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Table S8. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **I(− − −)**) in the sextet state (**HS**) at the B3LYP level. Units are in **Å**.

Table S9. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **I(− − −)**) in the doublet state (**LS**). Units are in **Å**.

Table S10. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II(− + −)**) in the sextet state (**HS**). Units are in **Å.**

Table S11. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II(− + −)**) in the doublet state (**LS**). Units are in **Å**.

Table S12. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II(+ − +)**) in the sextet state (**HS**). Units are in **Å.**

Table S13. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II(+ − +)**) in the doublet state (**LS**). Units are in **Å.**

Table S14. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **III(+ + −)**) in the sextet state (**HS**). Units are in **Å.**

Table S15. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **III(+ + −)**) in the doublet state (**LS**). Units are in **Å**.

Table S16. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **III(+ − −)**) in the sextet state (**HS**). Units are in **Å.**

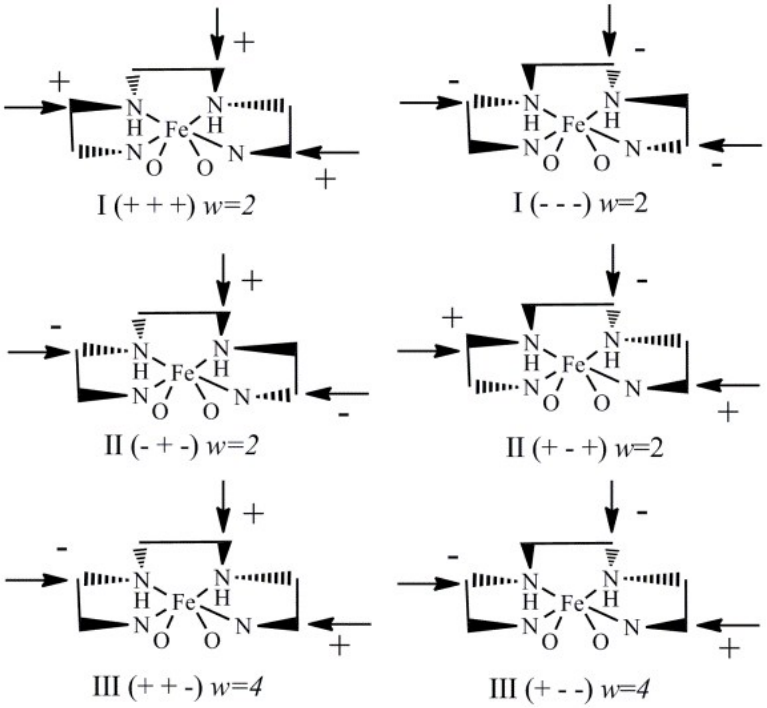

Fig. S1. Conformations of saltrien-type cation with classification of ethylene groups orientations. The arrows show the first carbon atom in each cycle. "*w*" is the statistical weight of conformer.

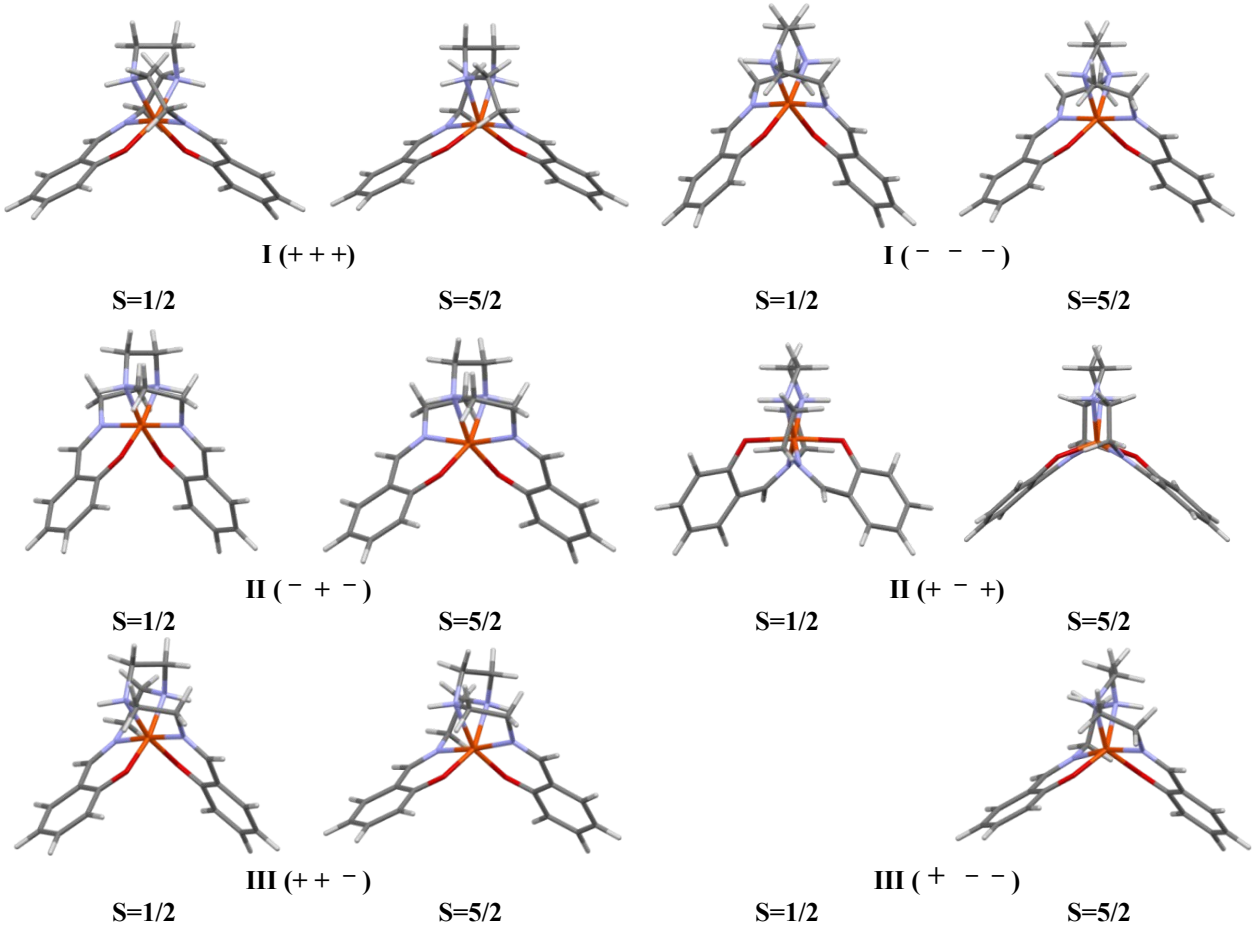

Fig. S2. Optimized structures (B3LYP/6-311++G(d,p)) of $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in HS (S=5/2) and LS (S=1/2) states.

Table S1. Comparison of $[Fe(Sal_2\text{-trien})]^+$ cation conformations presented in the CCDC database with the magnetic state.

