Supporting Information

Content

Figure S1. Photo of the crystalline sample of H_2thpy·⅓H_2O ligand.

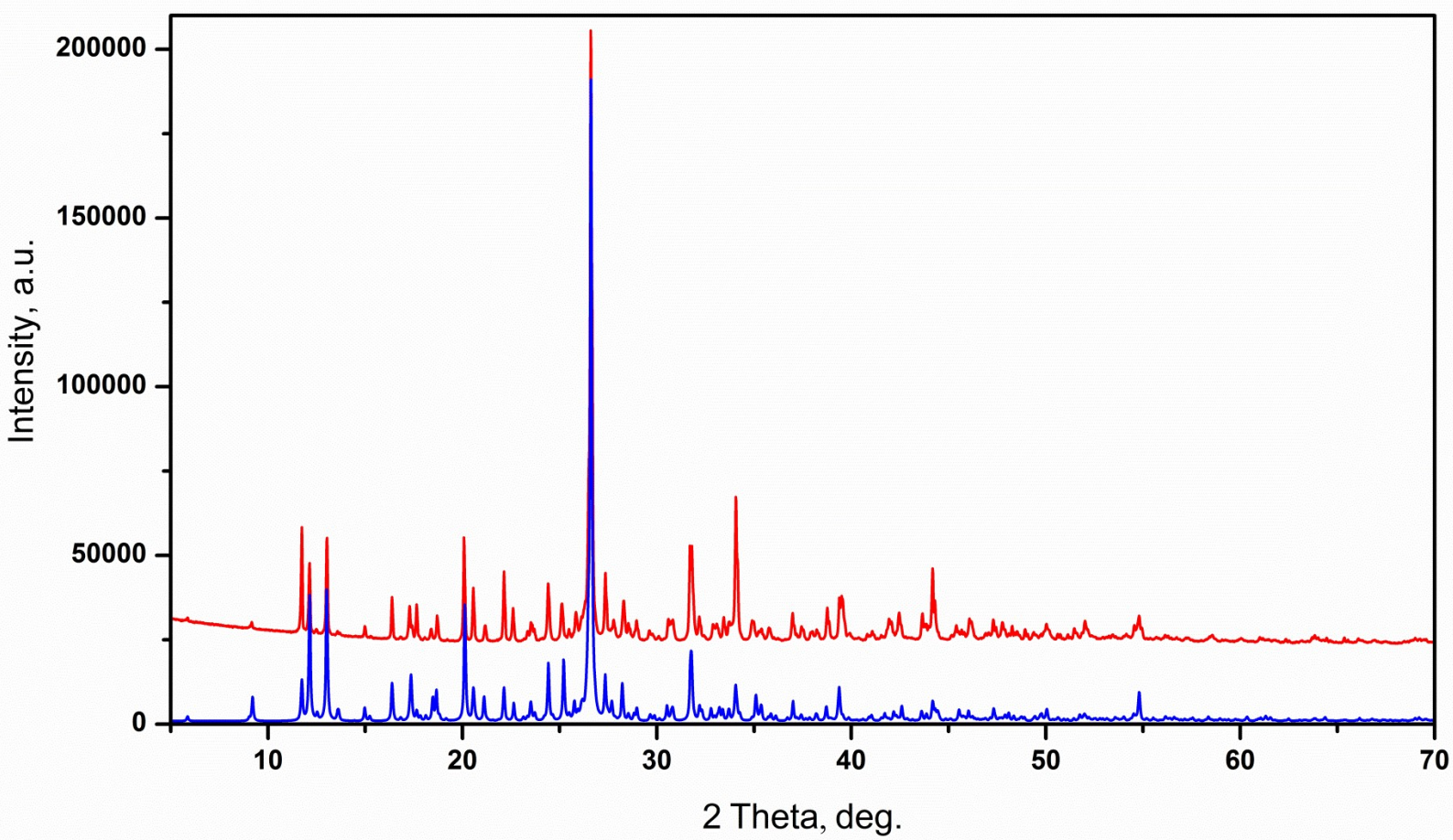


Figure S2. Powder diffractogram (XRPD) in the 2θ range from 5° to 70° of H_2thpy·⅓(H_2O) at 296K (red, experimental data; blue line, calculated data). The calculated XRPD was simulated base on single crystal structural data (cif-file) of H_2thpy·⅓(H_2O) ligand [1] from CCDC.

1. B. Ya. Antosyak, V.N. Biyushkin, L.F. Chapurina, T.I. Malinovsky. Dokl. Akad. Nauk. SSSR(Russ.)(Proc. Nat.Acad. Sci. USSR). **1992**, 327, 219. (CCDC refcode: YEBBUC).

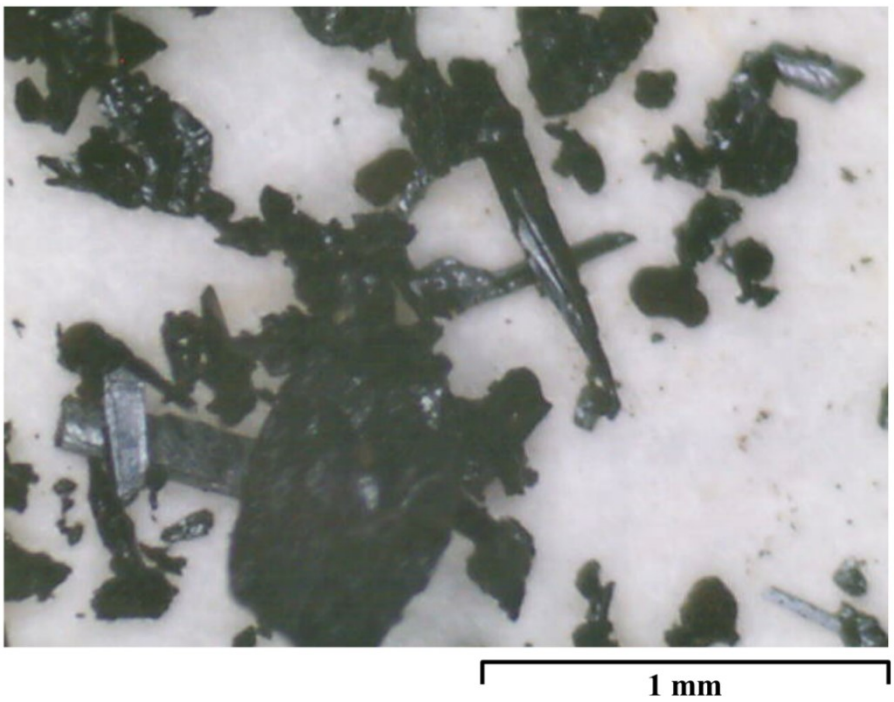


Figure S3. Photo of the crystalline sample of $Li[Fe(thpy)_2]\cdot 3H_2O$ (**1**). The scale bar represents 1mm.

Figure S4. Photo of the crystalline sample of $Li[Fe(thpy)_2]\cdot 3H_2O$ (**1**) (left) and $Li[Fe(thpy)_2]\cdot(0.6)H_2O$ (**2**) (right) after elimination of water molecules from (**1**).

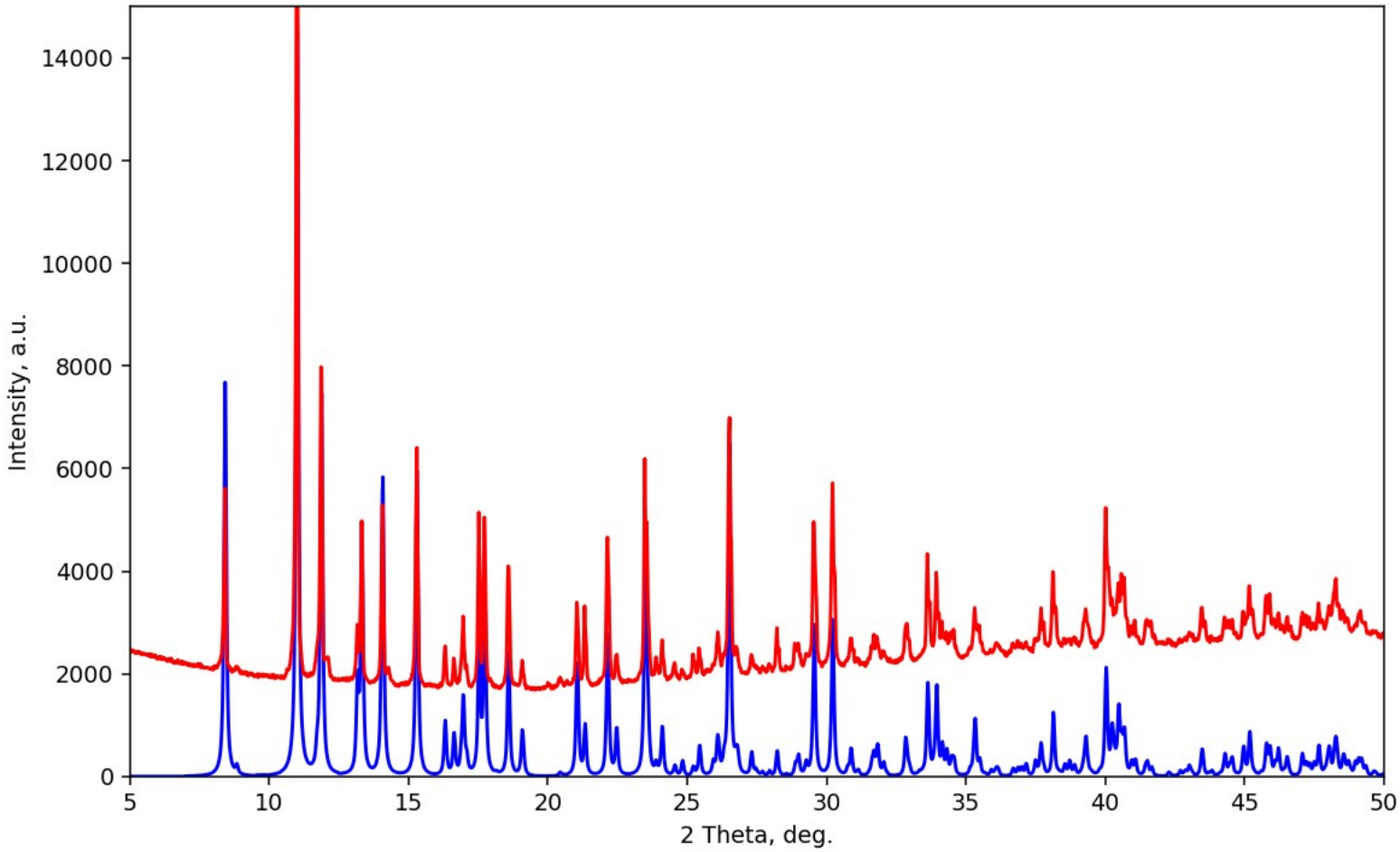


Figure S5. Powder diffractogram (XRPD) in the 2θ range from 5° to 50° of sample $Li[Fe(thpy)_2]\cdot 3H_2O$ (**1**) (red, experimental data; blue line, calculated data).

The adequacy of unit cell and space group for **1** was confirmed by the Rietveld method using Rigaku SmartLab Studio II software: triclinic, space group $P\bar{1}$ (no. 2), a=8.1408(7) Å , b=10.336(1) Å , c=11.401(1) Å ; α=96.826(6)°, β=110.275(6)°, γ= 99.372(5)°; T = 296 K.

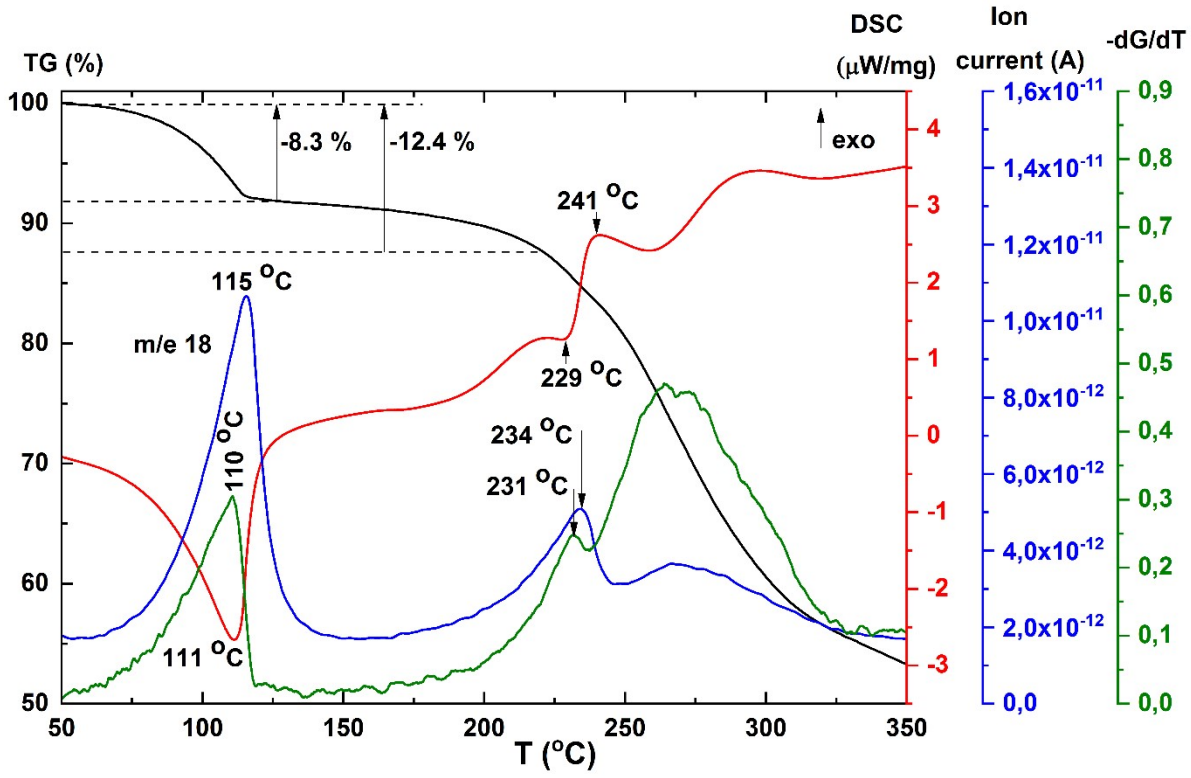


Figure S6. Thermogram of $Li[Fe(thpy)_2]\cdot 3H_2O$ (normal curve (black), DSC curve (red)) and ion current curve from $H_2O^{+\bullet}$ (m/e=18) (blue).

The thermogravimetric analysis was performed in high-purity argon atmosphere with a gas flow rate of 12 ml/min, at the heating rate of 10°C/min. The figure S3 demonstrates that temperature increasing leads to the gradual loss of water molecules of $Li[Fe(thpy)_2]\cdot 3H_2O$. The first gradual weight loss of 8.3% (calc. 8.3%, 2 molecules of H_2O) is observed in the temperature range 50-130 °C (peak at 110 °C) with *DSC* endothermic peak at 111°C and ion current (m/e 18 peak at 115°C), assigned to the loss of lattice water molecules. The second gradual weight loss of 4.1% (calc. 4.3%, 1 molecule of H_2O) step appears in the temperature range 150-240°C with *DSC* endothermic peak at 229°C, growth of ion current (m/e 18 peak at 234°C) and peak at 231°C in dG/dT curves. Changes in the mass of the sample in the region of 150–250°C, are of a complex nature, associated both with the release of water from the lattice and with the decomposition of the substance. The exothermic DSC peak at 241°C corresponds to the decomposition of the complex is also accompanied by the release of water.

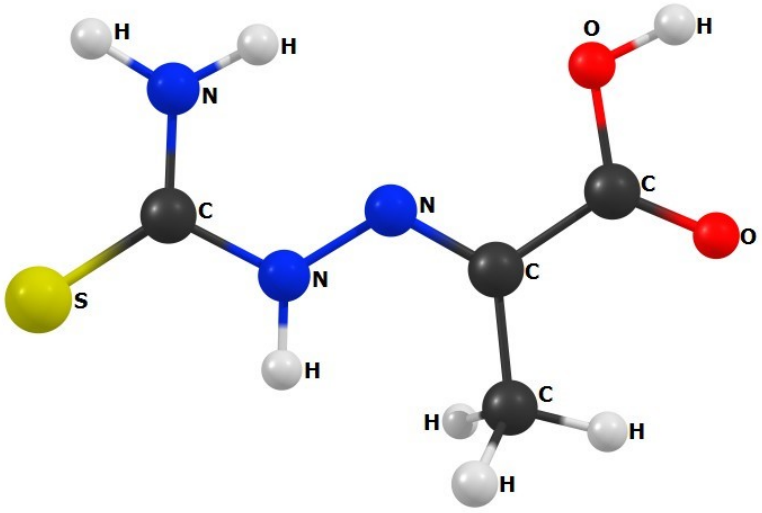


Figure S7. The optimized structure of the H_2thpy ligand (B3LYP/6-311++G(d,p)).

The atomic coordinates for starting geometry of the H_2thpy ligand were taken from the single crystal structural data. (CCDC refcode: YEBBUC). (see above).

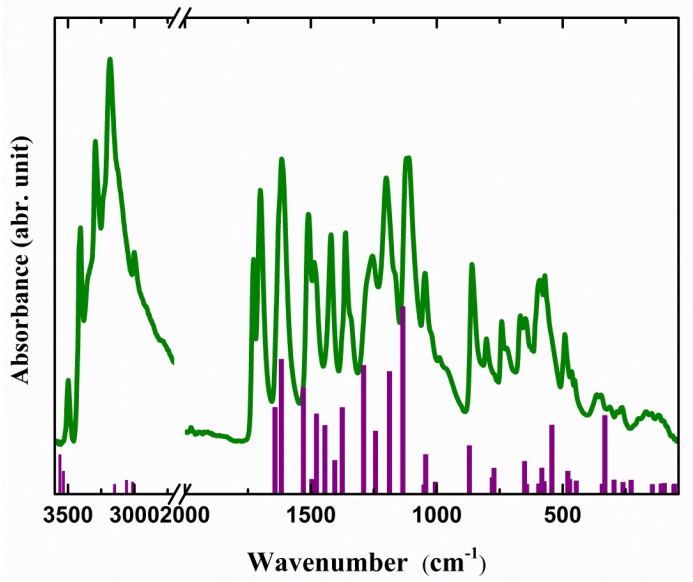


Figure S8. Experimental *ATR FT-IR* absorption spectrum for the sample of the H_2thpy·⅓(H_2O) ligand (green line) at T=298 K. DFT calculated IR vibration frequencies for the H_2-thpy ligand (298K, violet bars). B3LYP functional with 6-311++G(d,p) basis set was used.

