_4)·MeCN**, **1(PF_6)·MeCN, 1(BPh_4)·MeCN·Et_2O.**

1(ClO_4)		**1(BF_4)·MeCN**		**1(PF_6)·MeCN**		**1(BPh_4)·MeCN·Et_2O**		**2(ClO_4)·MeOH**		**3(ClO_4)·MeOH**	
T / K	296 K	*T* / K	163 K	*T* / K	163 K	*T* / K	163 K	*T* / K	153 K	*T* / K	153 K
Fe-N1	2.210	Fe-N1	1.978	Fe-N1	1.975	Fe-N1	2.171	Fe-N1	2.046	Fe-N1	2.208
Fe-N2	2.105	Fe-N2	1.901	Fe-N2	1.899	Fe-N2	2.117	Fe-N2	1.933	Fe-N2	2.141
Fe-N3	2.155	Fe-N3	1.980	Fe-N3	1.995	Fe-N3	2.170	Fe-N3	2.034	Fe-N3	2.208
Fe-N4	2.279	Fe-N4	1.980	Fe-N4	1.976	Fe-N4	2.201	Fe-N4	2.013	Fe-N4	2.227
Fe-N5	2.109	Fe-N5	1.904	Fe-N5	1.906	Fe-N5	2.120	Fe-N5	1.929	Fe-N5	2.148
Fe-N6	2.186	Fe-N6	1.984	Fe-N6	1.976	Fe-N6	2.229	Fe-N6	1.966	Fe-N6	2.224

Table S3. Summary of the structural parameters and spin state in the family of compounds reported in this work.

Entry	T (K)	Σ (°)	θ (°)	ϕ (°)	Fe−N_{av} (Å)	S (O_h)	S (T_h)	Spin State	ref.
1(ClO_4)	296	91.3	89.8	179.8	1.96	2.26	9.33	LS	this work
1(BF_4)·MeCN	163	88.6	89.4	179.3	1.96	2.16	9.38	LS	this work
1(PF_6)·MeCN	163	90.7	89.6	178.7	1.95	2.21	9.48	LS	this work
1(BPh_4)·MeCN·Et_2O	163	144.1	88.0	169.9	2.17	5.38	6.21	HS	this work
2(ClO_4)·MeOH	153	104.8	86.0	179.4	1.99	2.68	8.71	LS	this work
3(ClO4)·MeOH	153	151.2	89.7	171.2	2.19	5.82	6.05	HS	this work
(*S*)-1·3MeCN, Fe1	153	154.4	82.4	179.4	2.17	5.55	6.24	HS	1
(*S*)-1·3MeCN, Fe2	153	112.9	86.6	177.0	2.01	2.30	8.68	LS	1
(*S*)-1·3MeCN, Fe3	153	101.3	85.3	178.0	1.97	5.43	9.41	LS	1
(*S*)-1·3MeCN, Fe1	173	155.3	82.9	176.5	2.18	3.35	6.26	HS	1
(*S*)-1·3MeCN, Fe2	173	97.2	86.2	179.3	1.96	2.38	9.41	LS	1
(*rac*)-1·3MeCN	153	92.0	89.5	178.1	1.96	2.32	9.21	LS	1
(*S*)-2·$MeNO_2$	153	162.9	80.7	167.7	2.16	6.23	6.37	HS	1
(*rac*)-2·4$MeNO_2$	153	95.4	90.0	180	1.957	2.463	8.95	LS	1
***(S)*-2·MeCN, Fe1**	153	166.0	80.6	169.7	2.189	6.493	6.27	HS	1
(*S*)-2·MeCN, Fe2	153	169.5	78.9	167.3	2.195	6.553	6.28	HS	1
(*S*)-2·MeCN, Fe3	153	159.3	81.6	178.2	2.174	5.566	6.38	HS	1
(*S*)-2·MeCN, Fe4	153	165.7	80.9	166.1	2.191	6.593	6.12	HS	1
(*rac*)-2·3MeCN	153	143.7	86.9	177.6	2.165	5.119	6.37	HS	1
(*R*)-1-$MeNO_2$, Fe1	155	96.7	86.2	178.3	1.961	2.287	9.33	LS	3
(*R*)-1-$MeNO_2$, Fe2	155	92.4	87.0	178.4	1.962	2.199	9.48	LS	3
(*R*)-1-$MeNO_2$, Fe3	155	91.8	87.6	179.6	1.967	2.244	9.26	LS	3
(*R*)-1-$MeNO_2$	265	105.6	86.4	180	2.001	2.779	8.47	LS	3
(*R*)-1-$MeNO_2$	275	107.5	86.2	180	2.006	2.867	8.35	LS	3
(*rac)*-1-MeCN	120	91.9	89.2	178.2	1.959	2.308	9.22	LS	3
(*rac*)-1-MeCN	250	92.5	89.5	178.4	1.964	2.337	9.16	LS	3

Fe−N_{av}: the average value of the six Fe−N bond lengths in one FeN_6 coordination sphere; Σ: the sum of the deviations from 90° of the *cis* angles;[4] $S(O_h)$: the result of CShMs calculation denotes the deviation value of ideal O_h symmetry.[5]

Table S4. The calculated μ_{rms} values in the family of single crystal structures.

Entry	*T* (K)	μ_{rms} (Å)	ref.
1(ClO_4)	296	0.175	this work
1(BF_4)·MeCN	163	0.103	this work
1(PF_6)·MeCN	163	0.190	this work
1(BPh_4)·MeCN·Et_2O	163	0.119	this work
2(ClO_4)·MeOH	153	0.1558	this work
3(ClO4)·MeOH	153	0.1665	this work
(*S*)-1·3MeCN, Fe1	153	0.142	1
(*S*)-1·3MeCN, Fe2	153	0.125	1
(*S*)-1·3MeCN, Fe3	153	0.135	1
(*S*)-1·3MeCN, Fe1	173	0.146	1
(*S*)-1·3MeCN, Fe2	173	0.131	1
(*rac*)-1·3MeCN	153	0.093	1
(*S*)-2·$MeNO_2$	153	0.220	1
***(S)*-2·MeCN, Fe1**	153	0.170	1
***(S)*-2·MeCN, Fe2**	153	0.193	1
***(S)*-2·MeCN, Fe3**	153	0.212	1
***(S)*-2·MeCN, Fe4**	153	0.168	1
(*rac*)-2·3MeCN	153	0.079	1
(*R*)-1-$MeNO_2$, Fe1	155	0.1604	3
(*R*)-1-$MeNO_2$, Fe2	155	0.1428	3
(*R*)-1-$MeNO_2$, Fe3	155	0.1409	3
(*R*)-1-$MeNO_2$	265	0.1389	3
(*R*)-1-$MeNO_2$	275	0.1583	3
(*rac*)-1-MeCN	120	0.0922	3
(*rac*)-1-MeCN	250	0.0825	3

Table S5. Summary of dihedral angle between neighboring phenyl and pyridine in these Fe(II) complexes and their spin states.