№	Compound	Temp., K	Class	Confor-mation	α,°	*x*(HS), %	SCO	CCDC	Ref.
1	*t*-1-$[Fe(Sal_2\text{-trien})][Ni(dmit)_2]$	180	**II**	-+-	71.37	0^a	abrupt	246501	S1
2		R.T.	**I**	---	107.43	100^b		246500	
3	*m-1*-$[Fe(Sal_2\text{-trien})][Ni(dmit)_2]$	180	**I**	---	117.55	$100^{a,b}$	no	729925	S2
4		R.T.		---	115.72	$100^{a,b}$	no	729927	
5	*t*-1"-$[Fe(Sal_2\text{-trien})][Ni(dmit)_2]\cdot$ acetone	R.T.	**II**	-+-	71.94	0^a	no	729931	
6	$[Fe(Sal_2\text{-trien})]ClO_4$	R.T.	**III** **I** **II**	++- +++ -+-	97.96 107.85 78.64	$\approx 60^a$	gradual	221922	S3, S4
7	$[Fe(Sal_2\text{-trien})]BPh_4\cdot\frac{1}{2}CH_2Cl_2$	105	**I**	---	122.24	$\approx 85^a$	no	676636	S4
8	$[Fe(Sal_2\text{-trien})]BPh_4\cdot\frac{1}{2}$acetone	120	**I**	---	125.44	$\approx 85^a$	gradual	676635	
9	$[Fe(Sal_2\text{-trien})]BPh_4$	R.T.	**I**	---	124.92	$\approx 78^a$	gradual	-	S5
10	$[Fe(Sal_2\text{-trien})]PF_6$	R.T.	**I**	+++ ---	114.27 121.86	100^a	stepwise	-	
11		240		+++ ---	114.02 121.19	100^a		676633	S4, S5
12		140		+++ ---	114.67 120.83	$\approx 73^a$		676634	
13	$[Fe(Sal_2\text{-trien})]BPh_4\cdot$ acetone	R.T.	**T/S (II↔III)**	0+-	94.18	$\approx 40^a$ (0^b)	gradual	1187913	S6
14	$[Fe(Sal_2\text{-trien})]BF_4$	R.T.	**I**	---	104.86	100^a	no	746613	S7
15	$[Fe(Sal_2\text{-trien})]NO_3\cdot H_2O$	R.T.	**II**	-+-	63.61	$\approx 18^a$	not indicate	1254589	S8
16	$[Fe(Sal_2\text{-trien})]Cl\cdot 2H_2O$	R.T.	**II**	-+-	64.52	$\approx 6^a$	not indicate	1178434	
17	$[Fe(Sal_2\text{-trien})][Ni(dcbdt)_2]$	R.T.	**III** (disordered) **II** (disordered)	++- -+-	80.35	$\approx 85^a$	no	626997	S9
18	$[Fe(Sal_2\text{-trien})]_2[Mn_2(ox)_3]\cdot 4H_2O\cdot C_3H_7NO$	100	**I** (disordered) **III** (disordered) **III**	--- ++- ++-	102.01 108.82	$\approx 48^b$ (80K) $\approx 74^b$ (160K)	gradual	707311	S10
19	$[Fe(Sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CH_2Cl_2$	180	**II**	-+-	71.60	$\approx 6^b$ (165K)	gradual	749068	S11
20		92			71.38	0^b		813714	S12
21		120			70.57	0^b		807172	
22		250	**II** (disordered) **I** (disordered)	-+- ---	78.22	$\approx 50^b$		813345	
23		R.T.	**I** **II** (disordered)	--- -+-	81.51	$\approx 80^b$		807173	
24	$[Fe(Sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CH_3OH$	120	**III** **I**	++- ---	121.25 105.85	$\approx 70^b$	gradual	749069	S11
25	$[Fe(Sal_2\text{-trien})][Mn^{II}Cr^{III}(Cl_2An)_3]\cdot\frac{1}{2}CH_2Cl_2\cdot CH_3OH\cdot\frac{1}{2}(H_2O)\cdot 5CH_3CN$	120	**I**	---	116.9	$> 50^a$	gradual	998895	S13

[a] According to SQUID magnetic measurement; [b] according to Mössbauer spectroscopy of ^{57}Fe.

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S13. A. Abherv$\acute{e}$, M. Clemente-Le$\acute{o}$n, E. Coronado, C.J.G$\acute{o}$mez-Garc$\acute{i}$a and M.Verneret, *Inorg. Chem.*, 2014, **53**, 12014−12026.

Table S2. Calculated (B3LYP/6-311++G(d,p)) Fe-Ligand bond lengths (Å) and dihedral angle α (°) for $[Fe(Sal_2\text{-trien})]^+$ cation various conformations.

Conformation		Fe – N_{im}, Å	Fe – N_{am}, Å	Fe – O, Å	α, °
I (+ + +)	LS	1.96921	2.09390	1.87873	107.46
	HS	2.13492	2.30902	1.92070	113.59
I (– – –)	LS	1.98420	2.08226	1.87544	78.01
	HS	2.15887	2.27172	1.90976	93.84
II (– + –)	LS	1.96462	2.06091	1.87318	66.41
	HS	2.14261	2.27214	1.90712	81.75
II (+ – +)[a]	LS	1.96750	2.02383	1.92304	50.79
	HS	2.14409	2.28088	1.94075	97.60
III (+ + –)	LS	1.95779 1.98621	2.06608 2.08482	1.87926 1.87113	86.12
	HS	2.13138 2.15476	2.28237 2.29288	1.90802 1.91132	100.67
III (+ – –)	LS[b]	–	–	–	–
	HS	2.14000 2.17587	2.25570 2.33126	1.91280 1.92462	106.49

Note: [a] conformation **II (+ – +)** is not observed experimentally.

[b] conformation **III (+ – –)** is not an energy minimum for LS state.

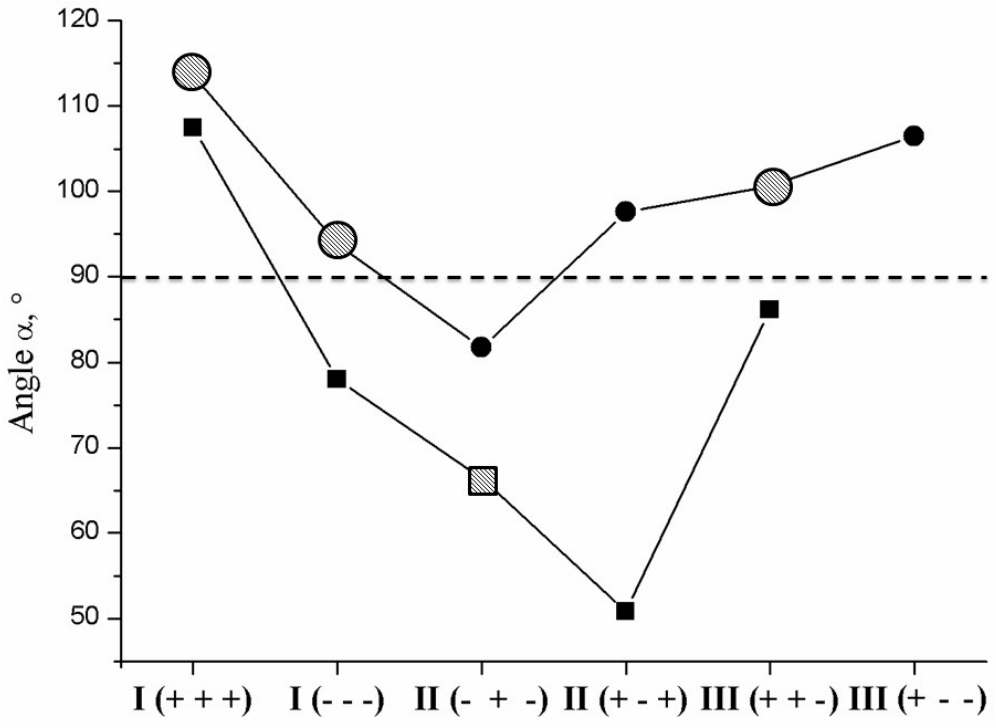
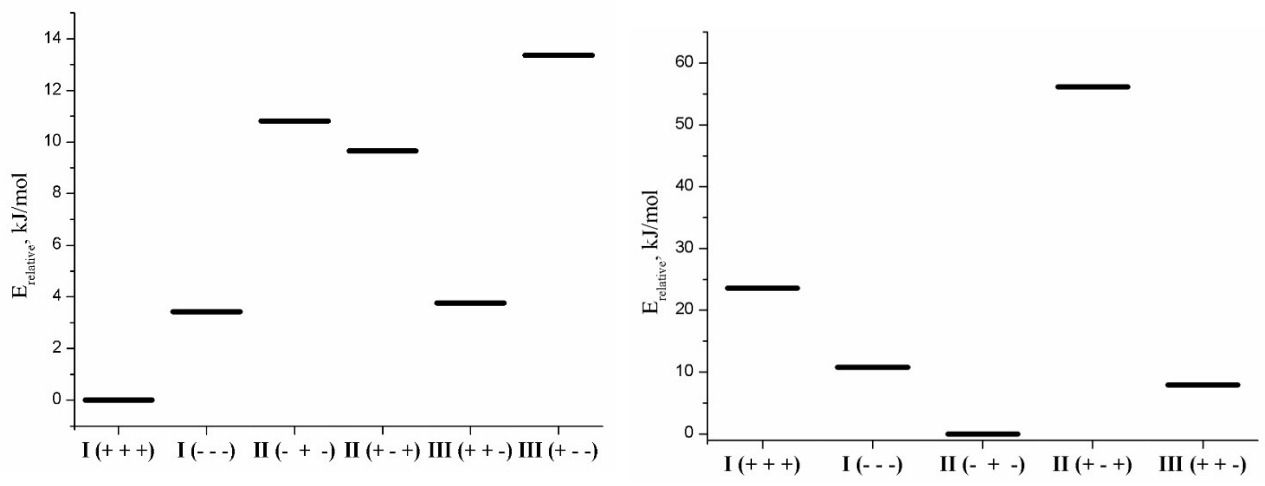