Several characteristic bands are available in the spectrum of ligand H_2thpy·⅓(H_2O) at 3501; 3407; 1701; 1616; 1256; 860 cm^{-1}; they are attributed to ν(OH), ν(NH_2), ν(C=O), ν(C=N), ν(C=S), ν(N-N) respectively.

1. Yin, H.D., Chen, S.W., Li, L.W., Wang, D.Q. Inorg. Chem. Act. **2007**, 360, 2215-2223.

Table S1. The table of experimental IR vibrational modes for H_2thpy·⅓(H_2O) ligand and Li[Fe(thpy)$_2$]·3H_2O salt. The selected values of calculated IR vibrational modes are showed in brackets.

Assignment of most essential vibrational mode	ν, cm^{-1}	
	H_2thpy·⅓(H_2O)	Li[Fe(thpy)$_2$]·3H_2O
ν(NH_2) ν(NH) ν (OH)	3501/(***3535***) 3407 3294 3184	3634 3433 3386 3283 3175
ν(CH_3)	3001/(***3014***)	—
ν(CO)	1 728 1 701	1657
ν(C-NH_2) ν(NH_2) ν(C=N)	1616/(***1617***) 1511	1618 1585/***(1594)***
ν(NCS)	1485 1420	1490 1437
δ(OH) ν(CH_3)	1364 —	 1357/***(1358)*** 1305
ν(C=S)	1256	—
δ(NCS) C-C(=O)-O system	1 200 1168 1 115	1216 1168 1064
ν(N-N)	860/(***871***)	1020 885/***(871)***
δ(CH)	802	766
ν(NCS) ν(NH)	742 721 671 645	679/***(689)***
ν(COO-H)	590/(***582***)	—
ν(Fe-O) ν(Fe- S) ν(Fe-N)	—	599/***(599)*** 550/**(550)** 516/**(516)**

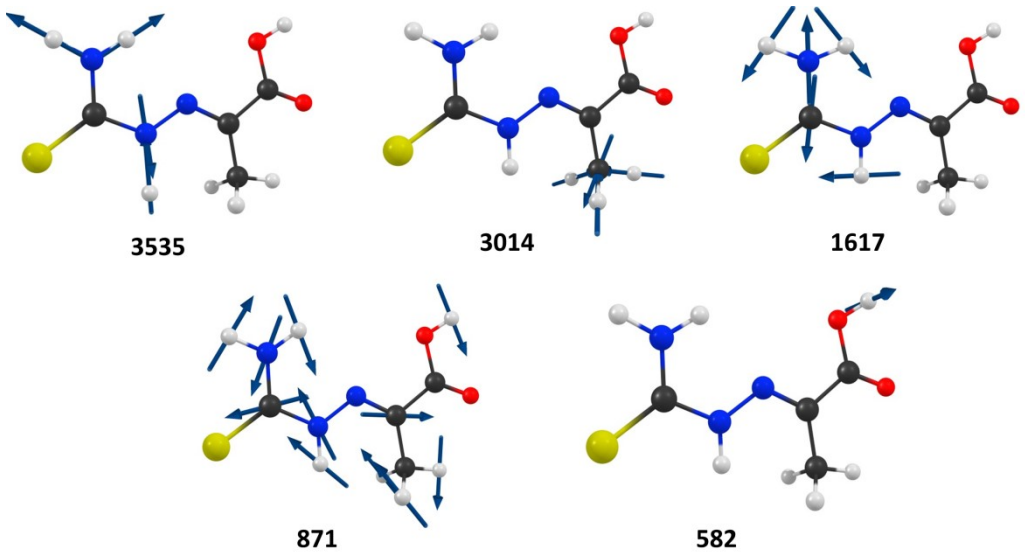


Figure S9. Selected calculated IR vibrational modes of the H_2thpy·⅓(H_2O) ligand (B3LYP/6-311++G(d,p)).

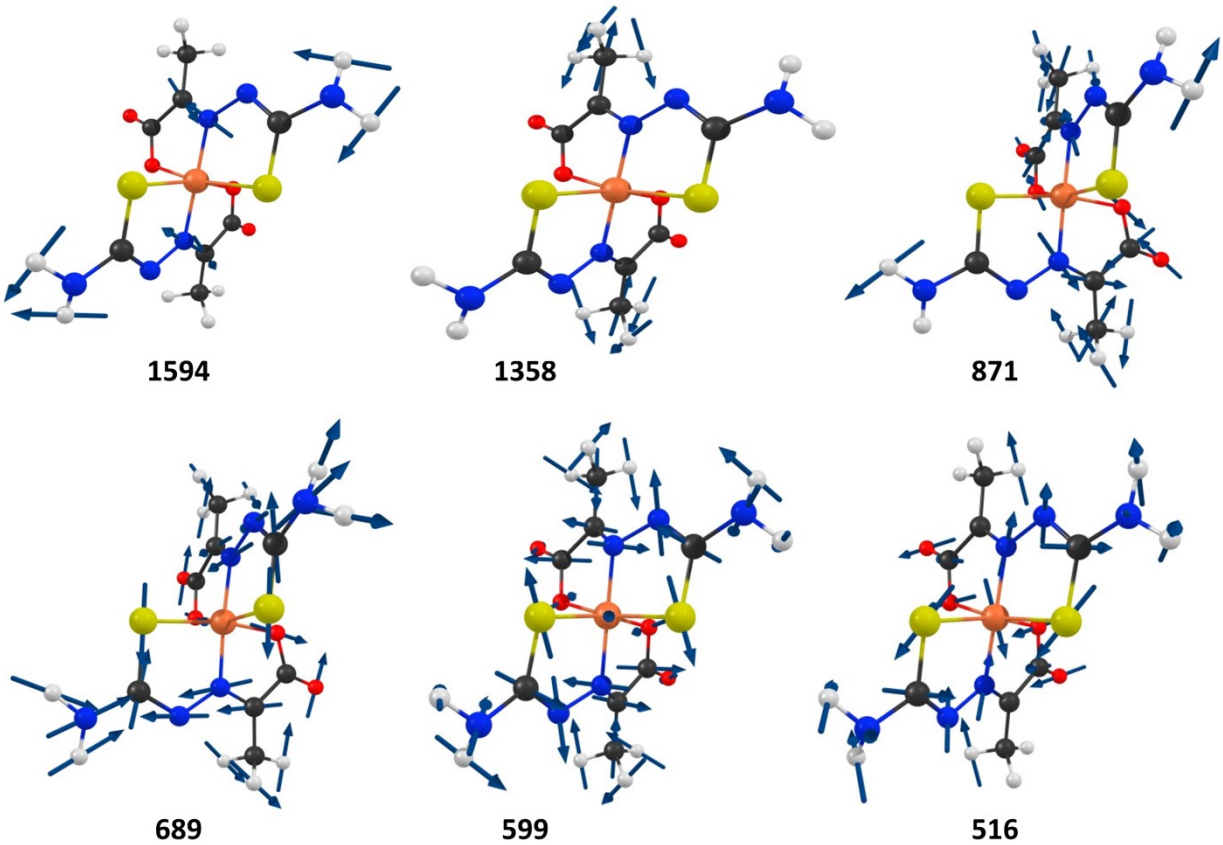


Figure S10. Selected calculated IR vibrational modes of the Li[Fe(thpy)$_2$]·3H_2O salt in LS state (OPBE/6-31G(d,p)).

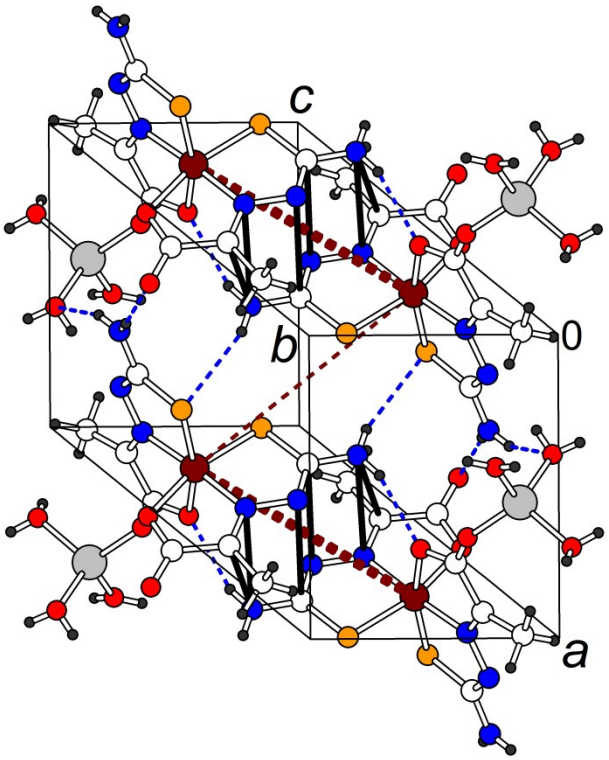


Figure S11. Two adjacent dimeric units in the structure **1**. C…N and N…N contacts are shown by black lines, N-H…O/S hydrogen bonds – by blue dashed lines. Fe…Fe distance in the dimer is 6.7861(4) Å (thick brown dashed line), the nearest Fe…Fe distance between the dimers is 7.2956(4) Å (thin brown dashed line).

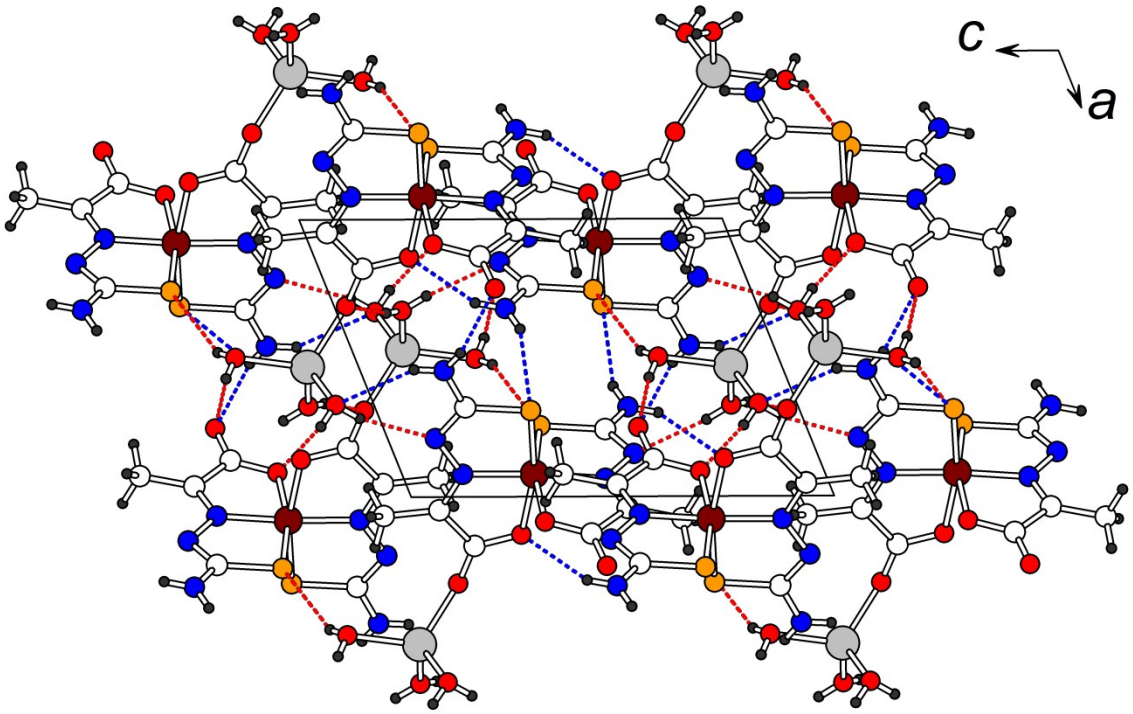


Figure S12. Projection of the structure **1** along *b*. N-H_{thpu}…O/S hydrogen bonds are shown by blue dashed lines, O-H_{water}…O/N/S hydrogen bonds are shown by red dashed lines.

Table S2. Selected bond lengths (Å) and angles (°) in **1**.

Bond	Bond length (Å)	Angle	Angle value (°)
Fe(1)-N(1)	1.9109(12)	O(1)-Fe(1)-S(1)	165.74(3)
Fe(1)-N(3)	1.9112(12)	O(2)-Fe(1)-S(2)	166.58(3)
Fe(1)-O(1)	1.9785(10)	N(1)-Fe(1)-N(3)	176.37(5)
Fe(1)-O(2)	1.9700(10)	O(1)-Fe(1)-O(2)	84.87(4)
Fe(1)-S(1)	2.2302(4)	O(1)-Fe(1)-N(1)	81.77(5)
Fe(1)-S(2)	2.2247(4)	O(1)-Fe(1)-N(3)	95.20(5)
Li(1)-O(3)	1.928(3)	O(1)-Fe(1)-S(2)	92.05(3)
Li(1)-O(5w)	1.957(3)	O(2)-Fe(1)-N(1)	95.62(5)
Li(1)-O(6w)	1.911(3)	O(2)-Fe(1)-N(3)	82.09(5)
Li(1)-O(7w)	1.984(3)	O(2)-Fe(1)-S(1)	90.40(3)
		N(1)-Fe(1)-S(1)	85.33(4)
		N(1)-Fe(1)-S(2)	96.87(4)
		N(3)-Fe(1)-S(1)	97.47(4)
		N(3)-Fe(1)-S(2)	85.20(4)
		S(1)-Fe(1)-S(2)	95.51(2)
		O(3)-Li(1)-O(5w)	115.09(15)
		O(3)-Li(1)-O(6w)	114.63(15)
		O(3)-Li(1)-O(7w)	105.36(14)
		O(5w)-Li(1)-O(6w)	100.18(14)
		O(5w)-Li(1)-O(7w)	110.02(14)
		O(6w)-Li(1)-O(7w)	111.69(15)

Table S3. Octahedral distortion parameters in **1**.*

Octahedron	Σ, °	Θ, °	<Fe-O/N/S>, Å	ζ, Å	Δ, Å
$FeN_2O_2S_2$	63.8617	209.7701	2.0376	0.759267	0.004501

*Σ is the sum of the deviation from 90° of the 12 *cis*-angles of the $FeN_2O_2S_2$ octahedron.

Θ is the sum of the deviation from 60° of the 24 trigonal angles of the projection of the $FeN_2O_2S_2$ octahedron onto the trigonal faces.

ζ is the distance distortion parameter, which is the sum of deviation from individual M-X bond distances with respect to the mean metal-ligand bond distance.

Δ is the scatter in metal-ligand bond lengths defined as normalized mean-square error [1].

1. R. Ketkaew, Y. Tantirungrotechai, P. Harding, G. Chastanet, P. Guionneau, M. Marchivie and D. J. Harding, *OctaDist*: a tool for calculating distortion parameters in spin crossover and coordination complexes, *Dalton Trans.* **2021**, *50(3),* 1086–1096.

Table S4. Hydrogen bond geometry in **1**.

Donor--H..Acceptor			[Symmetry of A]	D-H, Å	H...A, Å	D...A, Å	D-H...A, º
N5	--H5a	..O7w	[x+1,y,z]	0.79(2)	2.51(2)	3.189(2)	144(2)
N5	--H5b	..O4	[x+1,y,z]	0.82(2)	2.21(2)	3.009(2)	164(2)
N6	--H6a	..O1	[-x,1-y,1-z]	0.83(2)	2.21(2)	2.982(2)	156(2)
N6	--H6b	..S1	[1-x,1-y,1-z]	0.82(2)	2.64(2)	3.410(1)	157(2)
C7	--H7b	..O5w	[x,y,z]	0.98	2.50	3.451(2)	163.7
C8	--H8c	..S2	[-x,1-y,1-z]	0.98	3.03	3.938(2)	154.9
O5w	--H5wa	..S2	[-x,1-y,-z]	0.77(1)	3.04(2)	3.771(1)	158(2)
O5w	--H5wb	..O4	[-x-1,-y,-z]	0.79(1)	1.93(2)	2.715(2)	169(2)
O6w	--H6wa	..O3	[-x-1,1-y,-z]	0.79(1)	2.03(2)	2.805(2)	170(3)
O6w	--H6wb	..N4	[x-1,y,z-1]	0.78(1)	2.16(2)	2.936(2)	174(3)
O7w	--H7wa	..N2	[x-1,y,z]	0.76(1)	2.10(2)	2.840(2)	164(2)
O7w	--H7wb	..O2	[-x-1,-y,-z]	0.78(1)	2.05(1)	2.815(2)	169(2)

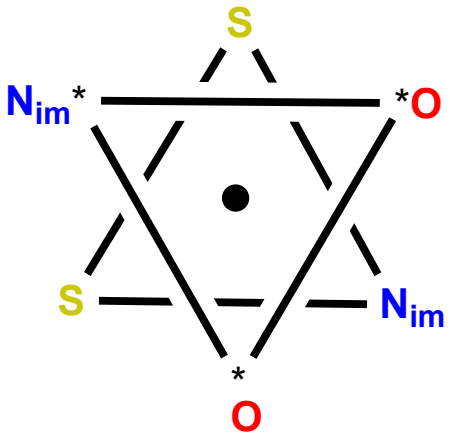


Figure S13. The pseudo C_2 axis in the coordinated octahedron of $[Fe(thpy)_2]^-$ anion in the salt **1**.