Entry	*T* / K	η_1	η_2	η_3	η_4	Spin State	ref.
1(ClO_4)	296	25.76	5.81	5.87	5.32	LS	this work
1(BF_4)·MeCN	163	9.21	3.88	4.33	1.84	LS	this work
1(PF_6)·MeCN	163	12.82	11.67	5.99	1.86	LS	this work
1(BPh_4)·MeCN·Et_2O	163	12.55	7.74	3.23	0.44	HS	this work
2(ClO_4)·MeOH	153	32.95	25.13	4.35	7.89	LS	this work
3(ClO_4)·MeOH	153	37.14	3.99	7.18	6.01	HS	this work
(*S*)-1·3MeCN, Fe1	153	30.49	27.62	1.20	5.05	HS	[1]
(*S*)-1·3MeCN, Fe2	153	26.17	20.42	3.08	5.70	LS	[1]
(*S*)-1·3MeCN, Fe3	153	18.55	17.67	5.28	5.54	LS	[1]
(*S*)-1·3MeCN, Fe1	173	30.56	30.12	1.41	4.52	HS	[1]
(*S*)-1·3MeCN, Fe2	173	18.08	17.98	6.01	6.86	LS	[1]
(*rac*)-1·3MeCN	153	9.15	6.81	4.14	3.59	LS	[1]
(*S*)-2·$MeNO_2$	153	53.38	9.01	6.08	4.69	HS	[1]
(*rac*)-2·4$MeNO_2$	153	6.78	/	3.04	/	LS	[1]
***(S)*-2·MeCN, Fe1**	153	53.49	12.62	14.87	10.68	HS	[1]
(*S*)-2·MeCN, Fe2	153	48.76	20.06	17.28	1.35	HS	[1]
(*S*)-2·MeCN, Fe3	153	41.51	25.46	7.17	2.70	HS	[1]
(*S*)-2·MeCN, Fe4	153	68.26	13.84	14.65	10.66	HS	[1]
(*rac*)-2·3MeCN	153	4.36	3.38	4.07	2.63	HS	[1]
(*R*)-1-$MeNO_2$, Fe1	155	34.63	27.34	4.72	2.68	LS	[3]
(*R*)-1-$MeNO_2$, Fe2	155	32.14	17.67	0.81	6.73	LS	[3]
(*R*)-1-$MeNO_2$, Fe3	155	29.54	11.65	2.06	5.32	LS	[3]
(*R*)-1-$MeNO_2$	265	22.42/30.18	/	3.73	/	LS	[3]
(*R*)-1-$MeNO_2$	275	22.62/30.22	/	3.68	/	LS	[3]
(*rac)*-1-MeCN	120	10.27	4.38	6.42	2.87	LS	[3]
(*rac*)-1-MeCN	250	10.45	4.84	6.79	3.91	LS	[3]

SI2.3 Magnetic characterization of Fe(II) complexes

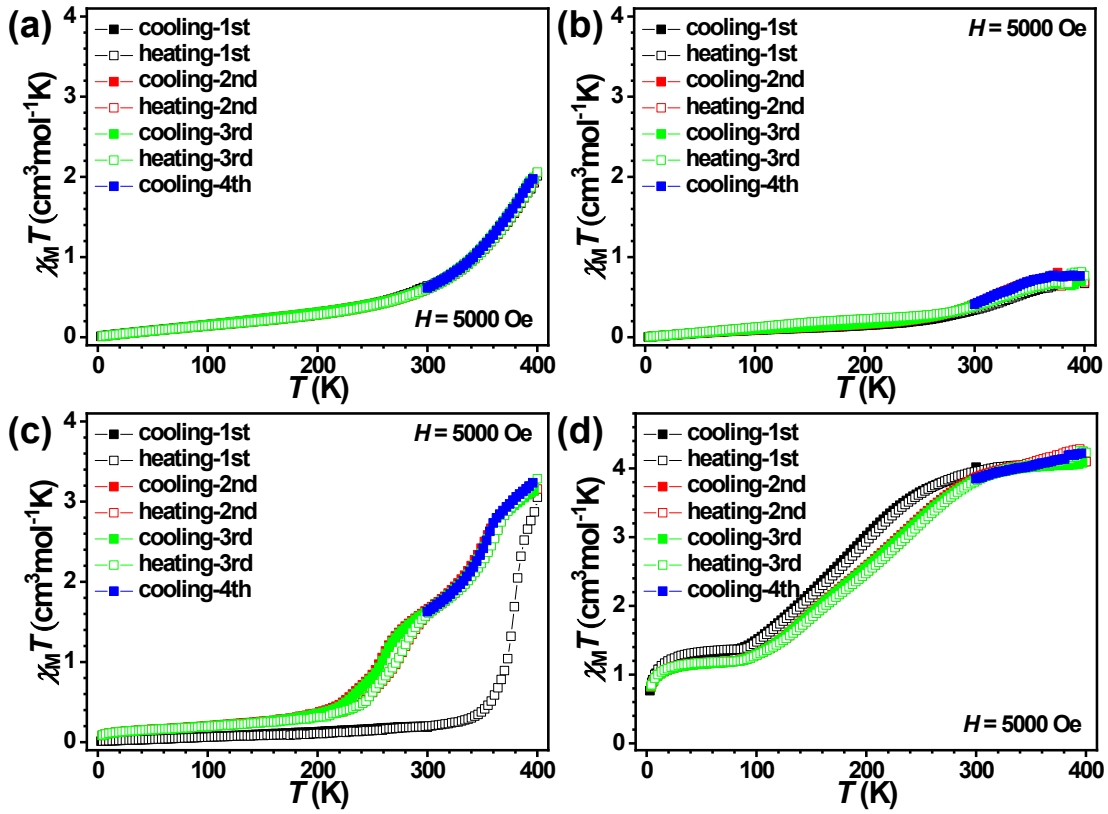

Fig. S43 Temperature dependence of $\chi_M T$ for **1(ClO$_4$)**, **1(BF$_4$)·MeCN**, **1(PF$_6$)·MeCN** and **1(BPh$_4$)·MeCN·Et$_2$O** upon successive scanning.