Fig. S3. Calculated (B3LYP/6-311++G(d,p) values of dihedral angle α between the least squares planes of the two phenoxy rings of $[Fe(Sal_2\text{-trien})]^+$ various cation conformations in **HS** (circle, ●) and **LS** (square, ■) states. Gray symbols correspond to the most thermodynamically stable conformers.



(*a*) (*b*)

Fig. S4. Total relative energies of conformers of $[Fe(Sal_2\text{-trien})]^+$ cation in HS (*a*) and LS (*b*) states.

Conformation	**Fe (21), *e***	**O(25), *e***	**O(49), *e***
I(+ + +)	0.553	-0.626	-0.626
I(− − −)	0.537	-0.604	-0.617
II(− + −)	0.507	-0.591	-0.591
II(+ − +)	0.540	-0.648	-0.648
III(+ + −)	0.531	-0.618	-0.600

Table S3. Selected natural atomic charges (B3LYP/6-311++G(d,p)) for $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in LS state.

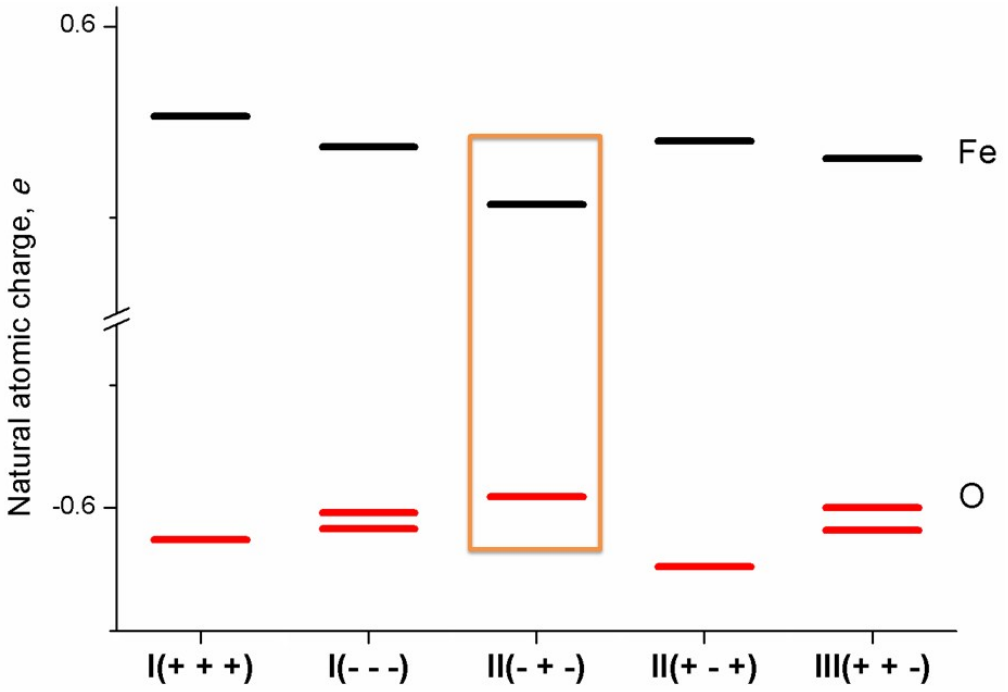


Fig. S5. Diagram of selected natural atomic charges (B3LYP/6-311++G(d,p)) for $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in LS state.

Table S4. Energy values for one singly-occupied (HOMO) molecular orbital of $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in the doublet state (**LS**).

Conformation	HOMO (№ 107)
	Energy, eV
I(+ + +)	-8,5768
I(⁻ ⁻ ⁻)	-8,5330
II(⁻ + ⁻)	-8,5251
II(+ ⁻ +)	-8,7630
III(+ + ⁻)	-8,5510

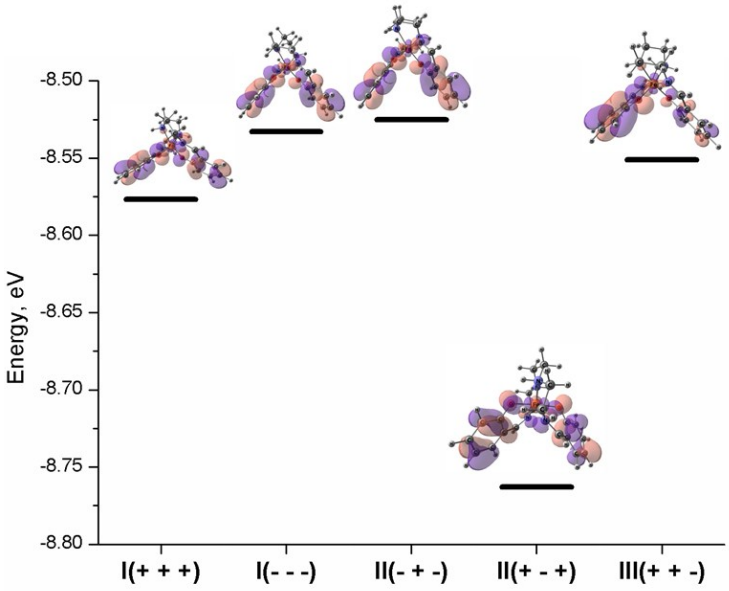


Fig. S6. Energy diagram of one singly-occupied (HOMO) molecular orbital for $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in the doublet state (**LS**).

Table S5. Energy values for five singly-occupied (HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4, respectively) molecular orbitals of $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in the sextet state (**HS**).