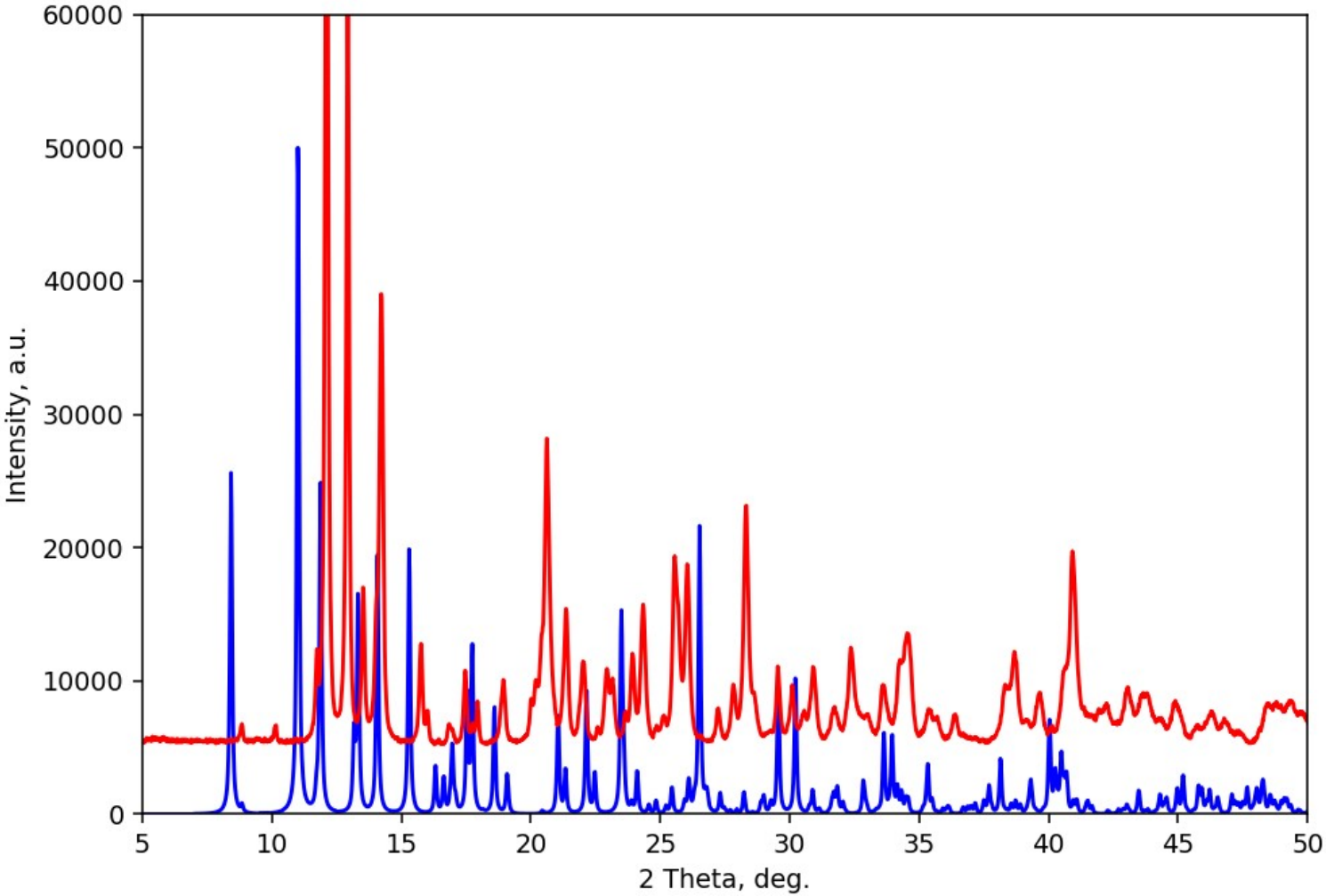


Figure S14. Comparison of powder diffractograms (XRPD) in the 2θ range from 5° to 50° for $Li[Fe(thpy)_2]\cdot 3H_2O$ (**1**) (blue line) and $Li[Fe(thpy)_2]\cdot(0.6)H_2O$ (**2**) (red line) samples at 296K.

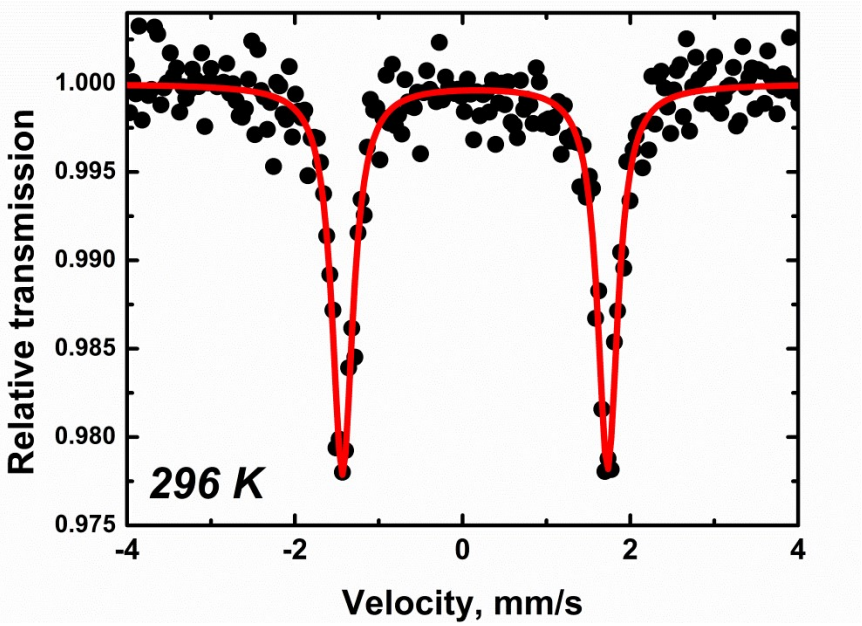


Figure S15. Mössbauer spectrum for the $Li[Fe(thpy)_2]\cdot(0.6)H_2O$ (**2**) sample at 296K. The parameters of spectrum are ΔE_Q=3.162(6) mm/s, δ=0.149(3) mm/s, Γ_-=0.30(1) mm/s, Γ_+=0.29(1) mm/s.

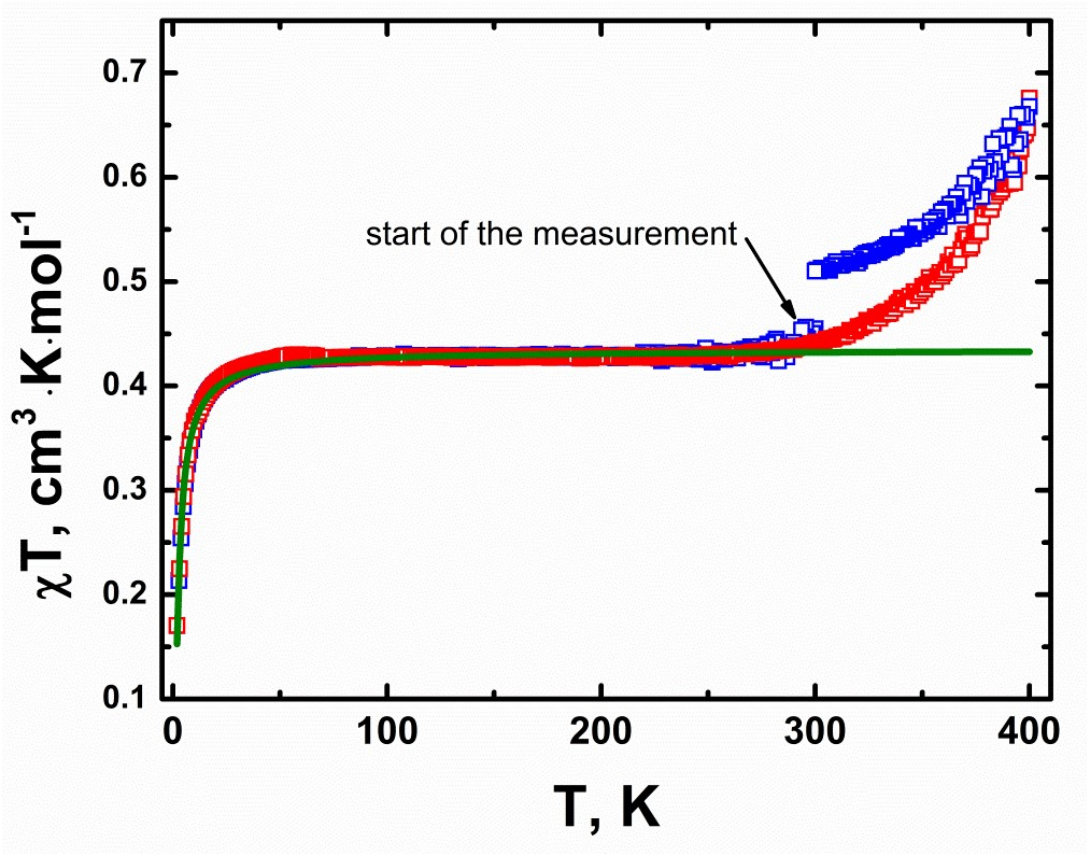


Figure S16. Temperature dependences of χT product for Li[Fe(thpy)$_2$]·(0.6)H$_2$O (**2**) sample at heating (red squares) and cooling (blue squares) modes. Green solid line is the fit of experimental data at cooling mode (2–250 K) according to equation 1 (see the text of the article). Parameters of the best fit of experimental data: g_{LS}=2.1536(7); J_1/k_B= –1.90(4)K; z·J_2/k_B= –1.6(1)K; R^2=0.988.

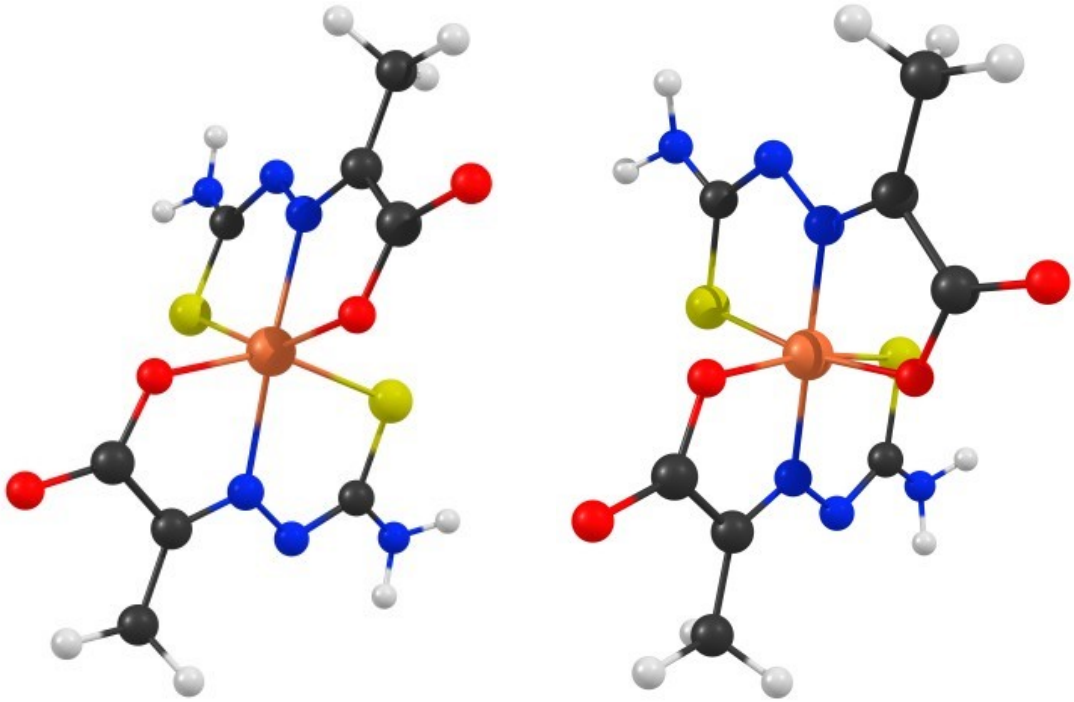


Figure S17. The optimized molecular geometries of $[Fe(thpy)_2]^-$ anion in HS (left) and LS (right) state (OPBE/6-31G(d,p)).

Table S5. Electronic energy (E_{el}), zero-point vibration energy (E_{ZPV}), total energy (E_0) and total energy difference between the HS and LS states (ΔE_0(HS-LS)) for the $[Fe(thpy)_2]^-$ anion and [Fe(Hthpy)(thpy)] complex.

no.	Functional	Type	HF, %	Spin state	Compound							
					$[Fe(thpy)_2]^-$				[Fe(Hthpy)(thpy)]			
					E_{el}, a.u.	E_{ZPV}, a.u.	E_0, a.u.	ΔE_0(HS-LS), kJ/mol	E_{el}, a.u.	E_{ZPV}, a.u.	E_0, a.u.	ΔE_0(HS-LS), kJ/mol
1	OLYP	GGA	—	HS	-3000.9447656	0.201752	-3000.7430136	0.41	-3001.4346440	0.213373	-3001.2212710	-4.33
				LS	-3000.9473965	0.204227	-3000.7431695		-3001.4355882	0.215966	-3001.2196222	
2	OPBE			HS	-3000.6866720	0.203406	-3000.4832660	17.41	-3001.1797792	0.215079	-3000.9647002	14.74
				LS	-3000.6959258	0.206028	-3000.4898978		-3001.1881689	0.217856	-3000.9703129	
3	TPSSh	GH-mGGA	10	HS	-3000.9398302	0.205148	-3000.7346822	35.86	-3001.4917995	0.216671	-3001.2751285	27.71
				LS	-3000.9559457	0.207606	-3000.7483397		-3001.5050261	0.219342	-3001.2856841	
4	PBE0-15	GH-GGA	15	HS	-2999.3515072	0.205209	-2999.1462982	5.47	-2999.8373621	0.216735	-2999.6206271	-0.70
				LS	-2999.3561993	0.207819	-2999.1483803		-2999.8398243	0.219462	-2999.6203623	
5	B3LYP*		15	HS	-3000.0898945	0.204198	-2999.8856965	9.53	-3000.5749858	0.215618	-3000.3593678	1.80
				LS	-3000.0960677	0.206741	-2999.8893267		-3000.5784066	0.218352	-3000.3600546	
6	B3LYP		20	HS	-3000.9842143	0.205947	-3000.7782673	-12.74	-3001.4705855	0.217430	-3001.2531555	-21.08
				LS	-3000.9817536	0.20834	-3000.7734136		-3001.4651900	0.220062	-3001.2451280	
7	PBE0		25	HS	-2999.3805333	0.208564	-2999.1719693	-35.11	-2999.8676414	0.220423	-2999.6472184	-41.31
				LS	-2999.3697155	0.211119	-2999.1585965		-2999.8544165	0.222933	-2999.6314835	

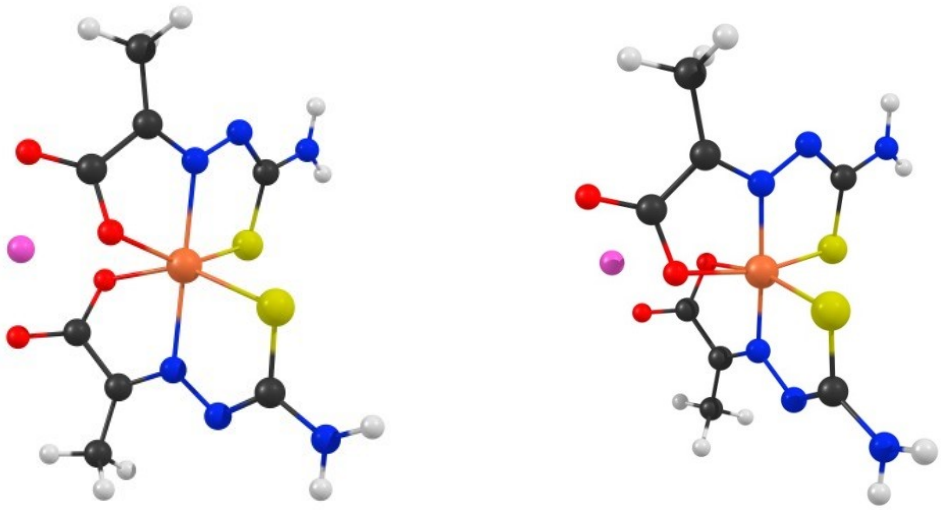


Figure S18. The optimized molecular geometries of Li[Fe(thpy)$_2$] complex in HS (left) and LS (right) state (OPBE/6-31G(d,p)).

Table S6. Electronic energy (E_{el}), zero-point vibration energy (E_{ZPV}), total energy (E_0) and total energy difference between the HS and LS states (ΔE_0(HS-LS)) for the Li[Fe(thpy)$_2$] complex.

no.	Functional	Type	HF, %	Spin state	E_{el}, a.u.	E_{ZPV}, a.u.	E_0, a.u.	ΔE_0(HS-LS), kJ/mol
1	OPBE	GGA	—	HS	-3008.1967986	0.205123	-3007.9916756	22.78
				LS	-3008.2083297	0.207977	-3008.0003527	
2	TPSSh	GH-mGGA	10	HS	-3008.5258597	0.207338	-3008.3185217	47.74
				LS	-3008.5458286	0.209125	-3008.3367036	
3	B3LYP*	GH-GGA	15	HS	-3007.6006167	0.206336	-3007.3942807	22.26
				LS	-3007.6108141	0.208055	-3007.4027591	

Table S7. The comparison of structural parameters of the X-ray crystal structure of Li[Fe(thpy)$_2$]·3H$_2$O at 150K and [Fe(thpy)$_2$]$^-$ anion/Li[Fe(thpy)$_2$] salt in the low-spin (S=1/2) optimized at the OPBE/6-31G(d,p) level.

X-ray crystal structure		Calculated parameters			
		[Fe(thpy)$_2$]$^-$	$\Delta_{calc-exp}$	Li[Fe(thpy)$_2$]	$\Delta_{calc-exp}$
Bond length, Å					
Fe-S	2.2264(5) 2.2322(6)	2.2717	0.0453(5) 0.0395(6)	2.2057	-0.0207(5) -0.0265(6)
Fe-N	1.915(2) 1.916(2)	1.873	-0.042(2) -0.043(2)	1.880	-0.035(2) -0.036(2)
Fe-O	1.972(1) 1.980(1)	1.898	-0.074(1) -0.082(1)	1.962	-0.010(1) -0.018(1)

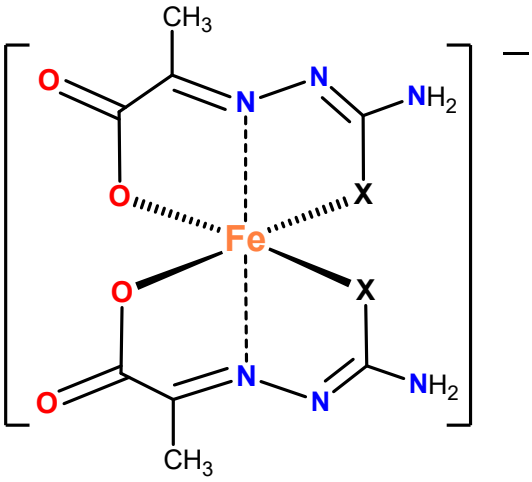


Figure S19. The scheme of $[Fe(Xpy)_2]^-$ anions with $X_2N_2O_2$ coordination sphere, where (X= O/sem; S/th; Se/se).