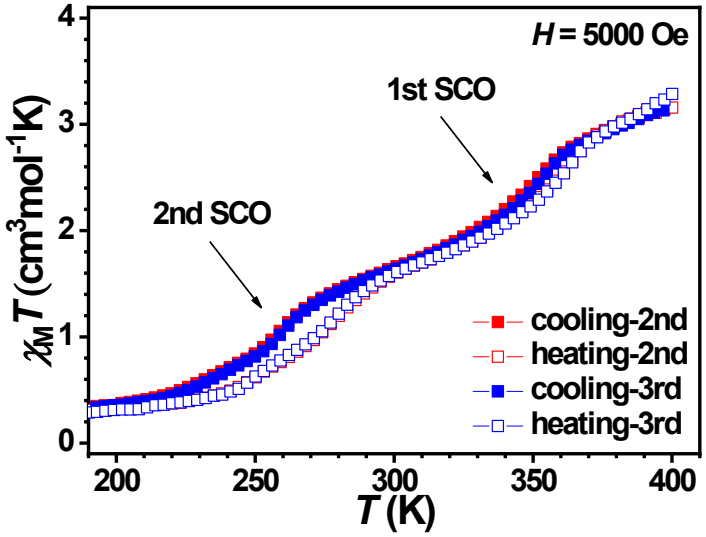

Fig. S44 Temperature dependence of $\chi_M T$ for **1(PF$_6$)·MeCN** in the second and third cycles.

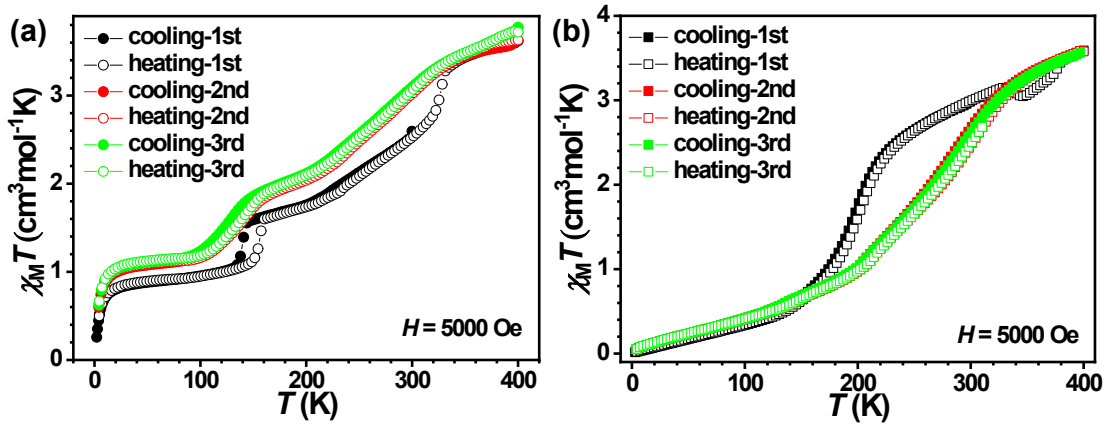

Fig. S45 Temperature dependence of $\chi_M T$ for (a) **2(ClO$_4$)·3MeCN**[1] and (b) **2(ClO$_4$)·MeOH** upon three repeated scanning.

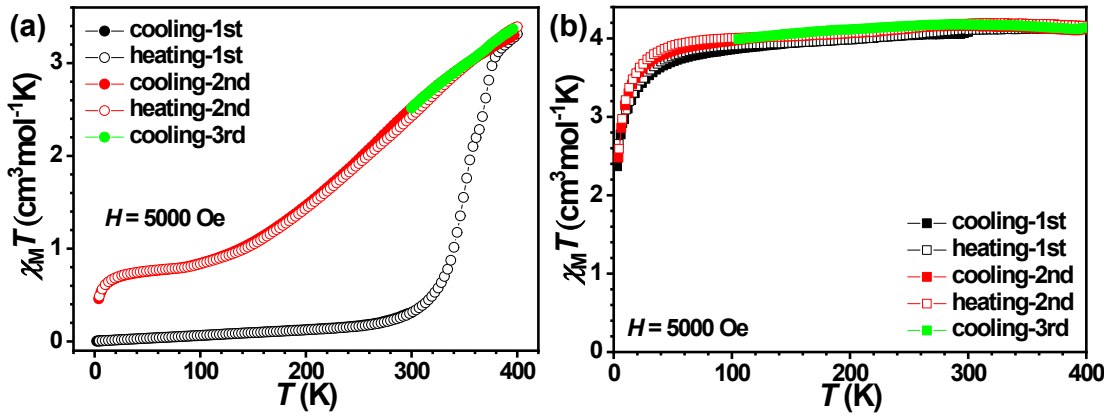

Fig. S46 Temperature dependence of $\chi_M T$ for (a) **3(ClO$_4$)·MeCN**[1] and **3(ClO$_4$)·MeOH** upon three repeated scanning.

SI3 Calculational results

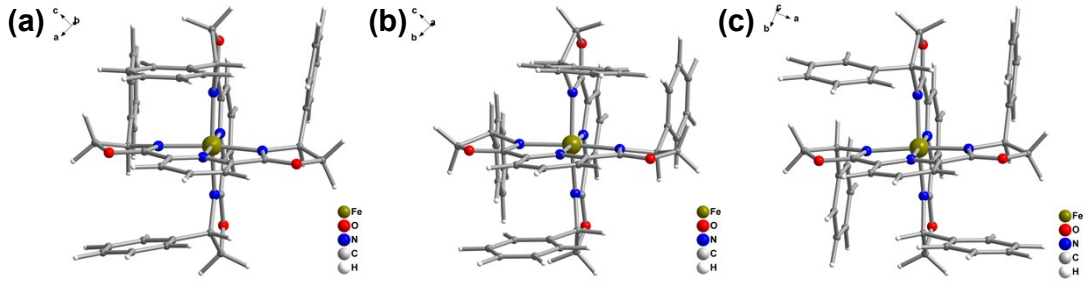

Fig. S47 The optimized singlet-state structures of (a−c) **1**−**3**.