Conformation	HOMO (№ 109)	HOMO-1 (№ 108)	HOMO-2 (№ 107)	HOMO-3 (№ 106)	HOMO-4 (№ 105)
	Energy, eV	Energy, eV	Energy, eV	Energy, eV	Energy, eV
I(+ + +)	-8,7156	-8,7847	-9,6326	-9,6985	-9,7665
I(⁻ ⁻ ⁻)	-8,6990	-8,7406	-9,6903	-9,6996	-9,7570
II(⁻ + ⁻)	-8,6985	-8,7602	-9,7102	-9,7200	-9,7662
II(+ ⁻ +)	-8,6903	-8,8394	-9,6068	-9,6947	-9,7165
III(+ + ⁻)	-8,7238	-8,7695	-9,6773	-9,7148	-9,7837
III(+ ⁻ ⁻)	-8,6898	-8,7747	-9,6569	-9,6743	-9,7581

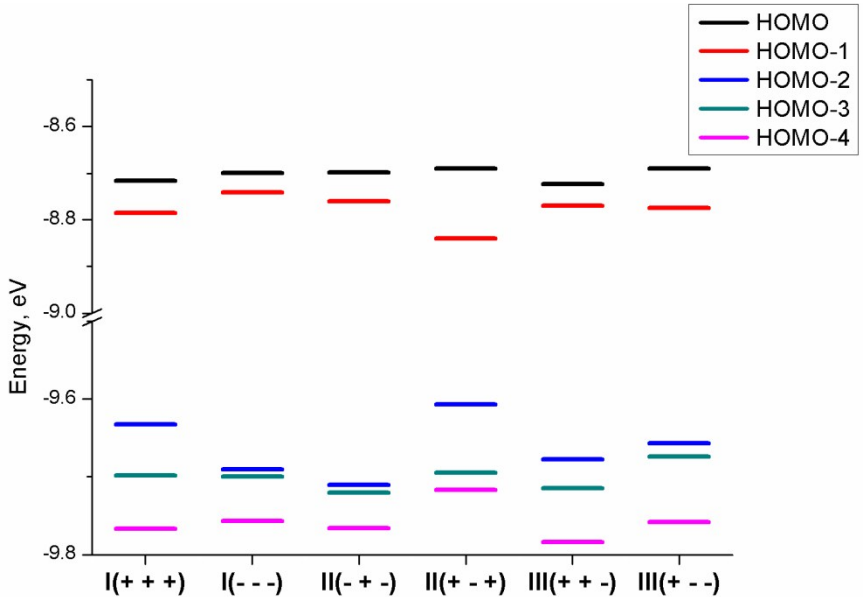


Fig. S7. Energy diagram of five singly-occupied (HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4, respectively) molecular orbital for $[Fe(Sal_2\text{-trien})]^+$ cation various conformations in the sextet state (**HS**).

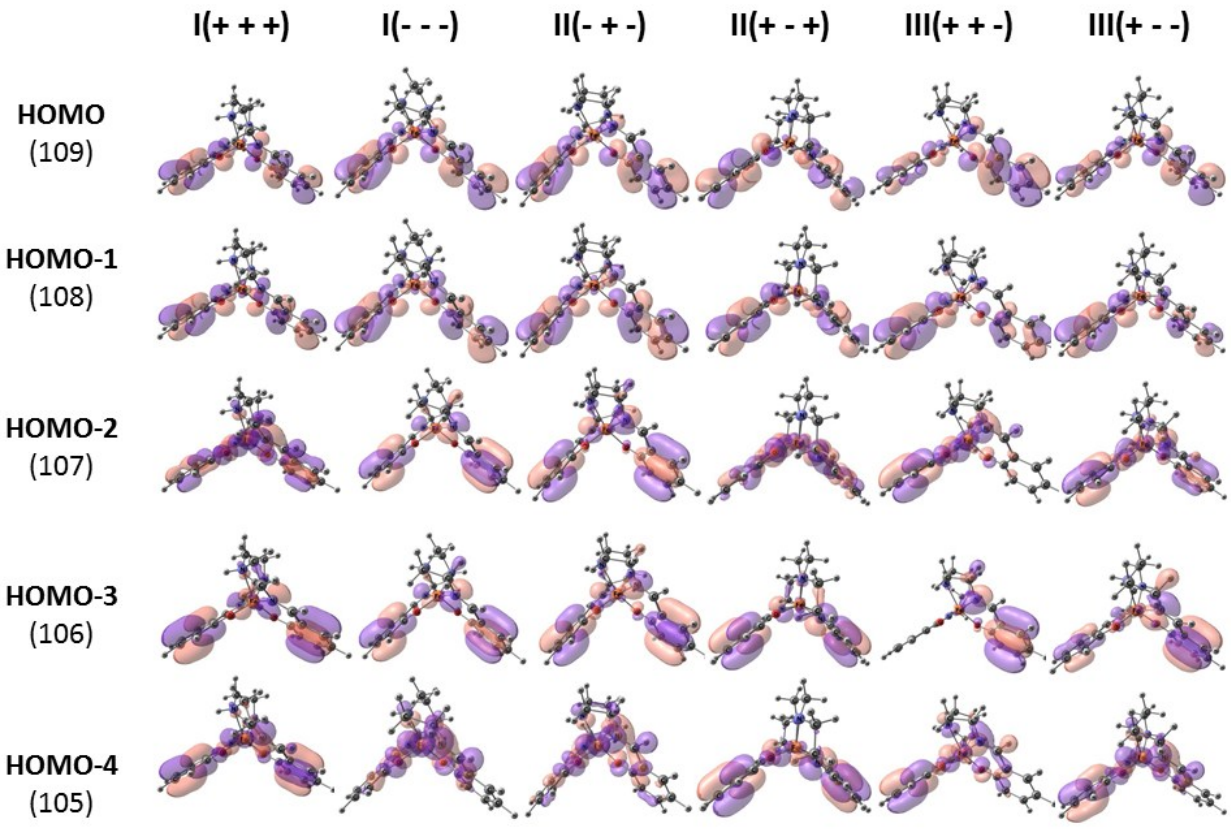


Fig. S8. Five singly-occupied (HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4, respectively) molecular orbital for the HS state of $[Fe(Sal_2\text{-trien})]^+$ cation various conformations.

Table S6. Optimized parameters of $[Fe(Sal_2\text{-trien}]^+$ (conformer: **I(+ + +)**) in the sextet state (**HS**). Units are in **Å.**