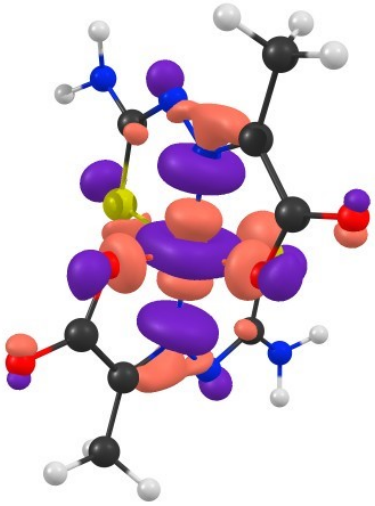
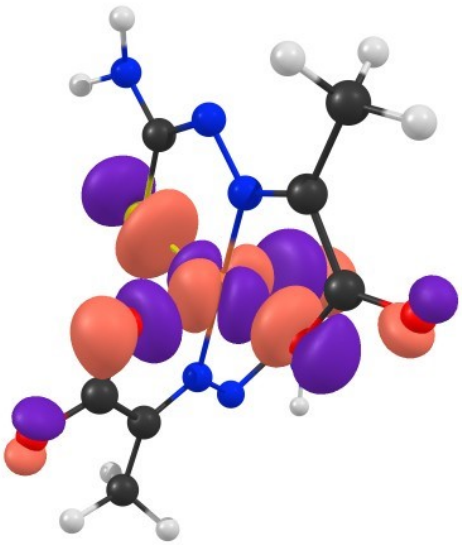
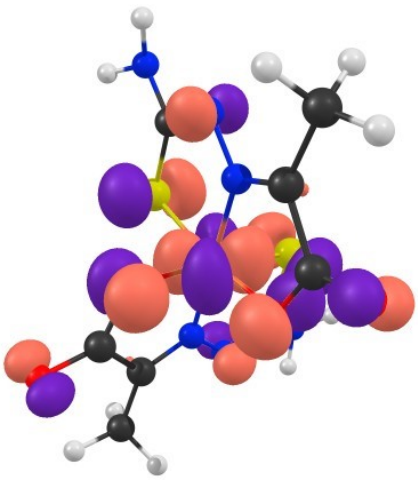
Table S8. Calculated values of electronic energy (E_{el}), zero-point vibration energy (E_{ZPV}) and total energy difference between HS and LS states (ΔE_0(HS-LS)) for the $[Fe(Xpy)_2]^-$ anions with $X_2N_2O_2$ coordination sphere, where (X= O/sem; S/th; Se/se). OPBE functional was used.

X	E_{el}, a.u.		E_{ZPV}, a.u.		E_0, a.u.		ΔE_0(HS-LS), kJ/mol
	HS	LS	HS	LS	HS	LS	
O	-2354.7626367	-2354.7542702	0.208499	0.211096	-2354.5541377	-2354.5431742	-28.78
S	-3000.6866720	-3000.6959258	0.203406	0.206028	-3000.4832660	-3000.4898978	17.41
Se	-7008.7429030	-7008.7515446	0.201874	0.204163	-7008.5410290	-7008.5473816	16.68

Table S9. The comparison of relative elongations of calculated iron(III)-ligand bonds in $[Fe(thpy)_2]^-$ anion.

$[Fe(thpy)_2]^-$ anion			
Bond	Spin state		Elongation relative to LS state, %
	HS	LS	
Fe-S	2.5056	2.2717	10.3
Fe-N	2.1874	1.8733	16.8
Fe-O	1.9590	1.8976	3.2

Table S10. Graphical representation of selected molecular orbitals (MOs) for the LS $[Fe(thpy)_2]^-$ anion at a contour level of 0.04 eÅ^{-3}. These representations were obtained from DFT calculations carried out at the OPBE/6-31G(d,p) level.

$[Fe(thpy)_2]^-$ complex in LS state		
Energy, eV	Type	MO
1.593 (LUMO+3/100th)	$\sigma^*(d_{z^2})$	
0.817 (LUMO/97th)	$\sigma^*(d_{x^2-y^2})$	
-1.629 (HOMO-2/94th)	$\pi^*(d_{xy})$	

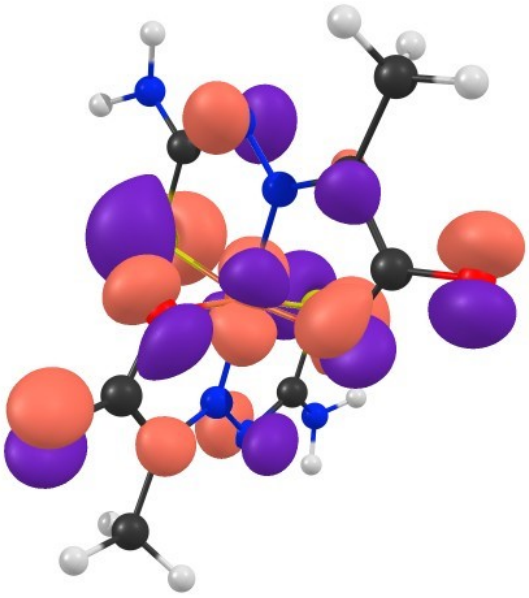
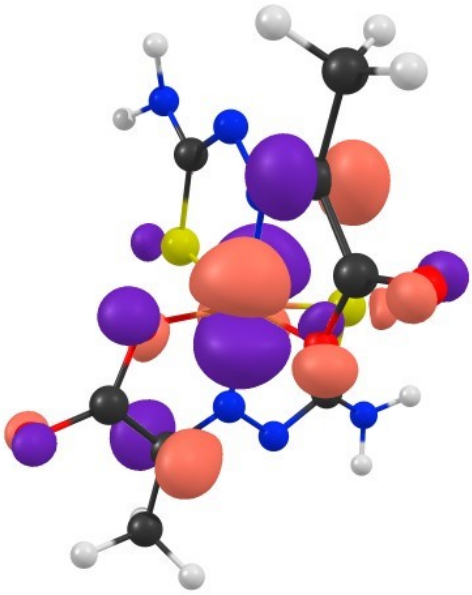
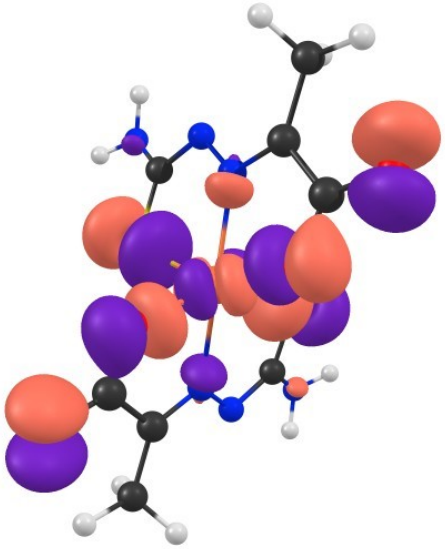
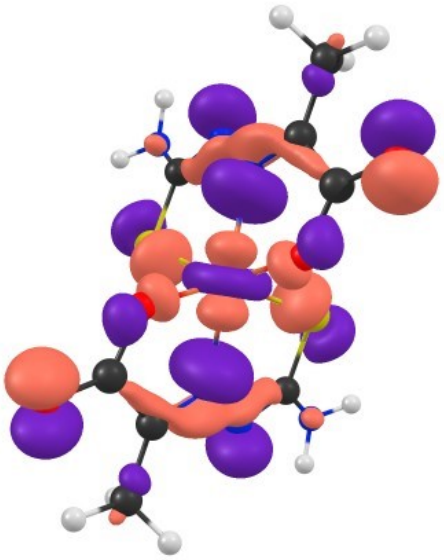
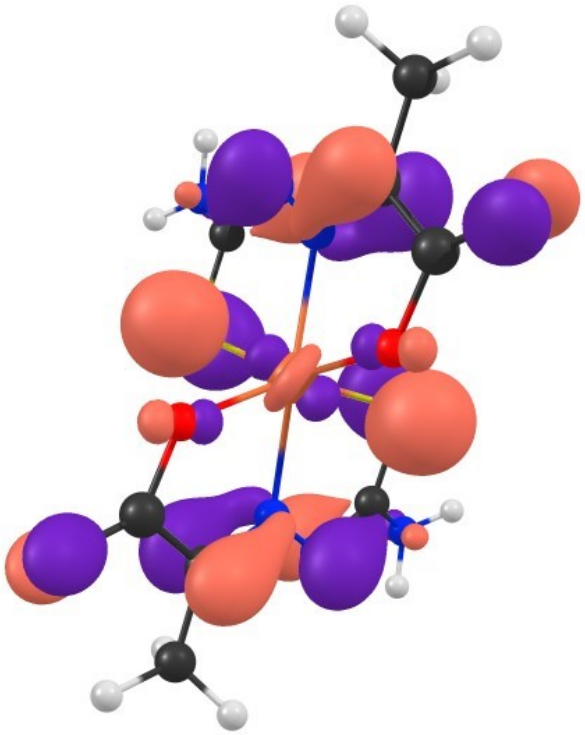
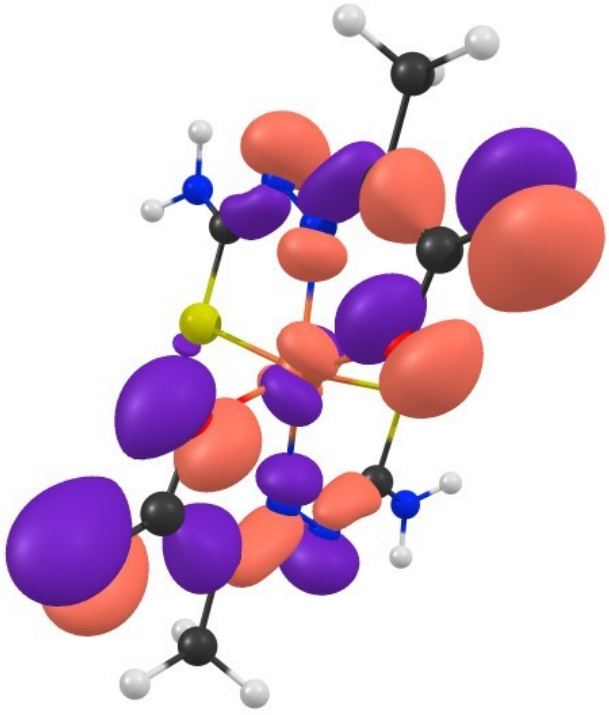
-1.778 (HOMO-3/93th)	$\pi^*(d_{xz/yz})$	α-	
-0.746 (HOMO/95th)		β-	

Table S11. Graphical representation of selected molecular orbitals (MOs) for the HS $[Fe(thpy)_2]^-$ anion at a contour level of 0.04 eÅ^{-3}. These representations were obtained from DFT calculations carried out at the OPBE/6-31G(d,p) level.

$[Fe(thpy)_2]^-$ complex in HS state		
Energy, eV	Type	MO
-1.451 (HOMO/98th)	$\sigma^*(d_{x^2-y^2})$	
-1.582 (HOMO-1/98th)	$\sigma^*(d_{z^2})$	

-1.994 (HOMO-3/95th)	π*(d_{xy})	
-2.462 (HOMO-6/92th)	π*($d_{xz/yz}$)	

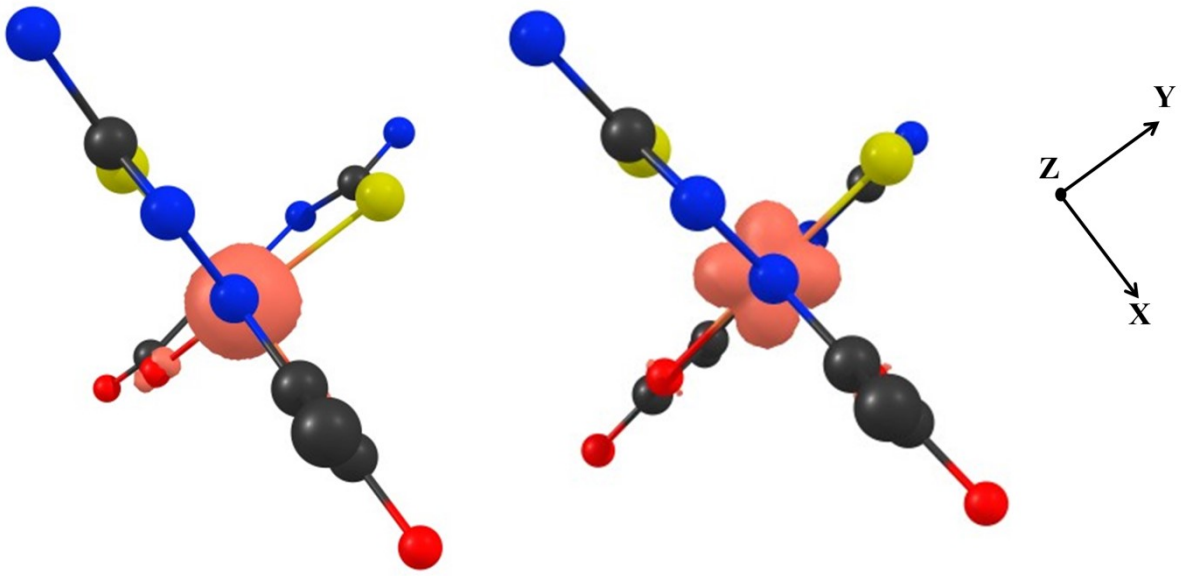


Figure S20. Calculated (OPBE/6-31G(d,p)) spin density distribution for the HS (left) and LS (right) structure of $[Fe(thpy)_2]^-$ anion. The isodensity surfaces are plotted with the cutoff values of 0.04 eÅ^{-3} for HS state and 0.015 eÅ^{-3} for LS state. Hydrogen atoms are omitted for clarity.

Table S12. Electronic energy (E_{el}), zero-point vibration (E_{ZPV}) energy, total energy ($E_0=E_{el}+E_{ZPV}$), relative energy (E_{rel}) and total spin angular momentum ($<S^2>$) of the optimized molecular geometry (top) and X-ray geometry with optimized hydrogen atoms (bottom), calculated and experimental values of exchange coupling constant J_1 and interlayer distance (l) for two $[Fe(thpy)_2]^-$ anions in HS ($S=S_A+S_B=1$) and BS ($S=S_A+S_B=0$) states. The $J_1(calc)$ values were calculated with formulas (eq. **4** and **5**, see in text). TPSSh functional was used. J_1 *(exp)*= –1.79(1)K; $l_{exp}(Fe-Fe)$= 6.7861(4)Å.

Optimized molecular geometry							
State	E_{el}, a.u.	E_{ZPV}, a.u.	E_0, a.u.	$<S^2>$	$l_{calc}(Fe-Fe)$, Å	J_1 *(calc)*, K	
						Yamaguchi	Noodelman
HS	-6002.0023124	0.416475	-6001.5858374	2.029811	7.352	**–0.92**	**–0.92**
BS	-6002.0023293	0.416489	-6001.5858403	1.029681	7.360		
X-ray geometry at 150K with optimized hydrogen atoms							
HS	-6001.9867862	—	-6001.9867862	2.052222	—	**-13.25**	**-13.26**
BS	-6001.9868282	—	-6001.9867862	1.05214			

Table S13. Optimized parameters (B3LYP/6-311++G(d,p)) of H_2thpy ligand in the singlet state. Units are in Å.

C	2.066026000000	0.332490000000	-0.000003000000
C	-1.380404000000	-0.485513000000	0.000000000000
C	-2.669679000000	0.262069000000	0.000003000000
C	-1.434455000000	-1.986392000000	0.000002000000
H	-0.937799000000	-2.398657000000	-0.885752000000
H	-2.469187000000	-2.321368000000	-0.000001000000
H	-0.937804000000	-2.398656000000	0.885759000000
N	-0.302650000000	0.222285000000	-0.000003000000
N	0.884936000000	-0.394827000000	-0.000005000000
S	3.528566000000	-0.469721000000	0.000002000000
O	-2.531429000000	1.605159000000	0.000000000000
O	-3.750536000000	-0.283515000000	0.000005000000
N	1.903093000000	1.664917000000	-0.000004000000
H	-3.428144000000	1.971384000000	0.000001000000
H	0.988042000000	-1.404698000000	0.000004000000
H	0.974406000000	2.064376000000	-0.000007000000
H	2.722572000000	2.247438000000	-0.000005000000

Table S14. Optimized parameters (OLYP/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	2.01669800	1.56281000	1.71883100	C	2.11491000	-1.46798300	-1.46713300
N	2.84064800	0.87007300	0.92974700	N	2.75643300	-0.66122700	-0.63413700
C	2.04153100	-1.76369700	-1.45773500	C	1.30120700	1.72279600	1.69042500
C	-2.01669200	1.56313200	-1.71854300	C	-2.11492900	-1.46775600	1.46734500
C	-2.88100500	-0.80450400	0.63581200	C	-2.37705600	0.97379200	-0.95746700
C	-2.04153800	-1.76395900	1.45741100	C	-1.30118800	1.72255700	-1.69067300
C	4.37453400	-0.79839600	-0.74177600	C	3.82981100	1.24770900	1.17579300
H	4.73773800	0.19167300	-1.05106400	H	4.36265700	0.34549500	1.50823500
H	4.68298900	-1.55381200	-1.46944300	H	3.92204000	2.03042600	1.93508500
H	4.83471000	-1.00741100	0.23413500	H	4.31565400	1.57775400	0.24651200
C	-4.37453800	-0.79853100	0.74161500	C	-3.82979600	1.24756300	-1.17598200
H	-4.73774100	0.19147300	1.05111400	H	-4.36265400	0.34530300	-1.50827900
H	-4.68299700	-1.55409900	1.46912100	H	-3.92201900	2.03016200	-1.93539800
H	-4.83470900	-1.00733600	-0.23434300	H	-4.31563400	1.57776100	-0.24675200
N	2.18704900	-0.01778100	0.14513300	N	1.89262800	0.07937100	0.12507500
C	2.88100200	-0.80438900	-0.63596800	C	2.37706700	0.97391900	0.95731800
N	-2.18704900	-0.01775200	-0.14514200	N	-1.89262600	0.07936300	-0.12508800
N	-2.84064600	0.87024600	-0.92959500	N	-2.75644500	-0.66111600	0.63422900
N	2.63516000	2.52787000	2.48940700	N	2.90621900	-2.29401800	-2.24565100
H	3.63307100	2.39033100	2.60162400	H	3.85864400	-1.96128300	-2.34299500
H	2.13337600	2.80516700	3.32102700	H	2.47847800	-2.59205700	-3.11200200
N	-2.63515200	2.52833600	-2.48894300	N	-2.90624300	-2.29366900	2.24598000
H	-3.63306200	2.39081300	-2.60119400	H	-3.85867000	-1.96092700	2.34327100
H	-2.13336300	2.80578500	-3.32051000	H	-2.47850700	-2.59160600	3.11236800
O	0.75297900	-1.66174200	-1.23814600	O	0.07526300	1.35944900	1.35100500
O	-0.75298500	-1.66196900	1.23784200	O	-0.07524800	1.35924200	-1.35119800
O	2.57903300	-2.55126700	-2.24508400	O	1.56182000	2.59009100	2.53321500
O	-2.57904300	-2.55166800	2.24461900	O	-1.56178700	2.58974200	-2.53358000
Fe	-0.00000100	-0.32738700	-0.00002900	Fe	0.00000200	0.00257000	0.00000100
S	0.29969800	1.39328900	1.84783700	S	0.38388600	-1.60988600	-1.61717000
S	-0.29969100	1.39364200	-1.84756900	S	-0.38390700	-1.60964800	1.61740600

Table S15. Optimized parameters (OPBE/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å. The complex was reoriented: *Z* along the N_{im}-Fe-N_{im} bond, *X* and *Y* along S-Fe-O bonds.