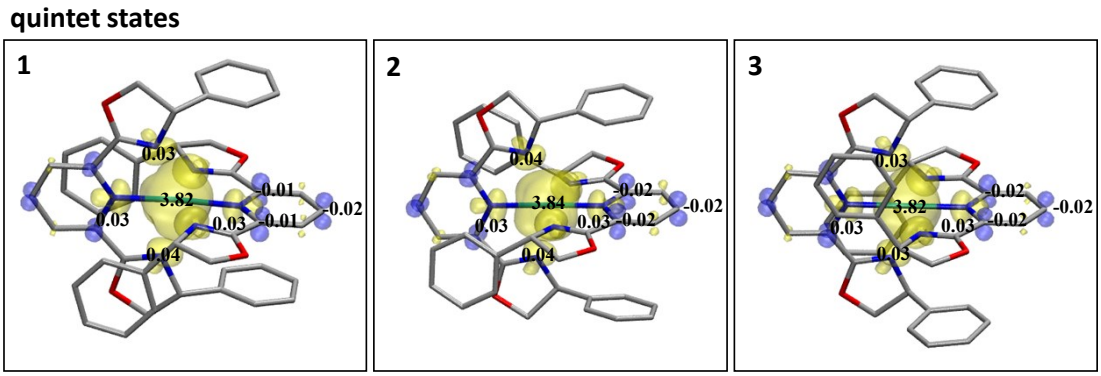

Fig. S48 The spin density plots for three complex cations at quintet states. Hydrogen atoms are not shown for clarity.

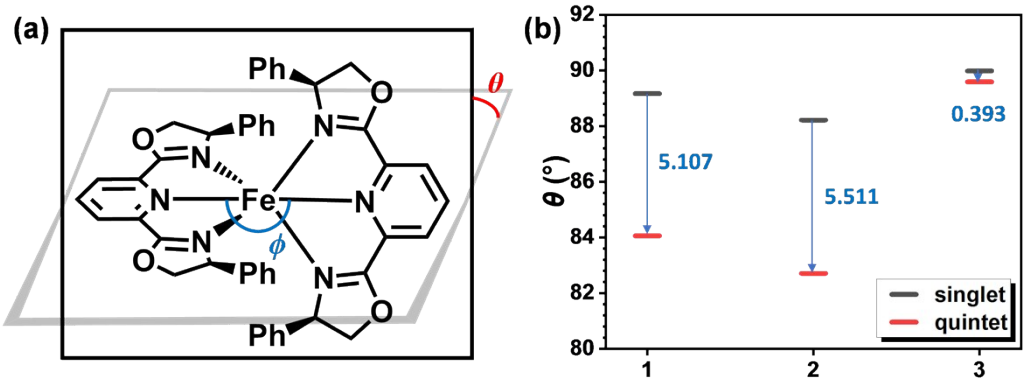

Fig. S49 (a) Definition of the angular Jahn-Teller distortion parameters θ and ϕ in this series complexes ($\theta < 90°$, $\phi < 180°$). (b) The θ values of three calculated structures in specific spin multiplicities.

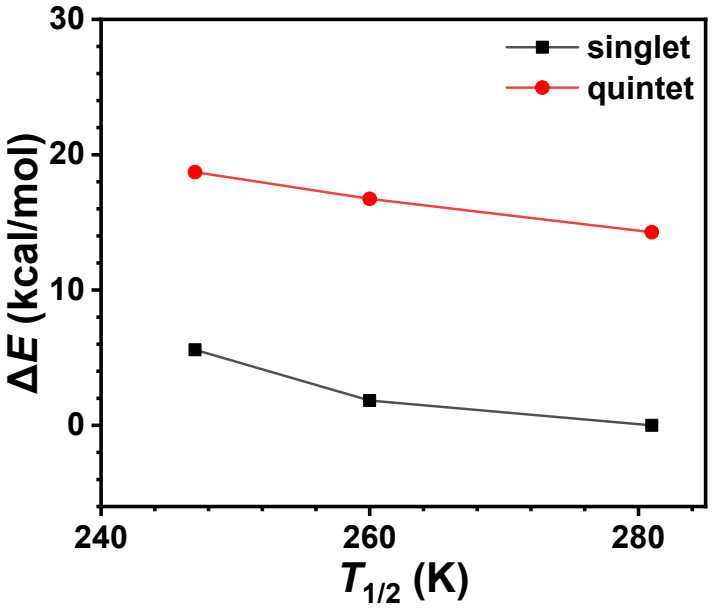

Fig. S50 The correlation of relative single point energy and $T_{1/2}$ for complexes **1**–**3** in specific spin multiplicities.

Table S6. Summary of the Fe–N bond lengths (Å) in the calculated structures of **1**–**3** in specific spin multiplicities.

	1		**2**		**3**	
spin state	**singlet**	**quintet**	**singlet**	**quintet**	**singlet**	**quintet**
Fe1-N6	1.992	2.172	1.989	2.201	1.992	2.167
Fe1-N7	1.911	2.127	1.912	2.146	1.916	2.124
Fe1-N8	1.984	2.185	1.985	2.198	1.992	2.167
Fe1-N9	1.992	2.172	1.989	2.151	1.991	2.173
Fe1-N10	1.911	2.127	1.912	2.139	1.916	2.124
Fe1-N11	1.984	2.185	1.985	2.148	1.993	2.173

Table S7. The calculated μ_{rms} values for calculated **1**–**3** in specific spin multiplicities.

	1		**2**		**3**	
spin state	**singlet**	**quintet**	**singlet**	**quintet**	**singlet**	**quintet**
ligand 1	0.1017	0.1033	0.1158	0.1915	0.0680	0.0856
ligand 2	0.1016	0.1030	0.1158	0.0813	0.0500	0.0652
complex	0.1016	0.1032	0.1158	0.1471	0.0597	0.0761

Table S8. Summary of dihedral angle between neighboring phenyl and pyridine in calculated structures of **1**–**3** in different spin multiplicities.

	spin state	η_1	η_2	η_3	η_4	η_{av}
1	**singlet**	11.411	5.241	11.403	5.245	8.325

	quintet	5.171	3.887	3.901	5.186	4.536
2	**singlet**	4.094	9.324	4.087	9.306	6.701
	quintet	14.192	14.910	1.658	1.818	8.145
3	**singlet**	7.564	7.469	7.350	7.469	7.463
	quintet	6.243	6.238	7.516	7.544	6.885

Table S9. Cartesian coordinates for the optimized geometries of **1** in singlet state.