C	2.497103000	-1.149644000	-0.655944000
C	3.182708000	-1.870527000	-1.654778000
C	4.402729000	-2.466203000	-1.386118000
H	4.907756000	-3.017462000	-2.171539000
C	4.993072000	-2.374015000	-0.114669000
H	5.945854000	-2.848507000	0.082106000
C	4.338164000	-1.676120000	0.878775000
H	4.776659000	-1.599802000	1.868628000
C	3.092377000	-1.052446000	0.638405000
C	2.460934000	-0.352415000	1.718841000
H	2.997249000	-0.372771000	2.673099000
C	0.796010000	0.910656000	2.865217000
H	1.535684000	0.958393000	3.671601000
H	-0.051708000	0.311249000	3.213965000
C	0.325068000	2.313558000	2.491224000
H	-0.183831000	2.796869000	3.331492000
H	1.191589000	2.925865000	2.232922000
C	-0.586723000	3.480854000	0.490570000
H	-1.533447000	3.505980000	-0.053482000
H	-0.552277000	4.377586000	1.119098000
Fe	0.000000000	0.415783000	0.000000000
N	1.333878000	0.281352000	1.661500000
N	-0.559048000	2.241425000	1.298480000
H	-1.499852000	2.005466000	1.602206000
O	1.338750000	-0.592334000	-0.938377000
C	-2.497101000	-1.149647000	0.655940000
C	-3.182704000	-1.870536000	1.654772000
C	-4.402726000	-2.466211000	1.386111000
H	-4.907751000	-3.017474000	2.171530000
C	-4.993071000	-2.374017000	0.114663000
H	-5.945853000	-2.848509000	-0.082112000
C	-4.338165000	-1.676117000	-0.878778000
H	-4.776661000	-1.599795000	-1.868631000
C	-3.092378000	-1.052444000	-0.638407000
C	-2.460935000	-0.352408000	-1.718841000
H	-2.997252000	-0.372761000	-2.673099000
C	-0.796013000	0.910667000	-2.865214000
H	-1.535689000	0.958408000	-3.671597000
H	0.051704000	0.311261000	-3.213966000
C	-0.325071000	2.313568000	-2.491217000
H	0.183827000	2.796882000	-3.331483000
H	-1.191591000	2.925874000	-2.232912000
C	0.586723000	3.480855000	-0.490559000
H	1.533447000	3.505979000	0.053494000
H	0.552277000	4.377590000	-1.119083000
N	-1.333879000	0.281359000	-1.661499000
N	0.559047000	2.241430000	-1.298473000
H	1.499851000	2.005472000	-1.602202000
O	-1.338748000	-0.592339000	0.938374000
H	2.723183000	-1.951099000	-2.632336000
H	-2.723178000	-1.951112000	2.632329000

Table S7. Optimized parameters of $[Fe(Sal_2\text{-trien}]^+$ (conformer: **I(+ + +)**) in the doublet state (**LS**). Units are in **Å.**

C	-2.280551000	-1.168268000	0.571556000
C	-2.966980000	-1.968376000	1.512002000
C	-4.170641000	-2.568592000	1.192106000
H	-4.668786000	-3.183605000	1.933411000
C	-4.752840000	-2.402727000	-0.076726000
H	-5.693324000	-2.882348000	-0.315497000
C	-4.100705000	-1.629823000	-1.012518000
H	-4.526794000	-1.498416000	-2.001997000
C	-2.869415000	-0.998005000	-0.715807000
C	-2.220819000	-0.245291000	-1.745458000
H	-2.679316000	-0.286099000	-2.736471000
C	-0.447355000	0.942460000	-2.799269000
H	-1.141243000	1.108777000	-3.629358000
H	0.276723000	0.180728000	-3.097962000
C	0.267919000	2.233133000	-2.432643000
H	1.043969000	2.480385000	-3.160444000
H	-0.444311000	3.059193000	-2.422213000
C	0.703497000	3.390221000	-0.292549000
H	1.452885000	3.405042000	0.500504000
H	0.872523000	4.267591000	-0.924178000
Fe	0.000000000	0.537327000	0.000000000
N	-1.136194000	0.444770000	-1.605706000
N	0.863349000	2.125319000	-1.057037000
H	1.850173000	1.897395000	-1.143678000
O	-1.143296000	-0.615520000	0.945217000
C	2.280555000	-1.168262000	-0.571560000
C	2.966987000	-1.968365000	-1.512009000
C	4.170646000	-2.568582000	-1.192112000
H	4.668793000	-3.183592000	-1.933420000
C	4.752843000	-2.402723000	0.076721000
H	5.693326000	-2.882345000	0.315492000
C	4.100705000	-1.629824000	1.012515000
H	4.526792000	-1.498421000	2.001996000
C	2.869416000	-0.998005000	0.715805000
C	2.220818000	-0.245296000	1.745459000
H	2.679313000	-0.286108000	2.736472000
C	0.447352000	0.942450000	2.799272000
H	1.141239000	1.108766000	3.629362000
H	-0.276725000	0.180716000	3.097962000
C	-0.267923000	2.233123000	2.432650000
H	-1.043975000	2.480372000	3.160451000
H	0.444305000	3.059185000	2.422222000
C	-0.703505000	3.390218000	0.292559000
H	-1.452893000	3.405040000	-0.500493000
H	-0.872534000	4.267585000	0.924192000
N	1.136192000	0.444766000	1.605707000
N	-0.863354000	2.125312000	1.057043000
H	-1.850177000	1.897386000	1.143683000
O	1.143301000	-0.615512000	-0.945222000
H	-2.513861000	-2.108726000	2.485798000
H	2.513869000	-2.108710000	-2.485806000

Table S8. Optimized parameters of $[Fe(Sal_2\text{-trien}]^+$ (conformer: **I(⁻ ⁻ ⁻)**) in the sextet state (**HS**). Units are in **Å.**

C	-2.286096000	-1.238520000	0.733606000
C	-2.785366000	-2.142443000	1.692685000
C	-3.934103000	-2.873204000	1.444337000
H	-4.294279000	-3.566325000	2.196470000
C	-4.637209000	-2.735444000	0.235726000
H	-5.532887000	-3.315538000	0.054347000
C	-4.169024000	-1.852278000	-0.714395000
H	-4.700679000	-1.732473000	-1.652943000
C	-2.998698000	-1.088329000	-0.494618000
C	-2.585597000	-0.176381000	-1.520319000
H	-3.235785000	-0.149046000	-2.401034000
C	-1.346743000	1.495555000	-2.652326000
H	-2.034715000	2.345418000	-2.575168000
H	-1.572713000	0.989364000	-3.596013000
C	0.102783000	1.979954000	-2.674635000
H	0.757109000	1.170015000	-2.998958000
H	0.212509000	2.817740000	-3.372350000
C	-0.061947000	3.587264000	-0.760393000
H	0.407943000	4.481672000	-1.183655000
H	-1.116641000	3.613895000	-1.041705000
Fe	0.000000000	0.560364000	0.000000000
N	-1.549985000	0.603827000	-1.502121000
N	0.531423000	2.344403000	-1.302108000
H	1.545718000	2.418457000	-1.286767000
O	-1.189264000	-0.559751000	0.989024000
C	2.286096000	-1.238521000	-0.733606000
C	2.785366000	-2.142443000	-1.692685000
C	3.934103000	-2.873205000	-1.444337000
H	4.294279000	-3.566325000	-2.196470000
C	4.637209000	-2.735445000	-0.235726000
H	5.532887000	-3.315538000	-0.054347000
C	4.169024000	-1.852278000	0.714395000
H	4.700679000	-1.732473000	1.652943000
C	2.998697000	-1.088329000	0.494618000
C	2.585597000	-0.176381000	1.520319000
H	3.235785000	-0.149046000	2.401034000
C	1.346743000	1.495554000	2.652326000
H	2.034715000	2.345418000	2.575168000
H	1.572713000	0.989364000	3.596013000
C	-0.102783000	1.979955000	2.674635000
H	-0.757109000	1.170015000	2.998958000
H	-0.212509000	2.817741000	3.372350000
C	0.061947000	3.587264000	0.760393000
H	-0.407942000	4.481672000	1.183655000
H	1.116641000	3.613895000	1.041705000
N	1.549985000	0.603827000	1.502121000
N	-0.531423000	2.344403000	1.302108000
H	-1.545717000	2.418457000	1.286767000
O	1.189264000	-0.559752000	-0.989023000
H	-2.238628000	-2.254550000	2.620934000
H	2.238627000	-2.254550000	-2.620934000

Table S9. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **I(− − −)**) in the doublet state (**LS**). Units are in **Å.**