HS				**LS**			
C	-2.47405000	-0.10693800	2.05488400	C	-2.24995600	-0.15376500	1.86587800
N	-1.41322200	-0.00413700	2.85520800	N	-1.16550500	-0.13057200	2.62298300
C	2.09827300	0.05450200	1.96019000	C	2.26717800	-0.01065100	1.50608300
C	-0.40576900	2.63341800	-1.80426400	C	0.11985500	2.15885700	-1.97205400
C	-0.21693500	-0.61935300	-2.89102200	C	0.27654500	-1.24583000	-2.40168600
C	0.01720700	-1.91043900	-2.14429400	C	0.22363300	-2.33489100	-1.38053500
C	0.97345900	0.07904500	4.31983300	C	1.33469700	-0.17098300	3.94273800
H	0.45103400	0.95568100	4.72742100	H	0.85406100	0.66632800	4.46815900
H	2.03104900	0.10894800	4.59762800	H	2.41203800	-0.15964800	4.13800100
H	0.49226800	-0.80444100	4.76196500	H	0.89662400	-1.09431500	4.34751800
C	-0.37910700	-0.60049500	-4.37155700	C	0.45801000	-1.51729700	-3.85219800
H	-1.34998100	-0.16705000	-4.64918400	H	-0.37703100	-1.11588700	-4.44359300
H	-0.30328100	-1.62475600	-4.74798900	H	0.52040900	-2.60170900	-3.99030700
H	0.38951600	0.03082100	-4.83870900	H	1.37417800	-1.04409700	-4.23300800
N	-0.25771100	0.01283600	2.17209900	N	-0.03715300	-0.05027400	1.87272200
C	0.86740800	0.04867500	2.83441400	C	1.13043200	-0.07927500	2.47288300
N	-0.25770600	0.43933400	-2.12724400	N	0.14713500	-0.05369500	-1.86656500
N	-0.45268300	1.64109700	-2.69282600	N	0.20068300	1.03854000	-2.67072400
N	-3.68566300	-0.06353200	2.70084800	N	-3.45646200	-0.19099400	2.52755800
H	-3.63726300	-0.26084400	3.69187700	H	-3.38447600	-0.53005400	3.47797100
H	-4.46179900	-0.46902100	2.20100500	H	-4.21835400	-0.58506000	1.99552600
N	-0.66374800	3.87929500	-2.32233300	N	0.12117300	3.33078200	-2.69417000
H	-0.55994300	3.94307100	-3.32661000	H	0.51385900	3.23234600	-3.62128200
H	-0.31174500	4.65688300	-1.78558200	H	0.44096600	4.14109000	-2.18430900
O	1.83624200	0.00528200	0.68266000	O	1.88386400	0.04818900	0.24664000
O	0.15808100	-1.75491800	-0.85621900	O	0.07557900	-1.89343900	-0.14773800
O	3.22332500	0.09814600	2.46532900	O	3.44550300	-0.00430100	1.87386800
O	0.06565900	-2.98360900	-2.75155800	O	0.30609900	-3.52829000	-1.68509500
Fe	0.00000000	0.00000000	0.00000000	Fe	0.00295500	-0.00298900	0.00046900
S	-2.46798700	-0.26148800	0.34420600	S	-2.26314900	-0.08647500	0.13632700
S	-0.08487900	2.50114200	-0.12204000	S	-0.03982300	2.25433300	-0.25117200

Table S16. Optimized parameters (TPSSh/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	1.83003300	1.57636600	1.76358800	C	-2.11897600	-1.45537500	1.43092200
N	2.71364200	0.92418600	1.01764600	N	-2.76506500	-0.65952700	0.59551200
C	2.10884300	-1.76532200	-1.34877400	C	-1.26315200	1.72613100	-1.69240000
C	-1.83004400	1.57637500	-1.76357400	C	2.11899300	-1.45549800	-1.43077700
C	-2.87096500	-0.76114700	0.51950800	C	2.35364200	0.97667400	0.98133200
C	-2.10883100	-1.76534100	1.34876100	C	1.26313100	1.72631300	1.69222300
C	4.36055100	-0.67485800	-0.58040800	C	-3.79852900	1.25463300	-1.22674700
H	4.67144500	0.32714300	-0.89745300	H	-4.32130500	0.34909900	-1.55493800
H	4.72418900	-1.42559600	-1.28379400	H	-3.86902900	2.02914900	-1.99321000
H	4.79420000	-0.83999600	0.41249100	H	-4.28901300	1.59303600	-0.30675000
C	-4.36054600	-0.67487500	0.58041600	C	3.79851300	1.25479000	1.22662600
H	-4.67144000	0.32712300	0.89747300	H	4.32129600	0.34929500	1.55491200
H	-4.72417800	-1.42562000	1.28379700	H	3.86900500	2.02938600	1.99301100
H	-4.79419900	-0.84000400	-0.41248200	H	4.28899900	1.59310300	0.30659600
N	2.11871100	-0.00809300	0.22695800	N	-1.89280700	0.08844500	-0.14909200
C	2.87097100	-0.76113400	-0.51950800	C	-2.35365400	0.97655300	-0.98143100
N	-2.11871100	-0.00809800	-0.22695600	N	1.89280500	0.08847900	0.14908200
N	-2.71364700	0.92418700	-1.01763200	N	2.76507300	-0.65956200	-0.59544400
N	2.35822500	2.57689600	2.54502500	N	-2.90503000	-2.28438600	2.20067800
H	3.35850400	2.51508800	2.68921900	H	-3.86726900	-1.97962100	2.28091900
H	1.80367000	2.85124100	3.34251600	H	-2.47981700	-2.60247200	3.06004900
N	-2.35824000	2.57691100	-2.54499900	N	2.90505600	-2.28459600	-2.20043100
H	-3.35852100	2.51510300	-2.68918900	H	3.86729500	-1.97983800	-2.28069900
H	-1.80369100	2.85126300	-3.34249200	H	2.47985100	-2.60278200	-3.05976800
O	0.81374100	-1.71897000	-1.16804400	O	-0.04859400	1.36792100	-1.32837600
O	-0.81373000	-1.71898500	1.16802300	O	0.04857700	1.36805600	1.32823100
O	2.71248800	-2.53171800	-2.10103100	O	-1.52671800	2.58692300	-2.53394800
O	-2.71247000	-2.53174600	2.10101200	O	1.52668600	2.58719500	2.53368200
Fe	0.000001000	-0.39021100	-0.00000500	Fe	0.00000000	0.02010000	-0.00000400
S	0.12060400	1.30933200	1.83549600	S	-0.39005000	-1.58176400	1.61425700
S	-0.12061500	1.30934200	-1.83549500	S	0.39006900	-1.58192300	-1.61410300

Table S17. Optimized parameters (PBE0-15/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	1.85536000	1.56940200	1.75477200	C	-2.12157900	-1.45400800	1.43530100
N	2.72392700	0.90829400	1.00248800	N	-2.75893900	-0.65462000	0.59957200
C	2.07896800	-1.76274600	-1.36950900	C	-1.24536800	1.71026100	-1.69596500
C	-1.85537100	1.56940900	-1.75475900	C	2.12159500	-1.45413900	-1.43514800
C	-2.85801400	-0.76907400	0.53907100	C	2.34184800	0.96855000	0.98021100
C	-2.07895600	-1.76276500	1.36949600	C	1.24534900	1.71044900	1.69578600
C	4.34292400	-0.70174800	-0.61130200	C	-3.77904600	1.26254500	-1.22163000
H	4.66641300	0.30033200	-0.92508800	H	-4.31756900	0.36062800	-1.54322900
H	4.69219200	-1.45556400	-1.32296900	H	-3.84209200	2.03658700	-1.99324600
H	4.78479700	-0.87561800	0.37948500	H	-4.26485300	1.61160300	-0.29982500
C	-4.34291800	-0.70176500	0.61131000	C	3.77903200	1.26270100	1.22150800
H	-4.66640800	0.30031100	0.92510700	H	4.31756000	0.36082200	1.54320400
H	-4.69218100	-1.45558800	1.32297100	H	3.84207000	2.03682400	1.99304400
H	-4.78479600	-0.87562700	-0.37947700	H	4.26484100	1.61166700	0.29966900
N	2.12269700	-0.01078200	0.21520600	N	-1.89079100	0.07884400	-0.14806800
C	2.85802000	-0.76906100	-0.53907200	C	-2.34185900	0.96842800	-0.98030900
N	-2.12269600	-0.01078700	-0.21520400	N	1.89079000	0.07887600	0.14806100
N	-2.72393300	0.90829500	-1.00247500	N	2.75894500	-0.65466000	-0.59949900
N	2.39703400	2.55470400	2.53829200	N	-2.90858200	-2.26598200	2.21396900
H	3.39889600	2.48954100	2.66997400	H	-3.86989900	-1.95752400	2.29221300
H	1.84504100	2.84683700	3.33131800	H	-2.48053000	-2.59528400	3.06781100
N	-2.39704900	2.55471700	-2.53826700	N	2.90860600	-2.26618900	-2.21372800
H	-3.39891200	2.48955500	-2.66994400	H	3.86992200	-1.95773100	-2.29200200
H	-1.84506100	2.84685700	-3.33129400	H	2.48056000	-2.59558400	-3.06753700
O	0.79005100	-1.70467000	-1.18246400	O	-0.03664800	1.34569000	-1.33749300
O	-0.79004000	-1.70468500	1.18244400	O	0.03663400	1.34583100	1.33734800
O	2.67263700	-2.52801800	-2.12661300	O	-1.50978400	2.56945700	-2.53501700
O	-2.67261900	-2.52804500	2.12659600	O	1.50975500	2.56973500	2.53474900
Fe	0.00000100	-0.37011100	-0.00000500	Fe	0.00000000	0.00151400	-0.00000200
S	0.14494700	1.32419000	1.83186400	S	-0.39544300	-1.59859400	1.60316200
S	-0.14495700	1.32419800	-1.83186400	S	0.39546000	-1.59875700	-1.60299800

Table S18. Optimized parameters (B3LYP*/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	1.52088200	0.87722100	2.14896400	C	1.58525300	0.86916100	2.23913000
N	1.03745600	1.48377100	1.07401100	N	0.97348500	1.38750700	1.18944900
C	-2.25740400	2.95558500	0.58399400	C	-2.27452100	3.03111700	1.15742600
C	-1.04052500	3.90498700	5.55004400	C	-0.93759700	3.97231900	5.52466200
C	-2.76802800	0.93723900	5.54313300	C	-2.59953100	0.97877100	5.22049700
C	-3.04762600	-0.06950300	4.44590600	C	-2.60762300	-0.01108800	4.08054200
C	-0.25785000	2.71257800	-1.08960600	C	-0.67005500	2.49719300	-0.84755400
H	0.65609500	3.31721100	-1.02248800	H	0.27881600	3.01600900	-1.03607300
H	-0.99704700	3.21208000	-1.72023300	H	-1.48730300	3.00735700	-1.36443500
H	0.03617800	1.75302600	-1.53476400	H	-0.55806600	1.47830200	-1.24147000
C	-3.30843200	0.74334700	6.92168100	C	-3.43342300	0.77930300	6.44119200
H	-2.49078200	0.70622300	7.65342600	H	-2.81273500	0.77750000	7.34662500
H	-3.88174600	-0.18632300	6.94677600	H	-3.96044000	-0.17366400	6.34406000
H	-3.94456200	1.59077400	7.20902300	H	-4.15819800	1.59634000	6.55521500
N	-0.23181800	1.93426400	1.25838300	N	-0.21810700	1.96648400	1.53085000
C	-0.84679400	2.50279500	0.26655200	C	-0.98459600	2.46880600	0.61036200
N	-2.04051000	1.94577100	5.17066600	N	-1.81496300	1.99200000	5.00847700
N	-1.73953200	2.91089800	6.07947700	N	-1.72354900	2.99358300	5.93591100
N	2.82225000	0.44651900	2.03971500	N	2.81361600	0.29419500	1.99966100
H	3.16904500	0.38143100	1.08979400	H	2.97695500	0.05559700	1.02844800
H	3.10493100	-0.28175900	2.68001500	H	3.10986500	-0.39608200	2.67616000
N	-0.66069200	4.88668500	6.43491300	N	-0.75441500	5.01223100	6.40887700
H	-1.17832700	4.89577200	7.30601800	H	-1.46267900	5.07133500	7.13118700
H	-0.42924300	5.78346900	6.03181100	H	-0.47687500	5.89151100	5.99446700
O	-2.63179000	2.68538500	1.80655300	O	-2.40601300	2.89248900	2.45859700
O	-2.52012900	0.25090200	3.29399100	O	-1.84269800	0.33621300	3.06869800
O	-2.93306000	3.51593700	-0.27806500	O	-3.09569100	3.56442500	0.41183600
O	-3.71974200	-1.07159700	4.68616300	O	-3.28372500	-1.03759700	4.14223100
Fe	-1.41421500	1.84890100	3.08624300	Fe	-0.94751800	2.00197900	3.30118800
S	0.69760700	0.59212000	3.65332400	S	1.00701200	0.88437900	3.89013000
S	-0.55459000	4.07954400	3.89005400	S	-0.08467800	4.04757400	3.99912600

Table S19. Optimized parameters (B3LYP/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	-2.09587900	1.50789900	-1.67073300	C	-2.15061200	-1.44525000	-1.45724500
N	-2.85374900	0.81511000	-0.83795800	N	-2.78353800	-0.60909600	-0.65755200
C	-1.86492900	-1.88669300	1.39523700	C	-1.26353300	1.69998700	1.71237500
C	1.84265100	1.60959100	1.76088100	C	2.15060400	1.44455200	-1.45794800
C	2.91011800	-0.67609700	-0.56081600	C	2.36288800	-0.97723300	0.96604800
C	2.16218200	-1.64356100	-1.45775000	C	1.26354300	-1.69916700	1.71318700
C	-4.24971800	-0.95001800	0.84390100	C	-3.80457500	1.22046800	1.26290000
H	-4.59729100	0.00883600	1.24561700	H	-4.34355200	1.53041900	0.36077300
H	-4.50082400	-1.75678700	1.53314000	H	-3.87280600	1.99600600	2.02732900
H	-4.76207000	-1.09116100	-0.11398300	H	-4.28528000	0.30255100	1.62032900
C	4.40219000	-0.61656200	-0.56977200	C	3.80458300	-1.21985400	1.26347600
H	4.74381200	0.39312600	-0.82368800	H	4.34355800	-1.53023700	0.36149500
H	4.77906200	-1.33772900	-1.29557100	H	3.87281700	-1.99502700	2.02827600
H	4.80014800	-0.83858800	0.42684600	H	4.28528800	-0.30176600	1.62046500
N	-2.14346400	-0.11132500	-0.13961700	N	-1.91507400	0.14620200	0.07995100
C	-2.76951600	-0.92581500	0.64764000	C	-2.36288200	0.97770100	0.96558500
N	2.14863800	0.05861400	0.18554500	N	1.91507500	-0.14616400	0.08001200
N	2.72816400	0.94963400	1.03528900	N	2.78353400	0.60878300	-0.65785600
N	-2.76071200	2.44048300	-2.43057900	N	-2.94657200	-2.22339300	-2.26616400
H	-3.67469900	2.69503000	-2.08069700	H	-3.90650300	-2.29652900	-1.95704200
H	-2.19616500	3.18669100	-2.80570600	H	-2.52654100	-3.07846400	-2.59758700
N	2.36890300	2.56027600	2.60374800	N	2.94655900	2.22231300	-2.26724000
H	3.35795600	2.45747800	2.78810200	H	3.90648800	2.29559900	-1.95814900
H	1.78965700	2.82610000	3.38490700	H	2.52652700	3.07723000	-2.59905700
O	-0.59964800	-1.73878400	1.11562000	O	-0.05381700	1.34317700	1.35404000
O	0.86673700	-1.58345000	-1.32577700	O	0.05382400	-1.34252600	1.35468800
O	-2.34870900	-2.70316700	2.17374100	O	-1.53700700	2.53871600	2.56680200
O	2.78527100	-2.38493800	-2.21201800	O	1.53702100	-2.53749100	2.56800800
Fe	0.02189500	-0.32928500	-0.08715000	Fe	0.00000100	-0.00000100	0.00413400
S	-0.38817000	1.31785100	-1.94255300	S	-0.41908400	-1.62730800	-1.61682600
S	0.11472500	1.41959500	1.73929500	S	0.41907200	1.62652800	-1.61760800

Table S20. Optimized parameters (PBE0/6-31G(d,p)) of $[Fe(thpy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	1.88161500	1.56043200	1.73501400	C	2.11145000	1.44459100	-1.45144000
N	2.73248200	0.89274100	0.98013900	N	2.75329500	0.61624400	-0.65615300
C	2.03956000	-1.75965100	-1.38749400	C	1.25012800	-1.68383500	1.70196400
C	-1.88162500	1.56044400	-1.73499700	C	-2.11146000	-1.44607400	-1.44995300
C	-2.83505900	-0.77765500	0.56015400	C	-2.34519700	0.96326300	0.95897400
C	-2.03954800	-1.75967300	1.38747600	C	-1.25011700	1.68557500	1.70024500
C	4.31683800	-0.72577600	-0.64251600	C	3.78004900	-1.19795000	1.25594900
H	4.64551800	0.27158700	-0.95452700	H	4.31929600	-1.50339700	0.35296200
H	4.65397000	-1.47860000	-1.35613600	H	3.84796000	-1.97450400	2.01982100
H	4.76025200	-0.90623500	0.34277700	H	4.25449000	-0.27772800	1.61451600
C	-4.31683300	-0.72579400	0.64252100	C	-3.78004000	1.19924600	1.25473400
H	-4.64551200	0.27156500	0.95454600	H	-4.31928700	1.50377200	0.35143600
H	-4.65395900	-1.47862800	1.35613400	H	-3.84794600	1.97658000	2.01781100
H	-4.76025100	-0.90624100	-0.34277200	H	-4.25448600	0.27939300	1.61424200
N	2.11756300	-0.01731800	0.19723900	N	1.89672500	-0.13521200	0.07691400
C	2.83506400	-0.77764100	-0.56015700	C	2.34520400	-0.96227700	0.95995100
N	-2.11756300	-0.01732300	-0.19723700	N	-1.89672400	0.13529100	0.07678400
N	-2.73248800	0.89274400	-0.98012400	N	-2.75329900	-0.61691200	-0.65551100
N	2.43565300	2.53259200	2.51697700	N	2.89038700	2.22684700	-2.25851200
H	3.43472100	2.46647400	2.63841500	H	3.85143400	2.30483100	-1.96218900
H	1.89054500	2.84085900	3.30379400	H	2.45905100	3.06919700	-2.60092200
N	-2.43566800	2.53261200	-2.51694500	N	-2.89040300	-2.22915500	-2.25621900
H	-3.43473600	2.46649500	-2.63837900	H	-3.85144900	-2.30683200	-1.95981300
H	-1.89056500	2.84088900	-3.30376200	H	-2.45907100	-3.07185600	-2.59776800
O	0.75974400	-1.68562500	-1.19351200	O	0.04755700	-1.33162500	1.34263900
O	-0.75973400	-1.68564200	1.19348800	O	-0.04754800	1.33299400	1.34127600
O	2.62073500	-2.52453700	-2.14473000	O	1.52702100	-2.51772200	2.55372600
O	-2.62071800	-2.52456900	2.14470600	O	-1.52700300	2.52033500	2.55115400
Fe	0.00000100	-0.35186200	-0.00000500	Fe	0.00000000	0.00000000	0.00367100
S	0.17157800	1.33883000	1.82240500	S	0.38974100	1.60617100	-1.59862200
S	-0.17158900	1.33884400	-1.82240000	S	-0.38975200	-1.60781100	-1.59697500