Atom	x	y	z	Atom	x	y	z
Fe	0.000052	0.000028	-0.519332	C	2.185795	0.370306	1.132446
O	0.799524	-3.035225	-3.064272	C	2.776504	-1.190028	2.573401
O	-3.120260	-0.114782	2.026798	C	1.738976	-1.761502	1.588254
O	-0.798893	3.035718	-3.063893	C	0.610448	-2.542229	2.205815
O	3.119965	0.114188	2.027295	C	0.364329	-3.848664	1.785689
N	0.884915	-1.098566	-1.925579	C	-0.665207	-4.594351	2.354045
N	-1.112902	-1.553066	-0.494931	C	-1.468119	-4.034223	3.342087
N	-1.317456	0.546240	0.859527	C	-1.237389	-2.725852	3.762154
N	-0.884650	1.098971	-1.925387	C	-0.202539	-1.989712	3.198422
N	1.113040	1.553083	-0.494451	H	2.003135	-0.123493	-3.410738
N	1.317221	-0.546424	0.859697	H	3.212271	-3.056195	-1.354640
C	2.071649	-1.037915	-2.803331	H	5.283010	-2.966672	-0.008264
C	3.340105	-0.993098	-1.989085	H	6.600413	-0.864837	0.116468
C	3.775875	-2.121859	-1.289974	H	5.837003	1.148264	-1.118455
C	4.939728	-2.075298	-0.530515	H	3.759290	1.064313	-2.468776
C	5.680510	-0.896894	-0.463172	H	1.584888	-2.069090	-4.709873
C	5.250160	0.232123	-1.152281	H	2.767274	-2.950760	-3.704372
C	4.084230	0.182671	-1.912232	H	-1.452555	-4.513354	-2.055609
C	1.891322	-2.296723	-3.684548	H	-3.357667	-4.658004	-0.432169
C	0.304829	-2.232700	-2.141662	H	-3.776281	-2.762243	1.158041
C	-0.867477	-2.568741	-1.337003	H	-2.366495	1.028060	3.578701
C	-1.660742	-3.708323	-1.354902	H	-3.697743	1.772313	2.643119
C	-2.718734	-3.778345	-0.447696	H	-2.243149	2.404800	0.845914
C	-2.960413	-2.729197	0.439597	H	-1.002052	4.296496	1.021900
C	-2.126954	-1.621028	0.378688	H	0.830218	5.620467	2.034287
C	-2.185902	-0.370662	1.132074	H	2.262476	4.619252	3.799849
C	-2.777135	1.189453	2.573099	H	1.853367	2.284382	4.544285
C	-1.739380	1.761130	1.588316	H	0.011632	0.973263	3.546369
C	-0.610921	2.541642	2.206267	H	-2.002791	0.124140	-3.410765
C	-0.364615	3.848165	1.786500	H	-3.211905	3.056856	-1.354730
C	0.664844	4.593633	2.355256	H	-5.282895	2.967524	-0.008702
C	1.467470	4.033235	3.343400	H	-6.600513	0.865803	0.115792
C	1.236587	2.724775	3.763055	H	-5.836977	-1.147413	-1.118882

C	0.201807	1.988828	3.198909	H	-3.759031	-1.063646	-2.468846
C	-2.071257	1.038523	-2.803293	H	-1.584162	2.069833	-4.709682
C	-3.339824	0.993766	-1.989189	H	-2.766581	2.951523	-3.704222
C	-3.775614	2.122575	-1.290158	H	1.453139	4.513583	-2.054637
C	-4.939594	2.076119	-0.530890	H	3.358080	4.657806	-0.430970
C	-5.680500	0.897777	-0.463679	H	3.776407	2.761751	1.158931
C	-5.250101	-0.231292	-1.152667	H	2.365560	-1.028649	3.578880
C	-4.084031	-0.181946	-1.912419	H	3.696995	-1.773027	2.643728
C	-1.890701	2.297390	-3.684373	H	2.242860	-2.405013	0.845780
C	-0.304399	2.233059	-2.141290	H	1.001968	-4.296772	1.021128
C	0.867816	2.568898	-1.336416	H	-0.830429	-5.621128	2.032815
C	1.661194	3.708410	-1.354057	H	-2.263239	-4.620371	3.798175
C	2.719082	3.778200	-0.446717	H	-1.854412	-2.285691	4.543316
C	2.960597	2.728876	0.440412	H	-0.012414	-0.974292	3.546341
C	2.127041	1.620801	0.379259				

Table S10. Cartesian coordinates for the optimized geometries of **1** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	0.000067	-0.000092	-0.580793	C	2.283432	-0.467181	1.231506
O	-0.823240	-3.463330	-2.843249	C	2.337358	-2.160243	2.652758
O	-3.062847	1.004108	2.151729	C	1.160876	-2.331318	1.669473
O	0.823959	3.463369	-2.842878	C	-0.173319	-2.640059	2.293365
O	3.062680	-1.004421	2.152180	C	-0.890526	-3.760402	1.877783
N	0.069427	-1.537215	-2.113283	C	-2.122760	-4.065907	2.450678
N	-1.784512	-1.135730	-0.359249	C	-2.653361	-3.244823	3.440093
N	-1.182895	1.058442	0.919940	C	-1.948293	-2.117463	3.856977
N	-0.069203	1.537494	-2.112896	C	-0.716030	-1.821848	3.287077
N	1.784859	1.135268	-0.359176	H	1.208140	-1.299214	-3.854173
N	1.182847	-1.058797	0.920190	H	1.799149	-4.056760	-1.339231
C	1.076416	-2.050201	-3.061689	H	3.896535	-4.240888	-0.043406
C	2.382614	-2.226923	-2.331583	H	5.658319	-2.504174	-0.265528
C	2.572635	-3.292294	-1.449825	H	5.332923	-0.605734	-1.834364
C	3.745435	-3.392449	-0.709318	H	3.244234	-0.439065	-3.164130
C	4.735529	-2.419417	-0.835591	H	0.111294	-3.240082	-4.669921
C	4.551497	-1.353783	-1.711697	H	0.987404	-4.238685	-3.481390
C	3.379911	-1.261128	-2.458321	H	-3.357011	-3.767304	-1.742472
C	0.402369	-3.324769	-3.619468	H	-5.074938	-3.082277	-0.048301
C	-0.885743	-2.398699	-2.065565	H	-4.626754	-1.101369	1.428548
C	-2.013678	-2.187817	-1.149881	H	-2.020109	1.929244	3.676475
C	-3.190516	-2.922379	-1.078831	H	-3.030530	3.004726	2.667095
C	-4.140975	-2.532122	-0.135066	H	-1.395108	3.120901	0.935606