C	1.902432000	-1.231899000	-0.758361000
C	2.286958000	-2.214038000	-1.697497000
C	3.299284000	-3.110892000	-1.412491000
H	3.566144000	-3.860252000	-2.149504000
C	3.982891000	-3.071745000	-0.184108000
H	4.771772000	-3.782241000	0.026817000
C	3.631898000	-2.116203000	0.743848000
H	4.149865000	-2.066644000	1.696280000
C	2.599049000	-1.183218000	0.483795000
C	2.301278000	-0.204544000	1.481544000
H	2.902965000	-0.256979000	2.392086000
C	1.197621000	1.592675000	2.572137000
H	1.864110000	2.459536000	2.502200000
H	1.446488000	1.074147000	3.501607000
C	-0.265655000	2.024186000	2.592734000
H	-0.895008000	1.190097000	2.896494000
H	-0.423224000	2.866478000	3.273835000
C	-0.069415000	3.673017000	0.755453000
H	-0.673861000	4.519055000	1.095632000
H	0.912792000	3.772723000	1.217177000
Fe	0.000000000	0.804245000	0.000000000
N	1.398125000	0.719964000	1.405418000
N	-0.655411000	2.376542000	1.197553000
H	-1.670531000	2.423803000	1.142628000
O	0.940878000	-0.395634000	-1.091927000
C	-1.902433000	-1.231898000	0.758361000
C	-2.286960000	-2.214036000	1.697497000
C	-3.299286000	-3.110889000	1.412491000
H	-3.566147000	-3.860249000	2.149505000
C	-3.982894000	-3.071742000	0.184108000
H	-4.771775000	-3.782237000	-0.026817000
C	-3.631900000	-2.116200000	-0.743848000
H	-4.149866000	-2.066641000	-1.696280000
C	-2.599050000	-1.183215000	-0.483795000
C	-2.301279000	-0.204542000	-1.481544000
H	-2.902965000	-0.256976000	-2.392086000
C	-1.197620000	1.592676000	-2.572137000
H	-1.864107000	2.459538000	-2.502200000
H	-1.446487000	1.074148000	-3.501607000
C	0.265657000	2.024185000	-2.592735000
H	0.895009000	1.190096000	-2.896494000
H	0.423227000	2.866478000	-3.273835000
C	0.069418000	3.673017000	-0.755453000
H	0.673866000	4.519054000	-1.095632000
H	-0.912788000	3.772724000	-1.217177000
N	-1.398124000	0.719966000	-1.405418000
N	0.655414000	2.376541000	-1.197553000
H	1.670533000	2.423801000	-1.142628000
O	-0.940878000	-0.395633000	1.091927000
H	1.756376000	-2.249476000	-2.641110000
H	-1.756378000	-2.249474000	2.641110000

Table S10. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II($^-$ + $^-$)**) in the sextet state (**HS**). Units are in **Å.**

C	-2.187305000	-1.349290000	0.768744000
C	-2.580198000	-2.376969000	1.648917000
C	-3.721148000	-3.120597000	1.402853000
H	-3.996981000	-3.911039000	2.092036000
C	-4.524974000	-2.870843000	0.277722000
H	-5.414147000	-3.461408000	0.098233000
C	-4.166005000	-1.861851000	-0.590785000
H	-4.778989000	-1.651568000	-1.461358000
C	-3.004045000	-1.083391000	-0.374224000
C	-2.719974000	-0.026731000	-1.300373000
H	-3.467497000	0.111937000	-2.088245000
C	-1.637688000	1.858213000	-2.265608000
H	-2.161544000	2.733664000	-1.864537000
H	-2.141783000	1.587248000	-3.199348000
C	-0.176567000	2.200773000	-2.553291000
H	0.269228000	1.398729000	-3.144614000
H	-0.108658000	3.129210000	-3.131295000
C	0.553449000	3.553300000	-0.533570000
H	1.525993000	3.685383000	-0.057319000
H	0.408013000	4.411997000	-1.198988000
Fe	0.000000000	0.521885000	0.000000000
N	-1.697537000	0.772148000	-1.283164000
N	0.610257000	2.284314000	-1.297711000
H	1.578675000	2.084958000	-1.524569000
O	-1.097326000	-0.657850000	1.020399000
C	2.187305000	-1.349289000	-0.768745000
C	2.580199000	-2.376967000	-1.648918000
C	3.721149000	-3.120595000	-1.402854000
H	3.996983000	-3.911036000	-2.092037000
C	4.524975000	-2.870842000	-0.277722000
H	5.414147000	-3.461407000	-0.098233000
C	4.166005000	-1.861851000	0.590785000
H	4.778988000	-1.651569000	1.461359000
C	3.004045000	-1.083391000	0.374224000
C	2.719973000	-0.026732000	1.300374000
H	3.467496000	0.111936000	2.088246000
C	1.637687000	1.858212000	2.265609000
H	2.161544000	2.733663000	1.864539000
H	2.141781000	1.587246000	3.199350000
C	0.176565000	2.200771000	2.553292000
H	-0.269230000	1.398727000	3.144613000
H	0.108656000	3.129208000	3.131296000
C	-0.553448000	3.553301000	0.533571000
H	-1.525992000	3.685385000	0.057319000
H	-0.408011000	4.411997000	1.198989000
N	1.697536000	0.772148000	1.283164000
N	-0.610258000	2.284314000	1.297711000
H	-1.578676000	2.084959000	1.524568000
O	1.097326000	-0.657849000	-1.020400000
H	-1.958058000	-2.571757000	2.513783000
H	1.958060000	-2.571755000	-2.513784000

Table S11. Optimized parameters of [Fe(Sal_2-trien)]$^+$ (conformer: **II(⁻ + ⁻)**) in the doublet state (**LS**). Units are in **Å.**

C	1.297799000	1.722155000	-0.861823000
C	2.364989000	1.944199000	-1.759909000
C	3.318797000	2.910828000	-1.504733000
H	4.133243000	3.049851000	-2.207093000
C	3.252967000	3.713767000	-0.351449000
H	4.007621000	4.466958000	-0.164678000
C	2.211715000	3.529660000	0.530707000
H	2.136861000	4.146779000	1.420364000
C	1.221957000	2.542137000	0.304774000
C	0.138455000	2.442195000	1.231448000
H	0.119675000	3.181849000	2.035384000
C	-1.880294000	1.591657000	2.189907000
H	-2.746826000	2.138337000	1.801345000
H	-1.559916000	2.105371000	3.101115000
C	-2.246098000	0.143538000	2.499503000
H	-1.437849000	-0.316415000	3.068110000
H	-3.171627000	0.075414000	3.079000000
C	-3.660814000	-0.566740000	0.514478000
H	-3.807373000	-1.527355000	0.019830000
H	-4.488388000	-0.438553000	1.219014000
Fe	-0.819845000	0.000000000	0.000000000
N	-0.816309000	1.568907000	1.182470000
N	-2.352718000	-0.628827000	1.225649000
H	-2.150745000	-1.600199000	1.444235000
O	0.409080000	0.798538000	-1.166563000
C	1.297799000	-1.722155000	0.861823000
C	2.364989000	-1.944199000	1.759909000
C	3.318797000	-2.910828000	1.504733000
H	4.133243000	-3.049851000	2.207093000
C	3.252967000	-3.713767000	0.351449000
H	4.007621000	-4.466958000	0.164678000
C	2.211715000	-3.529660000	-0.530707000
H	2.136862000	-4.146779000	-1.420365000
C	1.221958000	-2.542137000	-0.304774000
C	0.138455000	-2.442195000	-1.231448000
H	0.119675000	-3.181849000	-2.035385000
C	-1.880294000	-1.591657000	-2.189907000
H	-2.746826000	-2.138337000	-1.801345000
H	-1.559916000	-2.105371000	-3.101115000
C	-2.246097000	-0.143538000	-2.499503000
H	-1.437849000	0.316415000	-3.068110000
H	-3.171627000	-0.075414000	-3.079000000
C	-3.660814000	0.566739000	-0.514478000
H	-3.807373000	1.527354000	-0.019830000
H	-4.488388000	0.438553000	-1.219014000
N	-0.816309000	-1.568907000	-1.182470000
N	-2.352718000	0.628827000	-1.225649000
H	-2.150745000	1.600199000	-1.444235000
O	0.409080000	-0.798539000	1.166563000
H	2.417019000	1.325094000	-2.647071000
H	2.417019000	-1.325094000	2.647071000