Table S21. Optimized parameters (OPBE/6-31G(d,p)) of $[Fe(sepy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	-1.88492300	-1.74967000	-1.39456600	C	-2.11066400	-1.45927600	-1.22342100
N	-2.74852900	-0.99720200	-0.72779100	N	-2.73398800	-0.62278400	-0.41887200
C	-2.15371200	1.32593500	1.99595400	C	-1.33002500	1.69217900	1.97885300
C	1.88492300	1.74967100	-1.39456400	C	2.11066900	1.45928000	-1.22341000
C	2.91459700	-0.50549400	0.97813500	C	2.38142700	-0.95321200	1.21252600
C	2.15371100	-1.32593700	1.99595300	C	1.33001800	-1.69218600	1.97885000
C	-4.39891200	0.58512700	0.87980700	C	-3.83352700	1.20145400	1.41224500
H	-4.69855100	0.93477700	-0.11817400	H	-4.30513200	1.55838800	0.48538300
H	-4.76659300	1.27479600	1.64509200	H	-3.94414300	1.95680700	2.19712800
H	-4.85289900	-0.40649500	1.01236800	H	-4.36037900	0.28217900	1.70369900
C	4.39891200	-0.58512800	0.87980700	C	3.83352200	-1.20146300	1.41224900
H	4.69855100	-0.93477700	-0.11817400	H	4.30512800	-1.55839500	0.48538500
H	4.76659300	-1.27479900	1.64509100	H	3.94413500	-1.95682000	2.19712800
H	4.85289900	0.40649300	1.01236900	H	4.36037600	-0.28219100	1.70370700
N	-2.16087300	-0.23688900	0.21379500	N	-1.87513500	0.10711700	0.34385900
C	-2.91459800	0.50549200	0.97813500	C	-2.38143100	0.95320600	1.21252400
N	2.16087300	0.23688900	0.21379600	N	1.87513300	-0.10711900	0.34386300
N	2.74852900	0.99720200	-0.72779000	N	2.73398900	0.62278400	-0.41886300
N	-2.41768100	-2.50457700	-2.40673800	N	-2.89374900	-2.21604000	-2.06248600
H	-3.41965900	-2.63781900	-2.35961500	H	-3.85553600	-2.30302900	-1.75946900
H	-1.86889300	-3.29707300	-2.70183700	H	-2.47057800	-3.07608100	-2.37836900
N	2.41768100	2.50458000	-2.40673500	N	2.89375600	2.21604600	-2.06247000
H	3.41966000	2.63782100	-2.35961100	H	3.85554300	2.30303400	-1.75945000
H	1.86889400	3.29707700	-2.70183300	H	2.47058700	3.07608900	-2.37835000
O	-0.86403300	1.15107800	1.95461300	O	-0.10428900	1.35060700	1.64826400
O	0.86403300	-1.15108000	1.95461200	O	0.10428300	-1.35061100	1.64826000
O	-2.76102900	2.07068700	2.77097500	O	-1.61650900	2.53885100	2.83107900
O	2.76102800	-2.07069000	2.77097300	O	1.61649900	-2.53886200	2.83107300
Fe	0.00000000	0.00000000	0.61109200	Fe	-0.00000100	0.00000000	0.30490200
Se	-0.05542900	-1.84733300	-1.10404800	Se	-0.25299400	-1.62924700	-1.33428800
Se	0.05543000	1.84733500	-1.10404600	Se	0.25299900	1.62925400	-1.33428100

Table S22. Optimized parameters (OPBE/6-31G(d,p)) of $[Fe(sempy)_2]^-$ complex in the sextet (HS) and the doublet (LS) states. Units are in Å.

HS				LS			
C	1.45057000	-1.79428200	1.56127600	C	-1.33377300	1.71768400	1.55479200
N	2.54401300	-1.25770100	0.96748700	N	-2.36250000	1.18891900	0.87234500
C	2.12455100	1.34008300	-1.53033900	C	-1.65564500	-1.42922900	-1.51733600
C	-1.45057600	1.79429700	1.56125900	C	1.33377000	-1.71766700	1.55481100
C	-2.88127000	-0.38250900	-0.64346900	C	2.53386200	0.49123400	-0.75916800
C	-2.12454600	-1.34009600	-1.53033100	C	1.65564800	1.42921700	-1.51734600
C	4.36954600	0.30631800	-0.64425700	C	-4.01180500	-0.43959500	-0.92061200
H	4.77046800	0.49229100	0.36217900	H	-4.52774500	-0.62146000	0.03312700
H	4.76350300	1.04778100	-1.34596900	H	-4.30643900	-1.20398300	-1.64747100
H	4.70933500	-0.69768300	-0.93651800	H	-4.34092100	0.54672500	-1.27891600
C	-4.36954300	-0.30632800	-0.64426000	C	4.01180700	0.43958700	-0.92060900
H	-4.77046600	-0.49229300	0.36217600	H	4.52774500	0.62146000	0.03313000
H	-4.76349800	-1.04779700	-1.34596800	H	4.30644300	1.20396800	-1.64747400
H	-4.70933400	0.69767000	-0.93653000	H	4.34092300	-0.54673700	-1.27890400
N	2.09477500	-0.33902200	0.10323200	N	-1.82845400	0.25205000	0.05759200
C	2.88127300	0.38250200	-0.64346800	C	-2.53386000	-0.49124000	-0.75916800
N	-2.09477500	0.33902200	0.10322600	N	1.82845400	-0.25204900	0.05759700
N	-2.54401600	1.25770700	0.96747300	N	2.36249800	-1.18891100	0.87235900
N	1.71128000	-2.74282200	2.52954500	N	-1.64101800	2.68484400	2.49132800
H	2.62146700	-3.17356300	2.44742300	H	-2.51732500	3.15425700	2.31192900
H	0.94414800	-3.37904000	2.68973300	H	-0.86585700	3.30282000	2.68525000
N	-1.71128900	2.74284200	2.52952100	N	1.64101200	-2.68482900	2.49134700
H	-2.62147700	3.17358100	2.44739500	H	2.51731700	-3.15424400	2.31194800
H	-0.94415900	3.37906400	2.68970600	H	0.86584900	-3.30280300	2.68526800
O	0.82107000	1.24802200	-1.41962900	O	-0.36284600	-1.31002200	-1.22962800
O	-0.82106500	-1.24803100	-1.41962100	O	0.36284800	1.31001200	-1.22963900
O	2.72294300	2.12087800	-2.27582200	O	-2.09259900	-2.24969500	-2.32775500
O	-2.72293500	-2.12089700	-2.27580900	O	2.09260400	2.24967500	-2.32777000
Fe	0.00000100	0.00000000	-0.14929200	Fe	0.00000000	0.00000100	0.05524800
O	0.23872900	-1.48021700	1.32832800	O	-0.09656800	1.37519000	1.44273500
O	-0.23873400	1.48023000	1.32831400	O	0.09656500	-1.37517600	1.44274700

Table S23. Optimized parameters (OPBE/6-31G(d,p)) of Li[Fe(thpy)$_2$] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.38209400	-1.83414800	1.05450000	C	2.05196700	1.74636200	1.22649400
N	-2.99485000	-1.00806200	0.20081700	N	2.70351200	0.95687400	0.38022800
C	-1.58403300	2.00917400	-1.07680900	C	1.31739100	-1.90359400	-1.22353200
C	2.36786600	-1.84885100	-1.05712900	C	-2.05196800	1.74636300	-1.22649300
C	2.67120800	0.99962800	0.80988100	C	-2.38325900	-0.94854900	0.86307900
C	1.60052900	2.00041000	1.07624600	C	-1.31739000	-1.90359600	1.22353000
C	-4.10771800	1.30573200	-0.99662900	C	3.83468300	-1.20426800	-1.05220400
H	-4.54253900	0.62775800	-1.74416100	H	4.29174100	-0.41796500	-1.66833900
H	-4.24612500	2.33998700	-1.32195200	H	3.97507000	-2.17281900	-1.53999300
H	-4.65489400	1.13434100	-0.06055900	H	4.36352100	-1.20216500	-0.08984200
C	4.12053000	1.28587400	0.98010700	C	-3.83468200	-1.20427000	1.05220400
H	4.55783400	0.60356000	1.72219600	H	-4.29174200	-0.41796600	1.66833700
H	4.26552500	2.31849100	1.30773900	H	-3.97506900	-2.17282000	1.53999500
H	4.66043800	1.11544000	0.03962300	H	-4.36352000	-1.20217100	0.08984100
N	-2.16860200	-0.06210200	-0.24885600	N	1.86966200	0.06446400	-0.19002300
C	-2.66079600	1.01301400	-0.81731000	C	2.38326000	-0.94854700	-0.86307900
N	2.17075100	-0.07319200	0.24418700	N	-1.86966300	0.06446300	0.19002300
N	2.99036300	-1.02209800	-0.21110400	N	-2.70351300	0.95687300	-0.38022700
N	-3.12563900	-2.86036200	1.51795500	N	2.76352700	2.70857000	1.85103000
H	-4.09715600	-2.91513500	1.25229000	H	3.76778200	2.69964700	1.75880600
H	-2.75875900	-3.47658000	2.22269200	H	2.34570400	3.23747200	2.59791700
N	3.10547600	-2.87703900	-1.52578100	N	-2.76352900	2.70856700	-1.85103200
H	4.07974300	-2.93186300	-1.27038000	H	-3.76778300	2.69965600	-1.75879700
H	2.73109800	-3.49363700	-2.22623800	H	-2.34570200	3.23748600	-2.59790500
O	-0.38656900	1.52257700	-1.22940600	O	0.09935100	-1.41810200	-1.23241900
O	0.40199300	1.51908500	1.23702200	O	-0.09935000	-1.41810300	1.23241700
O	-1.79210800	3.24207700	-0.99284000	O	1.52136900	-3.13688900	-1.34214400
O	1.81370700	3.23234200	0.99026600	O	-1.52136700	-3.13689000	1.34214400
Fe	0.00007700	-0.07070300	0.00489800	Fe	0.00000000	0.10558000	0.00000000
S	-0.75869700	-1.67133200	1.63799000	S	0.35043600	1.60158700	1.58250100
S	0.73859100	-1.68609300	-1.62346200	S	-0.35043600	1.60158800	-1.58250000
Li	0.01096300	3.28035600	0.00032200	Li	0.00000000	-3.30080300	-0.00000100

Table S24. Optimized parameters (TPSSh/6-31G(d,p)) of Li[Fe(thpy)$_2$] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-1.67953100	-2.04925000	1.40489800	C	-2.04935400	1.77974800	-1.20174500
N	-2.63166700	-1.45567300	0.68516100	N	-2.71996500	0.99431400	-0.36388100
C	-2.25817700	1.60872300	-1.09521100	C	-1.34827300	-1.92746200	1.17048500
C	2.40807400	-1.52599000	-1.24243700	C	2.04934900	1.77975300	1.20174500
C	2.50749600	1.19737200	0.82715900	C	2.41586000	-0.95724700	-0.82904500
C	1.46480100	2.24506100	1.06199600	C	1.34827800	-1.92745900	-1.17048500
C	-4.47070300	0.40502300	-0.37315000	C	-3.87157800	-1.22020700	1.01215800
H	-4.90112400	-0.33254000	-1.06064600	H	-4.27404200	-0.61081400	1.82993700
H	-4.89189300	1.38713300	-0.59309200	H	-4.01813700	-2.27483800	1.25142100
H	-4.73481800	0.09348700	0.64150200	H	-4.42185800	-0.95510200	0.10517000
C	3.91431100	1.37403600	1.29096300	C	3.87158100	-1.22020000	-1.01215500
H	4.17778700	0.58482400	2.00395100	H	4.27404600	-0.61080300	-1.82993000
H	4.01774000	2.35041700	1.76529300	H	4.01814200	-2.27482900	-1.25142200
H	4.60627100	1.28526600	0.44728500	H	4.42185900	-0.95509700	-0.10516500
N	-2.14535900	-0.40993000	-0.01224900	N	-1.90159600	0.05993700	0.18475200
C	-2.98736100	0.44925600	-0.52438500	C	-2.41585700	-0.95725200	0.82904600
N	2.08149300	0.20589500	0.09679600	N	1.90159500	0.05994100	-0.18475300
N	2.93958000	-0.76573900	-0.28755000	N	2.71996300	0.99431800	0.36388400
N	-2.06168500	-3.13299700	2.11130700	N	-2.74768500	2.76409000	-1.80277000
H	-3.02969700	-3.41832500	2.08418900	H	-3.74025400	2.83534700	-1.63593400
H	-1.40917900	-3.60595600	2.71418600	H	-2.30768800	3.36383900	-2.48073000
N	3.17970600	-2.53155500	-1.70553500	N	2.74767500	2.76411200	1.80275200
H	4.06454500	-2.71087300	-1.25320200	H	3.74026200	2.83529900	1.63599600
H	2.80309900	-3.19928500	-2.35790700	H	2.30770400	3.36377400	2.48080700
O	-1.03487600	1.36885000	-1.49987100	O	-0.13110100	-1.44606100	1.21740100
O	0.25000200	1.89956300	0.64209900	O	0.13110500	-1.44606200	-1.21740100
O	-2.69243800	2.77942300	-1.01895000	O	-1.56037400	-3.16273400	1.22447400
O	1.73782700	3.35006500	1.51711700	O	1.56038300	-3.16273100	-1.22447200
Fe	-0.02959500	0.10129300	-0.26312600	Fe	0.00000000	0.08247600	-0.00000100
S	-0.01859000	-1.53260200	1.53416100	S	-0.35228500	1.60266800	-1.61642400
S	0.84712900	-1.28516500	-2.00438600	S	0.35228100	1.60267200	1.61642100
Li	-0.73397600	3.07930600	-0.48812300	Li	0.00000200	-3.32030800	-0.00000200

Table S25. Optimized parameters (B3LYP*/6-31G(d,p)) of Li[Fe(thpy)$_2$] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-1.76889200	-2.03333700	1.39607300	C	1.66303900	1.16875500	2.30300100
N	-2.68690900	-1.41875300	0.65530900	N	1.11019200	1.70239800	1.22056800
C	-2.21154000	1.64378600	-1.12000700	C	-2.36905000	2.50268000	0.91254000
C	2.43672200	-1.54528400	-1.23323600	C	-0.76050800	3.85746900	5.49610500
C	2.52610300	1.17752500	0.84202900	C	-2.85449600	1.17976400	5.03938700
C	1.48132300	2.23120000	1.07918600	C	-3.12119500	0.49058800	3.74631300
C	-4.46590000	0.48708100	-0.44962200	C	-0.57623000	2.31607000	-0.99863600
H	-4.89818000	-0.26166200	-1.12710800	H	0.00775100	3.20862400	-1.26102900
H	-4.86409300	1.47208000	-0.70483200	H	-1.47573500	2.28577200	-1.61857500
H	-4.76637000	0.20781800	0.56650300	H	0.05556500	1.44555900	-1.20725600
C	3.93372400	1.36183300	1.29966700	C	-3.73007300	1.05369800	6.23906200
H	4.21465000	0.56146600	1.99641800	H	-3.21314000	0.51129400	7.04225300
H	4.03339400	2.33207100	1.79065100	H	-4.63871000	0.50892800	5.97081500
H	4.62479300	1.29552100	0.45047400	H	-3.98575500	2.04383400	6.63242400
N	-2.17053100	-0.38290700	-0.03570800	N	-0.18197300	2.05440000	1.44428800
C	-2.97868000	0.49504200	-0.56379300	C	-0.96557100	2.34463200	0.43988600
N	2.10120000	0.18406300	0.11730100	N	-1.87310800	2.03128100	4.90197900
N	2.95848000	-0.78497000	-0.27717300	N	-1.57065600	2.89038700	5.90900700
N	-2.18996900	-3.10303000	2.10330900	N	2.95092900	0.77914800	2.20600100
H	-3.15996800	-3.37985100	2.03976200	H	3.43658800	0.90072500	1.32863800
H	-1.55159500	-3.60976600	2.69561100	H	3.42792300	0.37653000	2.99686900
N	3.21172000	-2.54762800	-1.69947400	N	-0.38521900	4.77597200	6.41009100
H	4.10832600	-2.71156800	-1.26224400	H	-0.73185600	4.69864900	7.35575300
H	2.84562900	-3.20535700	-2.36932800	H	0.23641700	5.52801500	6.15890500
O	-0.99038200	1.38105200	-1.50558600	O	-2.51872800	2.79805200	2.17454000
O	0.26339800	1.88471900	0.67944400	O	-2.13099800	0.46252300	2.89718500
O	-2.62183700	2.82166100	-1.03416200	O	-3.34588800	2.17884400	0.19544100
O	1.76512100	3.33996000	1.51565500	O	-4.27791600	0.13592100	3.41537300
Fe	-0.02164800	0.07827400	-0.24933600	Fe	-0.99288600	2.05386200	3.19015700
S	-0.09014700	-1.55688400	1.55838200	S	0.83083800	0.88617800	3.83204600
S	0.86530700	-1.31340700	-1.99536200	S	-0.18301200	4.05904300	3.84194300
Li	-0.68059700	3.07837600	-0.46367000	Li	-3.97214400	1.10640600	1.72667900

Table S26. Optimized (TPSSh/6-31G(d,p)) parameters of $[Fe(thpy)_2]_2^{2-}$ anion pair in the HS ($S=S_A+S_B=1$)/BS ($S=S_A+S_B=0$) state. Units are in Å.