C	-3.901011	-1.435112	0.690575	H	0.469723	4.414563	1.110234
C	-2.698149	-0.756658	0.534192	H	2.660727	4.957584	2.132703
C	-2.283448	0.466757	1.231257	H	3.607075	3.492421	3.900657
C	-2.337697	2.160107	2.652154	H	2.351955	1.478453	4.639270
C	-1.161184	2.331154	1.668878	H	0.152634	0.956115	3.634278
C	0.172925	2.640258	2.292786	H	-1.207454	1.299744	-3.854086
C	0.889939	3.760685	1.877115	H	-1.799643	4.057021	-1.339013
C	2.122064	4.066503	2.450084	H	-3.897373	4.240527	-0.043715
C	2.652736	3.245667	3.439662	H	-5.658618	2.503348	-0.266273
C	1.947862	2.118216	3.856635	H	-5.332393	0.605094	-1.835176
C	0.715718	1.822280	3.286659	H	-3.243363	0.439097	-3.164523
C	-1.075983	2.050620	-3.061451	H	-0.111042	3.241024	-4.669428
C	-2.382398	2.227105	-2.331669	H	-0.986692	4.239272	-3.480285
C	-2.572894	3.292360	-1.449875	H	3.357263	3.767427	-1.741391
C	-3.745893	3.392160	-0.709631	H	5.074951	3.082204	-0.047041
C	-4.735692	2.418866	-0.836158	H	4.626638	1.100984	1.429347
C	-4.551186	1.353336	-1.712288	H	2.019760	-1.929174	3.677034
C	-3.379422	1.261061	-2.458678	H	3.030080	-3.004955	2.667833
C	-0.401845	3.325306	-3.618871	H	1.394686	-3.121309	0.936451
C	0.886185	2.398720	-2.065199	H	-0.470378	-4.414442	1.111006
C	2.014064	2.187569	-1.149506	H	-2.661565	-4.956926	2.133367
C	3.190771	2.922289	-1.078022	H	-3.607793	-3.491324	3.901030
C	4.141078	2.531949	-0.134141	H	-2.352327	-1.477514	4.639489
C	3.901043	1.434768	0.691248	H	-0.152782	-0.955768	3.634646
C	2.698304	0.756184	0.534448				

Table S11. Cartesian coordinates for the optimized geometries of **2** in singlet state.

Atom	x	y	z	Atom	x	y	z
Fe	-0.000032	0.000041	-0.007972	C	1.348977	-1.822306	1.580184
O	-2.305024	-2.156729	-2.521564	C	0.233250	-3.127405	2.960718
O	-1.561641	2.729431	2.516059	C	-0.686606	-2.000241	2.460376
O	2.305181	2.156924	-2.521273	C	-2.058568	-2.431284	2.020112
O	1.561420	-2.729378	2.516158	C	-2.230792	-3.362606	0.992911
N	-0.549706	-1.295056	-1.413789	C	-3.503360	-3.758661	0.601002
N	-1.891347	0.278007	-0.001472	C	-4.623588	-3.233115	1.241696
N	-0.142098	1.396936	1.394668	C	-4.462789	-2.309606	2.269070
N	0.549759	1.295146	-1.413748	C	-3.185439	-1.910004	2.654393
N	1.891267	-0.277954	-0.001361	H	0.112892	-4.204611	-0.686255
N	0.141945	-1.396874	1.394703	H	2.074072	-5.509095	0.048833
C	1.238347	-2.940152	-2.026025	H	4.318686	-5.026991	-0.900997
C	1.098527	-3.964434	-1.085513	H	4.586370	-3.213458	-2.576390
C	2.200190	-4.705038	-0.673831	H	2.623028	-1.888428	-3.296369
C	3.459172	-4.433150	-1.205077	H	0.414324	-1.414474	-3.253129
C	3.609099	-3.416115	-2.142046	H	-1.222253	-2.973407	-4.085697
C	2.503537	-2.673152	-2.547095	H	-1.221318	-3.917154	-2.569228
C	0.061364	-2.119213	-2.479367	H	-4.670433	-0.928207	-1.457797
C	-1.153518	-2.909197	-2.998317	H	-5.681181	0.840839	0.005846
C	-1.829259	-1.353222	-1.587771	H	-4.194435	2.239999	1.462766
C	-2.675228	-0.466302	-0.793857	H	-0.263293	3.247138	4.044896
C	-4.054035	-0.305406	-0.813682	H	-0.006951	4.092907	2.488251
C	-4.605870	0.680398	0.004230	H	0.803484	1.228020	3.241679
C	-3.788106	1.461889	0.821014	H	1.356658	3.791986	0.503951
C	-2.422001	1.215377	0.796982	H	3.624192	4.493744	-0.192314
C	-1.349156	1.822337	1.580116	H	5.620493	3.555947	0.949708
C	-0.233471	3.127512	2.960603	H	5.332853	1.907052	2.784429
C	0.686375	2.000301	2.460404	H	3.063070	1.190239	3.465880
C	2.058420	2.431183	2.020267	H	-0.112789	4.204337	-0.685632
C	2.230912	3.362701	0.993290	H	-2.073925	5.508853	0.049491
C	3.503602	3.758452	0.601456	H	-4.318466	5.027195	-0.900746
C	4.623682	3.232382	1.241977	H	-4.586107	3.214133	-2.576649
C	4.462617	2.308663	2.269114	H	-2.622786	1.889113	-3.296734
C	3.185149	1.909375	2.654358	H	-0.414117	1.414814	-3.253190
C	-1.238179	2.940365	-2.025925	H	1.222552	2.973802	-4.085403
C	-1.098383	3.964399	-1.085137	H	1.221490	3.917360	-2.568815
C	-2.200029	4.705002	-0.673406	H	4.670467	0.928216	-1.457499
C	-3.458970	4.433348	-1.204860	H	5.681088	-0.840965	0.006102
C	-3.608872	3.416577	-2.142119	H	4.194192	-2.240179	1.462844
C	-2.503330	2.673608	-2.547214	H	0.263031	-3.246916	4.045024

C	-0.061204	2.119420	-2.479286	H	0.006765	-4.092843	2.488448
C	1.153723	2.909455	-2.998037	H	-0.803864	-1.227951	3.241623
C	1.829320	1.353342	-1.587586	H	-1.356396	-3.791478	0.503465
C	2.675218	0.466374	-0.793653	H	-3.623744	-4.493785	-0.192956
C	4.054016	0.305395	-0.813450	H	-5.620303	-3.556921	0.949370
C	4.605784	-0.680480	0.004440	H	-5.333143	-1.908409	2.784509
C	3.787944	-1.461996	0.821128	H	-3.063570	-1.191027	3.466087
C	2.421856	-1.215415	0.797051				