Table S12. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II(+ − +)**) in the sextet state (**HS**). Units are in **Å.**

C	2.561519000	-0.874576000	-0.603953000
C	3.367762000	-1.392376000	-1.638045000
C	4.372967000	-2.303543000	-1.364001000
H	4.973806000	-2.692028000	-2.178754000
C	4.627899000	-2.729905000	-0.050446000
H	5.418185000	-3.442017000	0.149859000
C	3.863451000	-2.221774000	0.980301000
H	4.055913000	-2.529970000	2.002953000
C	2.821612000	-1.301387000	0.732982000
C	2.102495000	-0.753030000	1.848270000
H	2.497631000	-0.993926000	2.840594000
C	0.519016000	0.645239000	2.961146000
H	1.115871000	0.427917000	3.853193000
H	-0.497251000	0.275542000	3.117365000
C	0.497273000	2.152942000	2.692644000
H	-0.003280000	2.692864000	3.502817000
H	1.523655000	2.520840000	2.627287000
C	0.254812000	3.665351000	0.718758000
H	-0.107281000	4.553611000	1.248730000
H	1.347803000	3.702685000	0.730204000
Fe	0.000000000	0.602371000	0.000000000
N	1.065623000	0.012536000	1.764560000
N	-0.155013000	2.410413000	1.381803000
H	-1.165754000	2.403803000	1.513532000
O	1.618874000	0.003464000	-0.887179000
C	-2.561519000	-0.874576000	0.603953000
C	-3.367763000	-1.392376000	1.638045000
C	-4.372968000	-2.303542000	1.364001000
H	-4.973806000	-2.692028000	2.178753000
C	-4.627900000	-2.729904000	0.050446000
H	-5.418186000	-3.442015000	-0.149860000
C	-3.863451000	-2.221773000	-0.980301000
H	-4.055914000	-2.529968000	-2.002953000
C	-2.821612000	-1.301386000	-0.732982000
C	-2.102495000	-0.753030000	-1.848270000
H	-2.497632000	-0.993925000	-2.840594000
C	-0.519016000	0.645239000	-2.961145000
H	-1.115871000	0.427917000	-3.853193000
H	0.497251000	0.275542000	-3.117365000
C	-0.497272000	2.152942000	-2.692644000
H	0.003280000	2.692864000	-3.502817000
H	-1.523655000	2.520840000	-2.627287000
C	-0.254811000	3.665351000	-0.718758000
H	0.107282000	4.553611000	-1.248730000
H	-1.347802000	3.702686000	-0.730204000
N	-1.065623000	0.012536000	-1.764560000
N	0.155014000	2.410413000	-1.381803000
H	1.165754000	2.403803000	-1.513532000
O	-1.618873000	0.003463000	0.887180000
H	3.177961000	-1.060151000	-2.651543000
H	-3.177961000	-1.060152000	2.651543000

Table S13. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **II(+ ⁻ +)**) in the doublet state (**LS**). Units are in **Å.**

C	-2.572226000	-0.471675000	0.019504000
C	-3.755772000	-0.677543000	0.762375000
C	-4.481777000	-1.847027000	0.632093000
H	-5.378026000	-1.983311000	1.227178000
C	-4.087320000	-2.854881000	-0.266378000
H	-4.671705000	-3.761094000	-0.361427000
C	-2.964872000	-2.659174000	-1.041513000
H	-2.666297000	-3.407907000	-1.767970000
C	-2.180020000	-1.491582000	-0.905055000
C	-1.144878000	-1.194540000	-1.847723000
H	-1.207078000	-1.665859000	-2.831836000
C	0.414620000	0.360704000	-2.789433000
H	0.093260000	-0.071303000	-3.740940000
H	1.500647000	0.278673000	-2.712328000
C	-0.014599000	1.839145000	-2.684880000
H	0.489924000	2.457941000	-3.433744000
H	-1.094088000	1.928795000	-2.821575000
C	-0.185846000	3.534937000	-0.746015000
H	0.235338000	4.406569000	-1.256814000
H	-1.271257000	3.556965000	-0.872092000
Fe	0.000000000	0.746602000	0.000000000
N	-0.217116000	-0.312401000	-1.643902000
N	0.324416000	2.260510000	-1.303358000
H	1.343603000	2.257181000	-1.224393000
O	-1.915467000	0.665407000	0.149886000
C	2.572226000	-0.471675000	-0.019504000
C	3.755772000	-0.677543000	-0.762374000
C	4.481777000	-1.847027000	-0.632093000
H	5.378026000	-1.983311000	-1.227178000
C	4.087320000	-2.854881000	0.266378000
H	4.671705000	-3.761095000	0.361427000
C	2.964871000	-2.659174000	1.041513000
H	2.666297000	-3.407908000	1.767970000
C	2.180020000	-1.491583000	0.905055000
C	1.144878000	-1.194540000	1.847723000
H	1.207078000	-1.665859000	2.831836000
C	-0.414620000	0.360705000	2.789434000
H	-0.093260000	-0.071303000	3.740940000
H	-1.500647000	0.278673000	2.712328000
C	0.014599000	1.839145000	2.684880000
H	-0.489924000	2.457941000	3.433744000
H	1.094088000	1.928795000	2.821575000
C	0.185846000	3.534937000	0.746015000
H	-0.235338000	4.406569000	1.256814000
H	1.271257000	3.556965000	0.872092000
N	0.217116000	-0.312401000	1.643902000
N	-0.324416000	2.260510000	1.303358000
H	-1.343603000	2.257181000	1.224393000
O	1.915467000	0.665407000	-0.149886000
H	-4.081132000	0.107325000	1.435049000
H	4.081132000	0.107325000	-1.435048000

Table S14. Optimized parameters of $[Fe(Sal_2\text{-trien})]^+$ (conformer: **III(+ + ⁻)**) in the sextet state (**HS**). Units are in **Å.**