HS				BS			
C	4.47742600	-3.33908800	-3.10580200	C	4.47768400	-3.33962000	-3.10742700
N	3.85031500	-2.79584900	-4.13632200	N	3.85059500	-2.79653300	-4.13799800
C	0.50730900	-1.38352800	-4.13012600	C	0.50668500	-1.38590900	-4.13286900
C	1.74881500	-0.55990300	0.28586500	C	2.16434600	-1.70456200	-6.12990100
C	0.33693800	-3.66737800	-0.15686000	H	3.06485000	-1.09646600	-6.27405800
C	0.38548300	-4.58147700	-1.33940800	H	1.31403000	-1.24156100	-6.63507400
C	2.16347200	-1.70396600	-6.12800600	H	2.36863800	-2.68976400	-6.56553400
H	3.06302600	-1.09486500	-6.27392700	N	2.61998200	-2.32037800	-3.77008700
H	1.31217400	-1.24282400	-6.63329500	C	1.83018100	-1.82650600	-4.68039700
H	2.36876300	-2.68954700	-6.56231800	N	5.75011400	-3.81550400	-3.36588800
C	-0.45142400	-3.97765500	1.07157900	H	5.91264800	-4.00542500	-4.34764000
H	0.20825400	-4.08485000	1.94122300	H	6.05719700	-4.54545900	-2.73770200
H	-0.99551100	-4.90986300	0.90431400	O	0.37393900	-1.58748700	-2.83522200
H	-1.14324000	-3.16113500	1.30713900	O	-0.35348200	-0.88603100	-4.86026300
N	2.62071800	-2.31771000	-3.76781100	Fe	1.88928900	-2.42761300	-2.02008500
C	1.83057900	-1.82409900	-4.67805200	S	3.87877200	-3.47019100	-1.48154700
N	1.03763400	-2.57709200	-0.32536600	C	1.74396600	-0.56819200	0.28432600
N	1.05032500	-1.63250900	0.64995000	C	0.33852100	-3.67832800	-0.16147800
N	5.74866200	-3.81770400	-3.36537300	C	0.38717800	-4.58969800	-1.34604400
H	5.90923600	-4.00901500	-4.34719400	C	-0.44792100	-3.99378000	1.06688700
H	6.05467500	-4.54801700	-2.73707800	H	0.21185100	-4.09369500	1.93724800
N	1.81456100	0.46849400	1.16015600	H	-0.98371700	-4.93086900	0.90006800
H	1.09746000	0.55804700	1.88530000	H	-1.14774700	-3.18361600	1.30084500
H	2.15649700	1.34499700	0.79545900	N	1.03654600	-2.58606000	-0.32864700
O	0.37545400	-1.58476800	-2.83233600	N	1.04742700	-1.64241300	0.64775300
O	1.10320200	-4.11537900	-2.34646200	N	1.80714200	0.46117500	1.15754700
O	-0.35387300	-0.88489500	-4.85712400	H	1.09239400	0.55028700	1.88482400
O	-0.20733600	-5.66437600	-1.34560600	H	2.14735400	1.33787100	0.79180400
Fe	1.89103300	-2.42237800	-2.01679300	O	1.10118400	-4.11952300	-2.35374900
S	3.88003600	-3.46689600	-1.47929500	O	-0.20301800	-5.67402500	-1.35332900
S	2.62801500	-0.41088200	-1.23433300	S	2.62399900	-0.41682600	-1.23496400
C	-4.47742600	3.33908800	3.10580200	C	-1.74396600	0.56819200	-0.28432600
N	-3.85031500	2.79584900	4.13632200	C	-0.33852100	3.67832800	0.16147800
C	-0.50730900	1.38352800	4.13012600	C	-0.38717800	4.58969800	1.34604400
C	-1.74881500	0.55990300	-0.28586500	C	0.44792100	3.99378000	-1.06688700
C	-0.33693800	3.66737800	0.15686000	H	-0.21185100	4.09369500	-1.93724800
C	-0.38548300	4.58147700	1.33940800	H	0.98371700	4.93086900	-0.90006800
C	-2.16347200	1.70396600	6.12800600	H	1.14774700	3.18361600	-1.30084500
H	-3.06302600	1.09486500	6.27392700	N	-1.03654600	2.58606000	0.32864700
H	-1.31217400	1.24282400	6.63329500	N	-1.04742700	1.64241300	-0.64775300
H	-2.36876300	2.68954700	6.56231800	N	-1.80714200	-0.46117500	-1.15754700
C	0.45142400	3.97765500	-1.07157900	H	-1.09239400	-0.55028700	-1.88482400
H	-0.20825400	4.08485000	-1.94122300	H	-2.14735400	-1.33787100	-0.79180400
H	0.99551100	4.90986300	-0.90431400	O	-1.10118400	4.11952300	2.35374900
H	1.14324000	3.16113500	-1.30713900	O	0.20301800	5.67402500	1.35332900
N	-2.62071800	2.31771000	3.76781100	Fe	-1.88928900	2.42761300	2.02008500

C	-1.83057900	1.82409900	4.67805200	S	-2.62399900	0.41682600	1.23496400
N	-1.03763400	2.57709200	0.32536600	C	-4.47768400	3.33962000	3.10742700
N	-1.05032500	1.63250900	-0.64995000	N	-3.85059500	2.79653300	4.13799800
N	-5.74866200	3.81770400	3.36537300	C	-0.50668500	1.38590900	4.13286900
H	-5.90923600	4.00901500	4.34719400	C	-2.16434600	1.70456200	6.12990100
H	-6.05467500	4.54801700	2.73707800	H	-3.06485000	1.09646600	6.27405800
N	-1.81456100	-0.46849400	-1.16015600	H	-1.31403000	1.24156100	6.63507400
H	-1.09746000	-0.55804700	-1.88530000	H	-2.36863800	2.68976400	6.56553400
H	-2.15649700	-1.34499700	-0.79545900	N	-2.61998200	2.32037800	3.77008700
O	-0.37545400	1.58476800	2.83233600	C	-1.83018100	1.82650600	4.68039700
O	-1.10320200	4.11537900	2.34646200	N	-5.75011400	3.81550400	3.36588800
O	0.35387300	0.88489500	4.85712400	H	-5.91264800	4.00542500	4.34764000
O	0.20733600	5.66437600	1.34560600	H	-6.05719700	4.54545900	2.73770200
Fe	-1.89103300	2.42237800	2.01679300	O	-0.37393900	1.58748700	2.83522200
S	-3.88003600	3.46689600	1.47929500	O	0.35348200	0.88603100	4.86026300
S	-2.62801500	0.41088200	1.23433300	S	-3.87877200	3.47019100	1.48154700

Table S27. X-ray geometry at 150K of $[Fe(thpy)_2]_2^{2-}$ anion pair with the optimized hydrogen atoms (TPSSh/6-31G(d,p)) in the HS ($S=S_A+S_B=1$)/BS ($S=S_A+S_B=0$) state. Units are in Å.

HS				BS			
C	4.34917500	-3.17494600	-3.01025700	C	6.00013000	-0.46048400	-1.35780500
N	3.77086700	-2.60815300	-4.06030900	N	6.04971200	0.67445400	-0.67387700
C	0.45310900	-1.16046500	-4.16820800	C	3.55138400	1.90053500	1.64350400
C	1.87917600	-0.13840400	0.23829300	C	5.92731500	2.87348200	1.06601400
C	0.16296400	-3.09402600	0.01505000	H	6.11477500	3.40469400	0.12542700
C	0.03843800	-4.03464100	-1.13680300	H	5.60932500	3.57922100	1.83680800
C	2.18306100	-1.54141200	-6.11429500	H	6.86732300	2.39101300	1.35644200
H	3.07369300	-0.91184500	-6.22536400	N	4.90935000	0.85748500	0.07678000
H	1.34944900	-1.11317200	-6.67553800	C	4.84555600	1.86389100	0.89249400
H	2.43752600	-2.53161400	-6.50886700	N	7.04638500	-0.77347100	-2.13190700
C	-0.62145000	-3.25934500	1.26323600	H	7.68240400	-0.01481900	-2.33926100
H	0.04108300	-3.44293200	2.11819200	H	6.87531900	-1.43397300	-2.87495500
H	-1.29422700	-4.10962400	1.13036100	O	2.69663700	0.98494500	1.34064900
H	-1.17794900	-2.34458900	1.49929400	O	3.34213000	2.78349200	2.49408500
N	2.52501300	-2.11498200	-3.74086600	Fe	3.38730200	-0.30219000	0.00426400
C	1.77772600	-1.62967100	-4.68338500	S	4.65717900	-1.58381600	-1.30994800
N	0.97275200	-2.11701400	-0.24053900	C	0.92322200	-0.30420500	-1.63170300
N	1.14598900	-1.13869100	0.71024100	C	1.79503900	-2.32071000	0.99595100
N	5.56778500	-3.70413000	-3.17395700	C	2.98795600	-2.25216300	1.88997500
H	6.06407500	-3.41606000	-4.00681800	C	0.67150100	-3.25758200	1.24199100
H	6.12093300	-3.82851500	-2.33966000	H	0.58011700	-3.98024600	0.42164100
N	2.03112800	0.92826500	1.02614000	H	0.86989600	-3.78628500	2.17704000
H	1.38920000	1.01958800	1.82155400	H	-0.28342200	-2.72025500	1.28331000
H	2.42646300	1.76949100	0.63724600	N	1.84642900	-1.44023600	0.04848000
O	0.27576300	-1.25653200	-2.89518400	N	0.78706500	-1.34783100	-0.82351200
O	0.77123000	-3.77503400	-2.17484400	N	-0.09201600	-0.03692900	-2.45562700
O	-0.39815700	-0.69901300	-4.94881900	H	-0.99267800	-0.48462600	-2.25184200
O	-0.76558600	-4.97123800	-1.08044500	H	-0.10027100	0.84028300	-2.95117800
Fe	1.80364000	-2.10772600	-1.96721000	O	3.89729900	-1.38376500	1.57226000
S	3.62010500	-3.28452100	-1.42145800	O	3.04463900	-2.96996300	2.89416500
S	2.63030200	-0.13571200	-1.34800700	S	2.33562600	0.73734200	-1.65985400
C	-4.34917500	3.17494600	3.01025700	C	-0.92322200	0.30420500	1.63170300
N	-3.77086700	2.60815300	4.06030900	C	-1.79503900	2.32071000	-0.99595100
C	-0.45310900	1.16046500	4.16820800	C	-2.98795700	2.25216300	-1.88997600
C	-1.87917600	0.13840400	-0.23829300	C	-0.67150000	3.25758300	-1.24199000
C	-0.16296400	3.09402600	-0.01505000	H	-0.58011700	3.98024600	-0.42164100
C	-0.03843800	4.03464100	1.13680300	H	-0.86989500	3.78628500	-2.17704100
C	-2.18306100	1.54141200	6.11429500	H	0.28342300	2.72025500	-1.28331000
H	-3.07369300	0.91184500	6.22536400	N	-1.84642900	1.44023700	-0.04848000
H	-1.34944900	1.11317200	6.67553800	N	-0.78706500	1.34783100	0.82351300
H	-2.43752600	2.53161400	6.50886700	N	0.09201700	0.03692900	2.45562700
C	0.62145000	3.25934500	-1.26323600	H	0.99267800	0.48462600	2.25184200
H	-0.04108300	3.44293200	-2.11819200	H	0.10027200	-0.84028300	2.95117800
H	1.29422700	4.10962400	-1.13036100	O	-3.89729900	1.38376500	-1.57226000
H	1.17794900	2.34458900	-1.49929400	O	-3.04463900	2.96996300	-2.89416400
N	-2.52501300	2.11498200	3.74086600	Fe	-3.38730200	0.30219000	-0.00426500
C	-1.77772600	1.62967100	4.68338500	S	-2.33562600	-0.73734200	1.65985400
N	-0.97275200	2.11701400	0.24053900	C	-6.00013000	0.46048400	1.35780500
N	-1.14598900	1.13869100	-0.71024100	N	-6.04971200	-0.67445500	0.67387600
N	-5.56778500	3.70413000	3.17395700	C	-3.55138400	-1.90053600	-1.64350400

H	-6.06407500	3.41606000	4.00681800	C	-5.92731500	-2.87348200	-1.06601400
H	-6.12093300	3.82851500	2.33966000	H	-6.11477400	-3.40469400	-0.12542700
N	-2.03112800	-0.92826500	-1.02614000	H	-5.60932500	-3.57922100	-1.83680800
H	-1.38920000	-1.01958800	-1.82155400	H	-6.86732300	-2.39101200	-1.35644200
H	-2.42646300	-1.76949100	-0.63724600	N	-4.90935000	-0.85748500	-0.07678000
O	-0.27576300	1.25653200	2.89518400	C	-4.84555600	-1.86389100	-0.89249400
O	-0.77123000	3.77503400	2.17484400	N	-7.04638500	0.77347200	2.13190700
O	0.39815700	0.69901300	4.94881900	H	-7.68240400	0.01481900	2.33926100
O	0.76558600	4.97123800	1.08044500	H	-6.87531900	1.43397300	2.87495400
Fe	-1.80364000	2.10772600	1.96721000	O	-2.69663700	-0.98494600	-1.34064900
S	-3.62010500	3.28452100	1.42145800	O	-3.34213000	-2.78349200	-2.49408500
S	-2.63030200	0.13571200	1.34800700	S	-4.65717900	1.58381700	1.30994900

Table S28. Optimized parameters (OLYP/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.93099200	0.29357600	-1.61132300	C	-2.21630800	-0.19518600	-2.00780300
C	-2.35784900	-0.43056100	1.70496100	C	-2.34003900	0.09991000	1.43082300
C	-1.05415100	-0.71868400	2.41763000	C	-1.21230700	0.17406600	2.41958700
C	1.32083900	2.55915600	0.21104100	C	1.18521100	2.45878900	-0.21207000
C	2.50736400	1.58249400	0.19053300	C	2.31441900	1.44809400	-0.15527800
C	2.64076100	-1.89140500	-0.53751000	C	2.12848400	-2.09244300	0.15450400
C	-3.67300300	-0.53602700	2.40490500	C	-3.77151100	0.16648200	1.84410500
H	-4.19239700	0.43201000	2.39230100	H	-4.26864800	1.03300800	1.38719000
H	-3.51086200	-0.85421000	3.43760800	H	-3.81953300	0.25014700	2.93337200
H	-4.32941800	-1.25062200	1.89057700	H	-4.32152800	-0.72570700	1.51606100
C	3.88804300	2.06116800	0.51772300	C	3.74869700	1.86214900	-0.13955900
H	4.24734800	1.62645500	1.46310100	H	4.25217800	1.58424600	0.80002100
H	3.85220000	3.14773300	0.63289300	H	3.77533800	2.95280700	-0.22585500
H	4.60922900	1.80950500	-0.27375600	H	4.31746900	1.43118000	-0.97744300
N	-3.26417900	0.16936200	-0.32750600	N	-2.80906500	-0.10176100	-0.82595500
N	-2.19658000	-0.11065500	0.44738700	N	-1.91400900	-0.03124000	0.19555000
N	2.15442900	0.37288100	-0.11033200	N	1.84279400	0.22696100	-0.12204200
N	3.05049300	-0.64333000	-0.13844900	N	2.68652200	-0.85932200	-0.03107100
H	4.01245800	-0.47268500	0.14163700	H	3.66015800	-0.68629600	0.19778500
N	-3.94683300	0.55475700	-2.47724900	N	-3.02098700	-0.31402000	-3.10157300
H	-4.83412200	0.82999100	-2.07750000	H	-3.99853400	-0.09104000	-2.96825500
H	-3.72224100	0.87141200	-3.40747200	H	-2.62413700	-0.11142700	-4.00662800
N	3.60283900	-2.84954100	-0.51335800	N	2.99555900	-3.12195900	0.33518400
H	4.45288700	-2.73431900	0.02362200	H	3.94891400	-3.06111300	0.00264700
H	3.29922800	-3.79757500	-0.68268100	H	2.59554900	-4.04889600	0.37267100
O	0.01190100	-0.56892100	1.64283300	O	-0.00497600	0.10572800	1.85257500
O	0.16629000	1.99614200	-0.02051100	O	-0.01622300	1.91272400	-0.17116000
O	-1.02269000	-1.06229100	3.59618100	O	-1.38753500	0.27245700	3.63080200
O	1.53501800	3.74958700	0.42908100	O	1.41650100	3.66299900	-0.29085900
Fe	-0.12605700	0.06202200	-0.18025300	Fe	-0.02599600	0.01661200	-0.03181700
S	-1.32929100	0.06252100	-2.28259000	S	-0.47687700	-0.23826300	-2.25527300
S	1.08065100	-2.19433400	-1.09151400	S	0.45256100	-2.30622700	0.15954300

Table S29. Optimized parameters (OPBE/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.92378200	0.60830400	-1.47233900	C	-2.15925300	-0.35378400	-1.99177800
C	-2.29126000	-0.74288500	1.61519900	C	-2.32737600	0.23590800	1.39109200
C	-0.97922100	-1.14956700	2.23387800	C	-1.21215600	0.38613500	2.37371900
C	1.35804500	2.46025000	0.65238700	C	1.19304500	2.40730700	-0.40507000
C	2.51667600	1.48296400	0.44785900	C	2.30919500	1.40395500	-0.25841300
C	2.53459200	-1.78384300	-0.90066100	C	2.06528200	-2.07667100	0.33862400
C	-3.58802700	-0.98821200	2.29745300	C	-3.75603600	0.34635100	1.77619900
H	-4.10944700	-0.03880400	2.48069200	H	-4.24070500	1.17336200	1.23982000
H	-3.40656100	-1.49983100	3.24627100	H	-3.81445200	0.52533600	2.85385800
H	-4.25067900	-1.59259600	1.66382700	H	-4.30870000	-0.56761300	1.52100800
C	3.90174500	1.85509300	0.84979400	C	3.74075200	1.79997400	-0.27263400
H	4.24480300	1.25334200	1.70519600	H	4.23940600	1.60359300	0.68968000
H	3.89025800	2.90543900	1.15609600	H	3.77372100	2.87991400	-0.45215000
H	4.61955800	1.73096400	0.02593500	H	4.30925400	1.29815800	-1.07025500
N	-3.23236900	0.22450700	-0.23663600	N	-2.76790900	-0.16095000	-0.83293500
N	-2.15403700	-0.18680800	0.44132200	N	-1.88851100	-0.00535800	0.17878900
N	2.13150800	0.36200100	-0.06947200	N	1.82230800	0.19736900	-0.12277900
N	2.98979500	-0.64886400	-0.28763200	N	2.64546700	-0.87829000	0.06266600
H	3.94851900	-0.57330400	0.03760900	H	3.62425200	-0.70313700	0.26009800
N	-3.95236000	1.02769300	-2.24657600	N	-2.94160400	-0.55985600	-3.08085600
H	-4.83899500	1.19197400	-1.79244600	H	-3.92157100	-0.33629900	-2.98486300
H	-3.75208100	1.50687300	-3.10858600	H	-2.52841400	-0.45311300	-3.99310600
N	3.44660300	-2.76861500	-1.05486700	N	2.89686300	-3.10959200	0.60132800
H	4.31781500	-2.77983600	-0.54397800	H	3.85701800	-3.10073200	0.28966400
H	3.10703100	-3.65142900	-1.40410600	H	2.47088400	-4.01642500	0.71901500
O	0.06519800	-0.83963700	1.49012300	O	-0.00789000	0.25944900	1.82424300
O	0.19694100	1.97197100	0.33441900	O	-0.00595400	1.87269500	-0.32565400
O	-0.92588200	-1.71646300	3.31945100	O	-1.39159900	0.59026900	3.56835700
O	1.60057500	3.58470600	1.07815700	O	1.42884500	3.59739200	-0.58285800
Fe	-0.11852700	0.11320600	-0.17374900	Fe	-0.02040700	0.01162100	-0.02845500
S	-1.34385900	0.53730200	-2.19144400	S	-0.42854100	-0.41563600	-2.19639800
S	0.97137400	-1.90747500	-1.48922100	S	0.39076900	-2.23698600	0.34892600