Table S12. Cartesian coordinates for the optimized geometries of **2** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	0.013071	0.048609	0.016057	C	1.672184	1.752851	1.764378
O	2.298389	-2.488738	-2.504785	C	3.020564	0.806829	3.239472
O	-2.734687	-2.092872	2.439451	C	1.980311	-0.216958	2.747098
O	-2.080212	2.569653	-2.632408	C	2.492161	-1.547892	2.269485
O	2.553076	2.076073	2.692830	C	3.500833	-1.606295	1.307965
N	1.452438	-0.675695	-1.482745	C	3.924633	-2.829092	0.802065
N	-0.199416	-2.086265	-0.029370	C	3.343762	-4.009807	1.262169
N	-1.518442	-0.447213	1.512992	C	2.337790	-3.959521	2.222133
N	-1.199848	0.784325	-1.601209	C	1.907684	-2.730883	2.717340
N	0.232691	2.176467	0.020102	H	4.676946	-0.246937	-1.039612
N	1.321016	0.518580	1.653672	H	5.935841	1.640864	-0.085940
C	3.195089	1.001112	-2.001109	H	5.206876	3.976092	-0.513060
C	4.329923	0.771199	-1.221041	H	3.211791	4.405805	-1.932717
C	5.043988	1.834673	-0.679118	H	1.938464	2.508995	-2.887553
C	4.636479	3.144434	-0.921160	H	1.680765	0.282734	-3.308760
C	3.517679	3.384170	-1.713115	H	3.083985	-1.478391	-4.129295
C	2.801744	2.316961	-2.246703	H	4.094508	-1.481223	-2.660840
C	2.343531	-0.124350	-2.526060	H	1.157048	-4.766961	-1.531014
C	3.072045	-1.379348	-3.042147	H	-0.570409	-5.900536	-0.106171
C	1.484034	-1.954790	-1.610955	H	-2.050188	-4.513582	1.371285
C	0.587166	-2.812643	-0.821653	H	-3.183832	-1.038929	4.158794
C	0.496774	-4.198063	-0.880634	H	-4.279730	-0.765697	2.783610
C	-0.464829	-4.818423	-0.084243	H	-1.586880	0.531921	3.348459
C	-1.291228	-4.056536	0.740874	H	-4.640661	0.480484	1.127339
C	-1.112290	-2.678510	0.738657	H	-5.575125	2.530197	0.119842
C	-1.821050	-1.695150	1.572605	H	-4.446800	4.715545	0.464371
C	-3.231775	-0.883652	3.078757	H	-2.399576	4.839465	1.865386
C	-2.302886	0.237004	2.563157	H	-1.449930	2.776212	2.862424
C	-2.956068	1.484382	2.027342	H	-4.026639	0.087201	-0.913548
C	-4.125540	1.431148	1.268526	H	-5.221643	-1.936366	-0.102430

C	-4.654378	2.584027	0.698163	H	-4.617523	-4.171225	-1.001442
C	-4.022778	3.809909	0.892965	H	-2.824182	-4.375903	-2.707035
C	-2.872216	3.877728	1.673192	H	-1.633016	-2.354704	-3.506203
C	-2.341159	2.719462	2.233301	H	-1.279810	-0.088131	-3.486473
C	-2.758879	-1.004777	-2.260806	H	-2.887355	1.551587	-4.246154
C	-3.766030	-0.897428	-1.301719	H	-3.822373	1.461140	-2.722780
C	-4.425545	-2.030397	-0.840547	H	-0.952026	4.889765	-1.575973
C	-4.085581	-3.285380	-1.343160	H	0.611733	5.996532	0.041781
C	-3.082030	-3.399847	-2.299988	H	1.921259	4.584495	1.651087
C	-2.415066	-2.263286	-2.750140	H	3.079363	0.913204	4.324031
C	-1.996650	0.212540	-2.702802	H	4.024056	0.631333	2.831871
C	-2.817355	1.429075	-3.164007	H	1.215156	-0.390338	3.523361
C	-1.281550	2.065525	-1.709401	H	3.946088	-0.677327	0.951812
C	-0.464576	2.921094	-0.841822	H	4.726247	-2.868291	0.065277
C	-0.365830	4.306878	-0.869406	H	3.691126	-4.969733	0.884761
C	0.503922	4.914543	0.036073	H	1.894817	-4.880045	2.598085
C	1.235353	4.137784	0.935079	H	1.123888	-2.691869	3.475846
C	1.057025	2.760445	0.893492				

Table S13. Cartesian coordinates for the optimized geometries of **3** in singlet state.

Atom	x	y	z	Atom	x	y	z
Fe	0.000625	0.000675	-0.001245	C	-0.892718	-2.067312	1.626647
O	3.241965	-1.387052	-1.976358	C	-1.576621	-3.978660	0.750579
O	-3.249927	1.368268	-1.975177	C	-1.314826	-2.951613	-0.375956
O	1.379194	3.254610	1.958363	C	-2.525325	-2.552639	-1.181186
O	-1.376623	-3.238186	1.987704	C	-2.458616	-2.488936	-2.571118
N	1.794870	-0.784370	-0.364256	C	-3.564935	-2.083601	-3.314135
N	-0.003461	-0.008242	-1.917447	C	-4.748174	-1.741122	-2.669002
N	-1.795271	0.781872	-0.363845	C	-4.826453	-1.813848	-1.278786
N	0.783189	1.796643	0.353466	C	-3.718398	-2.210563	-0.539092
N	0.002793	0.007508	1.914926	H	3.311478	-0.518551	1.059573
N	-0.782140	-1.794509	0.369487	H	2.765645	-1.512385	3.091935
C	2.950713	-1.311843	0.386514	H	2.046689	-3.476912	4.425185
C	2.550488	-2.516502	1.199913	H	1.435527	-5.595843	3.286153
C	2.485724	-2.440818	2.589283	H	1.578803	-5.756041	0.811532
C	2.079208	-3.542231	3.339014	H	2.268991	-3.792677	-0.522724
C	1.737072	-4.729563	2.701346	H	4.806304	-0.865773	-0.743917
C	1.810834	-4.816799	1.311708	H	4.373063	-2.602860	-0.739689
C	2.208545	-3.713689	0.565319	H	1.969382	-0.907080	-4.488108
C	3.979375	-1.582568	-0.736635	H	-0.011667	-0.025756	-5.754973
C	2.070176	-0.901881	-1.620186	H	-1.987227	0.867318	-4.487746