C	2.370566000	-1.231185000	-0.720395000
C	2.961587000	-2.014994000	-1.731595000
C	4.196761000	-2.608783000	-1.536650000
H	4.627100000	-3.209362000	-2.330320000
C	4.896522000	-2.451796000	-0.329113000
H	5.859700000	-2.925301000	-0.188699000
C	4.334852000	-1.692251000	0.676426000
H	4.858474000	-1.567403000	1.618841000
C	3.077217000	-1.067455000	0.511180000
C	2.549510000	-0.308240000	1.609274000
H	3.164263000	-0.301718000	2.515264000
C	0.999947000	1.027451000	2.839649000
H	1.814642000	1.137379000	3.563447000
H	0.212160000	0.425632000	3.307004000
C	0.445321000	2.395432000	2.447028000
H	0.000200000	2.903137000	3.308762000
H	1.260869000	3.021484000	2.080268000
C	-0.717029000	3.412378000	0.481993000
H	-1.666493000	3.292902000	-0.041151000
H	-0.780460000	4.339423000	1.064004000
Fe	-0.006632000	0.428160000	0.051989000
N	1.433744000	0.347236000	1.620928000
N	-0.541348000	2.227923000	1.349735000
H	-1.438463000	1.963050000	1.748053000
O	1.194207000	-0.680461000	-0.932636000
C	-2.396663000	-1.284561000	0.650945000
C	-2.943207000	-2.242680000	1.528457000
C	-4.133440000	-2.879963000	1.225270000
H	-4.529628000	-3.617991000	1.913892000
C	-4.833608000	-2.591134000	0.041371000
H	-5.762224000	-3.100000000	-0.183037000
C	-4.320717000	-1.651748000	-0.827863000
H	-4.849813000	-1.414557000	-1.745293000
C	-3.106276000	-0.980178000	-0.550751000
C	-2.649284000	0.003412000	-1.486289000
H	-3.307968000	0.163915000	-2.346062000
C	-1.327646000	1.719501000	-2.450265000
H	-1.883695000	2.632659000	-2.206267000
H	-1.687209000	1.379907000	-3.426980000
C	0.165978000	2.017374000	-2.531747000
H	0.685372000	1.158389000	-2.959603000
H	0.346427000	2.886862000	-3.173806000
C	0.440740000	3.519321000	-0.520135000
H	1.347547000	3.839711000	-0.003397000
H	0.212342000	4.294223000	-1.259451000
N	-1.565451000	0.713335000	-1.408058000
N	0.731426000	2.219318000	-1.174510000
H	1.736828000	2.098001000	-1.237913000
O	-1.261708000	-0.695849000	0.954494000
H	2.416496000	-2.145363000	-2.658463000
H	-2.399417000	-2.470730000	2.436945000

Table S15. Optimized parameters of $[Fe(Sal_2\text{-trien}]^+$ (conformer: **III(+ + ⁻))** in the doublet state (**LS**). Units are in **Å**.

C	1.924158000	-1.320531000	-0.659112000
C	2.374535000	-2.264338000	-1.610337000
C	3.496387000	-3.034996000	-1.372798000
H	3.810709000	-3.756569000	-2.118806000
C	4.231128000	-2.905261000	-0.180116000
H	5.105955000	-3.518369000	-0.005851000
C	3.813760000	-1.992798000	0.762855000
H	4.361571000	-1.882726000	1.693290000
C	2.669428000	-1.185236000	0.550918000
C	2.274842000	-0.279312000	1.583779000
H	2.849393000	-0.323357000	2.512128000
C	0.853096000	1.253903000	2.731397000
H	1.674653000	1.398878000	3.439855000
H	0.090274000	0.630981000	3.208315000
C	0.254006000	2.587268000	2.316053000
H	-0.311722000	3.048499000	3.129553000
H	1.050493000	3.277323000	2.034618000
C	-0.649799000	3.554709000	0.214539000
H	-1.536685000	3.470946000	-0.412305000
H	-0.727301000	4.493560000	0.773190000
Fe	-0.009885000	0.711786000	0.063162000
N	1.292810000	0.561370000	1.516882000
N	-0.621031000	2.379250000	1.118981000
H	-1.562677000	2.156487000	1.432689000
O	0.855238000	-0.610514000	-0.954047000
C	-2.094540000	-1.143739000	0.747041000
C	-2.581337000	-2.094674000	1.668652000
C	-3.604889000	-2.958153000	1.323499000
H	-3.951145000	-3.685915000	2.048998000
C	-4.198501000	-2.911183000	0.050312000
H	-4.997447000	-3.594494000	-0.207377000
C	-3.749095000	-1.980542000	-0.861373000
H	-4.200070000	-1.922896000	-1.846832000
C	-2.700286000	-1.085963000	-0.541725000
C	-2.309864000	-0.118360000	-1.520530000
H	-2.882381000	-0.122100000	-2.451199000
C	-1.070639000	1.657764000	-2.510244000
H	-1.613275000	2.600195000	-2.375846000
H	-1.397096000	1.234458000	-3.464215000
C	0.433660000	1.898006000	-2.527229000
H	0.942529000	0.994388000	-2.859502000
H	0.701003000	2.727129000	-3.189361000
C	0.627494000	3.538457000	-0.626461000
H	1.482600000	3.840025000	-0.019545000
H	0.554913000	4.252403000	-1.451567000
N	-1.358971000	0.749628000	-1.394089000
N	0.896782000	2.158894000	-1.132788000
H	1.899563000	1.995339000	-1.106960000
O	-1.129810000	-0.332917000	1.138097000
H	1.803350000	-2.373134000	-2.524237000
H	-2.122007000	-2.134164000	2.648745000

Table S16. Optimized parameters of [Fe(Sal_2-trien]$^+$ (conformer: **III(+ − −)**) in the sextet state (**HS**). Units are in **Å.**

C	2.433398000	-1.092976000	-0.712721000
C	3.100173000	-1.759906000	-1.759757000
C	4.300011000	-2.412244000	-1.532687000
H	4.792052000	-2.918923000	-2.355453000
C	4.884811000	-2.433713000	-0.256274000
H	5.821121000	-2.951334000	-0.091670000
C	4.244705000	-1.792914000	0.785074000
H	4.678159000	-1.806956000	1.779971000
C	3.022255000	-1.112782000	0.587139000
C	2.398205000	-0.485449000	1.717492000
H	2.911380000	-0.616033000	2.675880000
C	0.740323000	0.717526000	2.939257000
H	1.438153000	0.620557000	3.778111000
H	-0.159551000	0.139517000	3.169747000
C	0.382512000	2.186490000	2.719869000
H	-0.174612000	2.585245000	3.573315000
H	1.302952000	2.766236000	2.625692000
C	-0.171668000	3.642343000	0.770476000
H	-0.830134000	4.423224000	1.164462000
H	0.855190000	3.960973000	0.967328000
Fe	0.003709000	0.532856000	0.026047000
N	1.299292000	0.194729000	1.695399000
N	-0.375550000	2.340613000	1.448350000
H	-1.365953000	2.199553000	1.635152000
O	1.292722000	-0.480744000	-0.958770000
C	-2.425148000	-1.146035000	0.656382000
C	-3.033082000	-1.964781000	1.629612000
C	-4.147897000	-2.723053000	1.318015000
H	-4.593153000	-3.349845000	2.082707000
C	-4.709437000	-2.697176000	0.030060000
H	-5.580457000	-3.297540000	-0.199154000
C	-4.136022000	-1.895507000	-0.934267000
H	-4.559304000	-1.858637000	-1.932947000
C	-2.994547000	-1.109759000	-0.650879000
C	-2.471264000	-0.269859000	-1.685991000
H	-3.039154000	-0.281598000	-2.622409000
C	-1.129966000	1.334272000	-2.783863000
H	-1.899385000	2.109007000	-2.876594000
H	-1.152608000	0.749016000	-3.708194000
C	0.251148000	1.968960000	-2.624861000
H	1.025467000	1.239016000	-2.859512000
H	0.356582000	2.823693000	-3.302173000
C	-0.371476000	3.487369000	-0.733306000
H	-0.127837000	4.424562000	-1.246997000
H	-1.415535000	3.254509000	-0.952124000
N	-1.426935000	0.494715000	-1.612924000
N	0.461605000	2.362802000	-1.210815000
H	1.444389000	2.596659000	-1.084398000
O	-1.365252000	-0.433751000	0.972501000
H	2.643429000	-1.753544000	-2.741922000
H	-2.598480000	-1.990506000	2.621430000