Table S30. Optimized parameters (TPSSh/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-3.01693100	0.09073500	-1.43292100	C	-2.25999700	-0.16082000	-1.95834100
C	-2.11760000	-0.22063900	1.85524600	C	-2.28285900	0.06300300	1.47111800
C	-0.75968000	-0.43584800	2.47072600	C	-1.12342000	0.11988700	2.42224100
C	1.24678700	2.55495700	-0.17891700	C	1.13733500	2.44818300	-0.18873800
C	2.43036400	1.59715100	-0.06468000	C	2.28572800	1.45379600	-0.16070400
C	2.53520200	-1.91636500	-0.38405400	C	2.13302300	-2.07442100	0.08820400
C	-3.36168200	-0.22798000	2.67593300	C	-3.69668500	0.13311400	1.93400400
H	-3.86766200	0.74097600	2.60203100	H	-4.18965500	1.01903900	1.51900900
H	-3.10125700	-0.43555200	3.71431700	H	-3.70241300	0.18243100	3.02395100
H	-4.06162500	-0.98130700	2.29933100	H	-4.26150500	-0.74035200	1.59181500
C	3.79420800	2.10772200	0.26708700	C	3.70781200	1.90048900	-0.12496000
H	4.07432700	1.83216600	1.29244600	H	4.19431300	1.62161000	0.81925300
H	3.76623900	3.19643300	0.20102100	H	3.70472000	2.98948400	-0.20327200
H	4.55263200	1.71476800	-0.42046400	H	4.28840300	1.48156100	-0.95625600
N	-3.22506300	0.14060900	-0.12515500	N	-2.83218600	-0.09540800	-0.76844400
N	-2.07528600	-0.05672900	0.56624300	N	-1.90468200	-0.04848500	0.22973300
N	2.08501600	0.37157200	-0.25787100	N	1.84766200	0.23468000	-0.15943500
N	2.98066700	-0.64732100	-0.14167300	N	2.69816000	-0.84338700	-0.08900200
H	3.86566900	-0.47445000	0.32706300	H	3.67084800	-0.66824800	0.14414200
N	-4.10144300	0.25513100	-2.22852800	N	-3.08189200	-0.24671500	-3.03583000
H	-4.95489000	0.57658100	-1.79327700	H	-4.06040400	-0.04622100	-2.88197400
H	-3.96583800	0.41988500	-3.21306200	H	-2.69994900	-0.04975600	-3.94769200
N	3.42401100	-2.90302600	-0.16894900	N	2.99275200	-3.10277600	0.24710800
H	4.35142700	-2.74358200	0.19846700	H	3.96700500	-3.02883000	-0.00950600
H	3.11494600	-3.85489300	-0.29512700	H	2.60114300	-4.03080000	0.31349800
O	0.22636200	-0.38976000	1.58976000	O	0.06322700	0.06448900	1.81792300
O	0.10383700	1.95136400	-0.35261800	O	-0.04923500	1.88669400	-0.14517500
O	-0.62738800	-0.63843000	3.67063500	O	-1.27590100	0.19583700	3.63323500
O	1.45441100	3.75903300	-0.10438600	O	1.37596700	3.64720000	-0.24427800
Fe	-0.11977800	0.02687000	-0.26311800	Fe	-0.02971400	0.00965700	-0.04542200
S	-1.48764300	-0.25506900	-2.21938900	S	-0.52757900	-0.20184200	-2.25509700
S	0.98534100	-2.21789100	-0.98422400	S	0.45903400	-2.29312700	0.09312900

Table S31. Optimized parameters (PBE0-15/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.98227300	-0.17163100	-1.47043900	C	-2.25546100	-0.04548900	-1.96123900
C	-2.15664200	0.09357900	1.83720700	C	-2.27563600	-0.01155400	1.47080600
C	-0.80911700	-0.00322800	2.50894900	C	-1.11384200	-0.00866000	2.42490100
C	1.23184400	2.49208500	-0.58020200	C	1.14802700	2.44976100	-0.06114700
C	2.42147300	1.56967200	-0.31495100	C	2.29045000	1.44486500	-0.08374400
C	2.55842100	-1.94188600	-0.05041500	C	2.11217500	-2.08296200	-0.02441200
C	-3.41047100	0.22464700	2.62167500	C	-3.68272800	0.03368400	1.93955400
H	-3.92074700	1.16368500	2.36754600	H	-4.17824200	0.94506100	1.57839300
H	-3.16840700	0.20632300	3.68777000	H	-3.68560700	0.01906400	3.03349000
H	-4.10611200	-0.58748700	2.37245100	H	-4.25463300	-0.81723400	1.54694900
C	3.77848100	2.13433800	-0.08133500	C	3.70976000	1.87861300	-0.01824800
H	4.07619600	2.02107000	0.97247100	H	4.19278500	1.55117400	0.91533300
H	3.73621100	3.20376600	-0.31027800	H	3.71168200	2.97371400	-0.03963500
H	4.53839300	1.65309300	-0.71348300	H	4.29692600	1.50280000	-0.86893100
N	-3.21632500	0.09813000	-0.19687600	N	-2.82203200	-0.04563000	-0.76919100
N	-2.09103200	0.03055700	0.54263000	N	-1.90229900	-0.05355700	0.22612500
N	2.08765900	0.32795200	-0.30040400	N	1.84775200	0.23231300	-0.14715900
N	2.98543600	-0.64620900	-0.02549200	N	2.68272000	-0.84877600	-0.12625100
H	3.89097500	-0.39083000	0.36105200	H	3.66134000	-0.69411300	0.10004600
N	-4.04386600	-0.14483400	-2.30639500	N	-3.07564500	-0.06556300	-3.03858600
H	-4.91364100	0.22491400	-1.94756400	H	-4.05675600	0.11380300	-2.87329100
H	-3.88982100	-0.17046000	-3.30199600	H	-2.69334100	0.16318200	-3.94323600
N	3.46808600	-2.86678300	0.29881100	N	2.96124400	-3.12370700	0.07105700
H	4.40433600	-2.63693300	0.60299600	H	3.94234400	-3.04101600	-0.15686200
H	3.17236200	-3.83143100	0.33386200	H	2.56328600	-4.05169500	0.09955700
O	0.19160500	-0.10735700	1.65761400	O	0.06769700	-0.02874900	1.82164300
O	0.09448100	1.86692800	-0.64830300	O	-0.03784100	1.89710800	-0.04832100
O	-0.70700100	0.00988400	3.72603100	O	-1.27244300	-0.00166300	3.63509400
O	1.43791900	3.68991300	-0.70422300	O	1.39984100	3.64485500	-0.05352900
Fe	-0.12025200	-0.02054800	-0.24577200	Fe	-0.03041300	0.01445000	-0.04538800
S	-1.43685600	-0.64055100	-2.15034700	S	-0.52596400	-0.07052800	-2.25907500
S	1.00252900	-2.35779600	-0.54918900	S	0.43810700	-2.28872000	-0.03352500

Table S32. Optimized parameters (B3LYP*/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.97758700	-0.35619700	-1.48292100	C	-2.29028200	0.04599500	-1.95922200
C	-2.21327300	0.28349200	1.79619000	C	-2.28775900	-0.10507100	1.47874100
C	-0.87549600	0.26991600	2.50208300	C	-1.11994300	-0.14748900	2.43174800
C	1.22199700	2.43107400	-0.82640200	C	1.13570300	2.46794600	0.06318400
C	2.42462700	1.55033500	-0.46962700	C	2.29013200	1.47106900	-0.01436600
C	2.61769200	-1.92139400	0.16899100	C	2.16173900	-2.06929200	-0.13586600
C	-3.48577600	0.49457800	2.54224100	C	-3.69734800	-0.09201200	1.95811400
H	-3.99553700	1.39548000	2.17705000	H	-4.19802400	0.83569200	1.65234100
H	-3.26473600	0.59730000	3.60675500	H	-3.69728500	-0.16885900	3.04806900
H	-4.17304500	-0.34411800	2.37526400	H	-4.26786900	-0.92057900	1.52071400
C	3.78236400	2.15264200	-0.31263700	C	3.70957900	1.91781800	0.07360200
H	4.09335100	2.15354500	0.74258700	H	4.19446400	1.54825400	0.98940300
H	3.73021000	3.18957300	-0.65352500	H	3.70539700	3.01091900	0.10485700
H	4.53941500	1.61244700	-0.89740600	H	4.29967100	1.58587900	-0.79204700
N	-3.23647900	0.05583600	-0.25310800	N	-2.84780600	-0.01783500	-0.76435300
N	-2.12148600	0.07824500	0.51801300	N	-1.91961700	-0.07732900	0.23202000
N	2.10472100	0.31375400	-0.31644000	N	1.86170100	0.25846900	-0.14128800
N	3.02349800	-0.62102800	0.05253500	N	2.71398100	-0.81900800	-0.17767700
H	3.93060400	-0.31462800	0.39622600	H	3.68799200	-0.66469500	0.06886900
N	-4.02519200	-0.43103400	-2.33945800	N	-3.12152400	0.08003300	-3.03250200
H	-4.90166100	-0.02113900	-2.04441100	H	-4.10187600	0.25043800	-2.85015000
H	-3.84990400	-0.55921700	-3.32410800	H	-2.74822500	0.36291500	-3.92614000
N	3.55202200	-2.78867400	0.60359600	N	3.03594800	-3.09711000	-0.08976900
H	4.48905600	-2.51064000	0.86404200	H	4.01391200	-2.98143800	-0.32032100
H	3.27961100	-3.75128300	0.74171800	H	2.65973800	-4.03482100	-0.10982000
O	0.14447600	0.07332500	1.68433400	O	0.06311600	-0.12965000	1.82408400
O	0.08769800	1.79030600	-0.82507200	O	-0.04847300	1.90561200	0.05133500
O	-0.79436200	0.42200700	3.71195200	O	-1.27551800	-0.20619300	3.64184100
O	1.41400800	3.61224600	-1.07694400	O	1.37879000	3.66378600	0.13138900
Fe	-0.12077500	-0.04861800	-0.22491200	Fe	-0.03471500	0.01801200	-0.04551700
S	-1.40912200	-0.89561400	-2.07954000	S	-0.55397800	0.03849400	-2.27771300
S	1.05920700	-2.41955400	-0.26134300	S	0.48783200	-2.31254400	-0.15679700

Table S33. Optimized parameters (B3LYP/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.97433000	-0.38304300	-1.47983100	C	-2.30068300	0.18185200	-1.94457600
C	-2.21862200	0.30762800	1.78582600	C	-2.28788100	-0.21940600	1.46879000
C	-0.88191500	0.30412900	2.49651400	C	-1.11525800	-0.32777200	2.41466700
C	1.21324000	2.41899900	-0.85904600	C	1.12359900	2.46041200	0.23227400
C	2.42002300	1.54764400	-0.49135600	C	2.28620200	1.47553200	0.08621000
C	2.62901200	-1.90937600	0.19828000	C	2.17912500	-2.04510000	-0.28223100
C	-3.49334700	0.53157300	2.52440800	C	-3.69573400	-0.24353100	1.95344100
H	-3.99908300	1.42577200	2.14362500	H	-4.19433200	0.70467800	1.72373200
H	-3.27732200	0.65042500	3.58613900	H	-3.69351700	-0.40588100	3.03179400
H	-4.17890800	-0.30787300	2.36798200	H	-4.26653800	-1.03286000	1.45354500
C	3.77643300	2.15663200	-0.34831800	C	3.70232500	1.92560100	0.20872300
H	4.08644300	2.17927900	0.70484500	H	4.18043400	1.50432100	1.10296500
H	3.72382900	3.18421900	-0.70967600	H	3.69396800	3.01260700	0.30416400
H	4.53197700	1.60577700	-0.92109100	H	4.29706300	1.64636200	-0.66956400
N	-3.23563700	0.05039000	-0.26131000	N	-2.85502100	0.03189900	-0.75839900
N	-2.12317500	0.08345600	0.51438400	N	-1.92612100	-0.09975900	0.22958500
N	2.10558200	0.31507100	-0.31818600	N	1.87017300	0.27484200	-0.12408600
N	3.02881100	-0.61122100	0.06152200	N	2.72448800	-0.79280500	-0.23471800
H	3.92875600	-0.29621200	0.40856400	H	3.69602600	-0.65406800	0.02070700
N	-4.01787900	-0.47288500	-2.33836100	N	-3.13469100	0.29404200	-3.00916200
H	-4.89305800	-0.05728700	-2.05501200	H	-4.11238500	0.45032200	-2.81220600
H	-3.83890100	-0.61450000	-3.31837800	H	-2.76512100	0.64075700	-3.87916500
N	3.56609700	-2.76451700	0.64499700	N	3.06020300	-3.06519100	-0.30768700
H	4.50625600	-2.48263700	0.88040700	H	4.03870700	-2.92611800	-0.51207500
H	3.30206500	-3.72627000	0.79017500	H	2.69429600	-4.00128200	-0.38991600
O	0.13829200	0.09343300	1.68706800	O	0.06345100	-0.26239100	1.80973800
O	0.08303900	1.77598800	-0.84272700	O	-0.05448800	1.89672800	0.18429900
O	-0.80685800	0.47538100	3.70147300	O	-1.27248300	-0.47466400	3.61444700
O	1.40175400	3.59335300	-1.12977200	O	1.36662900	3.64622700	0.38047300
Fe	-0.12297500	-0.05351300	-0.22044600	Fe	-0.03825300	0.02164200	-0.04306600
S	-1.40558100	-0.93527200	-2.06365800	S	-0.56735400	0.19575500	-2.27234900
S	1.07345300	-2.42233900	-0.22099900	S	0.50971100	-2.30171900	-0.32505300

Table S34. Optimized parameters (PBE0/6-31G(d,p)) of [Fe(Hthpy)(thpy)] complex in the sextet (HS) and the doublet (LS) states. Units are in in Å.

HS				LS			
C	-2.97925700	-0.14807400	-1.45778400	C	-2.26918100	0.22237900	-1.92973800
C	-2.13821000	0.06374500	1.83627200	C	-2.26177400	-0.22791400	1.45974700
C	-0.78866900	-0.04443500	2.50042000	C	-1.09002200	-0.35384200	2.39551400
C	1.21971200	2.49325800	-0.54408100	C	1.12595900	2.43291800	0.26412700
C	2.40952300	1.57007800	-0.29562000	C	2.27867100	1.44835200	0.10516900
C	2.55061400	-1.93149200	-0.08228600	C	2.12531200	-2.04378500	-0.31358000
C	-3.38640500	0.18495700	2.62540400	C	-3.66120100	-0.25163000	1.94405600
H	-3.89159700	1.12746800	2.38832300	H	-4.15281600	0.70362600	1.73060300
H	-3.14288600	0.14776400	3.68745800	H	-3.65548900	-0.43186000	3.01984000
H	-4.08234500	-0.61856000	2.36358600	H	-4.23694300	-1.02838500	1.43100800
C	3.76360000	2.13149900	-0.05670900	C	3.69019600	1.88382300	0.23556300
H	4.05460100	2.01371600	0.99515600	H	4.16195400	1.44925500	1.12622900
H	3.72513200	3.19884400	-0.28060800	H	3.68429400	2.97015200	0.34588400
H	4.52171000	1.65158900	-0.68637400	H	4.28509800	1.61528300	-0.64550700
N	-3.20459500	0.10179000	-0.18545800	N	-2.82639400	0.05351300	-0.75102200
N	-2.07844200	0.02109400	0.54742300	N	-1.90446000	-0.09324100	0.22527300
N	2.07901600	0.33371500	-0.29842600	N	1.85522800	0.25802700	-0.12095700
N	2.97539200	-0.64153500	-0.03907100	N	2.68829100	-0.80802900	-0.24326700
H	3.87103000	-0.39217400	0.36343600	H	3.66621200	-0.68249600	-0.01324100
N	-4.03970800	-0.10676500	-2.28710200	N	-3.09412600	0.35730700	-2.98918000
H	-4.90928800	0.24473900	-1.91984400	H	-4.07269500	0.49913600	-2.79681700
H	-3.89340400	-0.12953400	-3.28035000	H	-2.71992300	0.69734600	-3.85744200
N	3.45533500	-2.85806900	0.25419500	N	2.97796000	-3.07705000	-0.36370300
H	4.39678500	-2.63530000	0.53508700	H	3.96480700	-2.95940100	-0.52562000
H	3.16424700	-3.82134700	0.26482800	H	2.59266000	-4.00351300	-0.44437000
O	0.20266000	-0.13475300	1.64752100	O	0.07925600	-0.28269600	1.79066500
O	0.08893800	1.86915200	-0.61235000	O	-0.04757600	1.87829900	0.20795300
O	-0.68688300	-0.05086700	3.71153000	O	-1.24691100	-0.51778100	3.58887900
O	1.42610500	3.68597600	-0.65444900	O	1.37953400	3.61000900	0.42913800
Fe	-0.12267700	-0.01700400	-0.24690300	Fe	-0.03489400	0.02079400	-0.04340000
S	-1.44189900	-0.60695500	-2.15342400	S	-0.54794000	0.23910500	-2.24548100
S	0.99906400	-2.34117000	-0.58681800	S	0.45871500	-2.26210100	-0.35704500