C	1.056743	-0.486552	-2.585504	H	-4.807796	0.854410	-0.731605
C	1.094567	-0.516519	-3.973153	H	-4.378565	2.592596	-0.744548
C	-0.009333	-0.020768	-4.667741	H	-3.305195	0.526961	1.068978
C	-1.110220	0.481424	-3.973011	H	-2.274400	3.788205	-0.547241
C	-1.066473	0.464087	-2.585332	H	-1.582526	5.764699	0.766771
C	-2.075995	0.887823	-1.619597	H	-1.429993	5.627096	3.242167
C	-3.982554	1.573257	-0.734119	H	-2.034062	3.517756	4.402553
C	-2.948612	1.314539	0.387044	H	-2.754312	1.540013	3.089607
C	-2.547087	2.527154	1.187877	H	0.525319	3.302054	-1.083908
C	-2.209601	3.719140	0.541229	H	1.531744	2.738054	-3.104518
C	-1.811151	4.829614	1.276226	H	3.505509	2.010032	-4.419226
C	-1.732105	4.755039	2.666315	H	5.618905	1.414550	-3.261847
C	-2.070267	3.573090	3.315952	H	5.764212	1.582343	-0.787739
C	-2.477530	2.464273	2.577637	H	3.791725	2.281277	0.528129
C	1.314234	2.947648	-0.402577	H	2.593815	4.384101	0.718927
C	2.524898	2.542586	-1.204589	H	0.854338	4.808015	0.713867
C	2.457527	2.464082	-2.593727	H	0.890054	1.997003	4.476818
C	3.564227	2.053049	-3.333053	H	0.005996	0.023027	5.752309
C	4.748596	1.719945	-2.685060	H	-0.881132	-1.960715	4.494354
C	4.827491	1.807447	-1.295726	H	-2.595450	-4.375924	0.759914
C	3.719015	2.209606	-0.559641	H	-0.856849	-4.803168	0.755687
C	1.575717	3.984885	0.714632	H	-0.526480	-3.312865	-1.054390
C	0.896197	2.080095	1.608069	H	-1.533558	-2.769813	-3.079451
C	0.477907	1.072352	2.578170	H	-3.506747	-2.052107	-4.400727
C	0.502617	1.118564	3.965679	H	-5.618243	-1.440165	-3.248470
C	0.005086	0.018638	4.665060	H	-5.762437	-1.581506	-0.772690
C	-0.493924	-1.086763	3.975424	H	-3.790548	-2.270409	0.549439
C	-0.471587	-1.051872	2.587521				

Table S14. Cartesian coordinates for the optimized geometries of **3** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	-0.000062	-0.000124	-0.000397	C	-1.766158	1.464362	-1.858207
O	2.279898	2.702526	2.300260	C	-3.334493	2.849406	-1.133459
O	-2.280741	-2.701416	2.301033	C	-2.658232	2.143287	0.062244
O	2.748427	-2.224623	-2.306420	C	-3.530517	1.218455	0.873214
O	-2.747411	2.223257	-2.308795	C	-3.390160	1.162108	2.259020
N	1.395250	1.550479	0.587678	C	-4.142257	0.261858	3.009279
N	-0.000380	0.000501	2.123849	C	-5.046444	-0.586165	2.376750
N	-1.395581	-1.550296	0.588099	C	-5.191025	-0.536492	0.991282
N	1.589212	-1.361199	-0.586787	C	-4.429903	0.355694	0.243661
N	0.000473	-0.000634	-2.123922	H	2.900953	2.143823	-0.743427

N	-1.588985	1.360669	-0.588227	H	1.845987	2.647638	-2.764076
C	2.170390	2.618695	-0.070680	H	0.218148	3.972695	-4.087746
C	1.233610	3.483803	-0.875930	H	-1.301518	5.571183	-2.949480
C	1.164850	3.337817	-2.260551	H	-1.186148	5.844941	-0.481592
C	0.248946	4.077114	-3.004432	H	0.408588	4.501783	0.843215
C	-0.602067	4.974909	-2.366626	H	3.955308	3.065395	1.160038
C	-0.539034	5.126261	-0.982417	H	2.739565	4.379599	1.175369
C	0.368614	4.377417	-0.241109	H	1.424440	1.633410	4.693086
C	2.886197	3.297343	1.118057	H	-0.001284	0.001846	5.959310
C	1.509999	1.726701	1.856873	H	-1.426495	-1.630532	4.693558
C	0.763034	0.871584	2.788284	H	-3.955750	-3.065335	1.160549
C	0.794193	0.912922	4.176838	H	-2.739703	-4.379195	1.176895
C	-0.001029	0.001460	4.871911	H	-2.901031	-2.144288	-0.743003
C	-0.795931	-0.910473	4.177100	H	-0.409266	-4.502051	0.844902
C	-0.764130	-0.870098	2.788524	H	1.185759	-5.845563	-0.479182
C	-1.510745	-1.725807	1.857361	H	1.302134	-5.572017	-2.947048
C	-2.886563	-3.296999	1.118977	H	-0.216956	-3.973512	-4.086047
C	-2.170570	-2.618836	-0.069919	H	-1.845216	-2.648210	-2.763124
C	-1.233605	-3.484222	-0.874662	H	2.183555	-2.878526	0.731953
C	-0.368917	-4.377831	-0.239423	H	2.693591	-1.838373	2.760178
C	0.538912	-5.126862	-0.980324	H	4.041239	-0.237568	4.094204
C	0.602503	-4.975636	-2.364519	H	5.652005	1.275385	2.964351
C	-0.248183	-4.077819	-3.002734	H	5.914528	1.181497	0.494561
C	-1.164314	-3.338386	-2.259276	H	4.550048	-0.386790	-0.840287
C	2.658305	-2.143356	0.064508	H	4.418409	-2.713489	-1.183548
C	3.530471	-1.217893	0.874905	H	3.093091	-3.916635	-1.185659
C	3.389689	-1.160278	2.260612	H	1.688955	-1.359991	-4.692022
C	4.141716	-0.259492	3.010306	H	0.001060	-0.001990	-5.958481
C	5.046284	0.587764	2.377307	H	-1.687299	1.356813	-4.693501
C	5.191256	0.536873	0.991921	H	-4.418058	2.711990	-1.186872
C	4.430203	-0.355841	0.244859	H	-3.093304	3.915727	-1.189060
C	3.334764	-2.850394	-1.130515	H	-2.183576	2.878998	0.729172
C	1.766928	-1.465552	-1.856637	H	-2.694340	1.840763	2.758199
C	0.899637	-0.730689	-2.787240	H	-4.042163	0.240957	4.093230
C	0.944225	-0.758580	-4.175839	H	-5.652215	-1.273380	2.964213
C	0.000886	-0.001616	-4.871060	H	-5.914072	-1.181640	0.494266
C	-0.942683	0.755826	-4.176658	H	-4.549429	0.385687	-0.841550
C	-0.898527	0.728920	-2.788026				

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