Supplementary Information

Incorporation of Redox-Inactive Cations Promotes Iron Catalyzed Aerobic C-H Oxidation at Mild Potentials

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General Information & Synthesis

All reagents were purchased from commercial suppliers and used without purification. Unless otherwise noted, all organic chemical manipulations were performed in air. Cyclohexene was passed through a short basic alumina plug before catalytic studies to get rid of stabilizers. Compounds were purified via flash column chromatography using Sorbent Technologies 60 Å, 230–400 mesh silica gel, unless otherwise stated. Unless otherwise noted, inorganic metal complexations were performed in a Vacuum Atmospheres Co. drybox under a nitrogen atmosphere. Anhydrous solvents were sparged with UHP argon (Praxair) and passed through columns containing Q-5 and molecular sieves before use. ^{1}H NMR spectra were recorded at 500 MHz on Bruker instruments. ^{1}H NMR spectra chemical shifts are reported as δ values in ppm relative to residual protio solvent: $CDCl_3$ (7.26 ppm), CD_3CN (1.94 ppm). Electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass LCT and collected at the University of California-Irvine Mass Spectrometry Facility. Elemental analyses were performed on a Perkin Elmer 2400 Series II CHNS elemental analyzer. Ultraviolet-visible (UV–vis) spectra were collected in a 10 mm pathlength quartz cuvette or 1 mm pathlength, using an Agilent Technologies Cary 60 UV–vis spectrometer and 8453 Diode-array UV-vis spectrometer equipped with Unisoku cryostat.

Electrochemical experiments were performed under an atmosphere of nitrogen in a solution containing 0.2 M Bu_4NPF_6 in acetonitrile. Glassy carbon was used as the working and auxiliary electrode and a silver wire was used as a pseudoreference electrode. Ferrocene and cobaltocene were used as internal standards, and all potentials are referenced to the ferrocenium/ferrocene couple. Cyclic voltammetry experiments were performed with a Pine Wavedriver 10 or 20 potentiostat and Pine Aftermath software version 1.2.7359.

Synthesis of FeMsalen (**2M**)

In 5 mL CH_3OH, **1M** (0.15 mmol, 1 equiv) and $Fe(OAc)_2$ (28.5 mg, 0.165 mmol, 1.1 equiv) were dissolved and heated at 65°C for 1 h. The reaction changed color from yellow to dark brown. The volume was reduced under vacuum before recrystallization by Et_2O diffusion. Crystals suitable for X-ray crystallography were obtained with Et_2O diffusion into an CH_3CN solution. **2K**: Yield 75.8 mg (77.3 %) ESI-MS *m/z* calcd $C_{23}H_{24}F_3FeKN_2O_9S$ 656.0 (M), found 656.0, Calcd $C_{23}H_{24}F_3FeKN_2O_9S$ (656.45 g·mol^{-1}): C, 42.08; H, 3.69; N, 4.27. Found: C, 41.86; H, 3.31; N, 4.09. **2Ba**: Yield 114.8 mg (85.0 %) ESI-MS *m/z* calcd $[C_{24}H_{27}BaF_3FeN_2O_{10}S]^+$ 786.0 (M-$CF_3SO_3^-$ +CH_3O^-), found 785.9, Calcd $C_{24}H_{24}F_6FeBaN_2O_{12}S_2$ (903.74 g·mol^{-1}): C, 31.90; H, 2.68; N, 3.10. Found: C, 32.18; H, 2.72; N, 2.87.

Synthesis of FeClMsalen (**3M**)

In 5 mL EtOH, **1M** (0.1 mmol, 1 equiv), $FeCl_3$ (18 mg, 0.11 mmol, 1.1 equiv), and triethylamine (30 μL, 0.2 mmol, 2 equiv) were dissolved and heated at 80°C for 1 h. The reaction changed color from yellow to dark brown with precipitate. The precipitate was collected after vacuum filtration. Crystals suitable for X-ray crystallography were obtained with Et_2O diffusion into an CH_3CN solution. **3K**: Yield 53.8 mg (77.8 %) ESI-MS *m/z* calcd $C_{22}H_{24}ClFeKN_2O_6$ 542.0 (M-$CF_3SO_3^-$), found 542.0, Calcd $C_{23}H_{24}ClF_3FeKN_2O_9S$ (691.90 g·mol^{-1}): C, 39.93; H, 3.50; N, 4.05. Found: C, 40.21; H, 3.56; N, 3.83. **3Ba**: Yield 32.0 mg (34.0 %) ESI-MS *m/z* calcd $[C_{23}H_{27}BaClFeN_2O_7]^+$ 671.9 (M-$CF_3SO_3^-$+CH_3O^-) found 671.9 Calcd $C_{31}H_{41}BaClF_6FeN_3O_{14}S_2$ (1086.00 g·mol^{-1}): C, 34.27; H, 3.80; N, 3.87. Found: C, 34.36; H, 3.64; N, 3.65.

Synthesis of [Fe_2(μ-Oxo) (salenM)$_2$] (**4M**)

In 2 mL CH_3CN, **2M** (0.033 mmol) were exposed to air overnight. The resulting solution was recrystallized. Crystals suitable for X-ray crystallography were obtained with Et_2O diffusion into an CH_3CN solution. **4K**: Yield 29.3 mg (87.7 %) ESI-MS *m/z* calcd for $C_{45}H_{48}F_3Fe_2K_2N_4O_{16}S_1^+$ 1179.1 (M-CF_3SO_3) found 1179.1, Calcd $C_{46}H_{48}F_6Fe_2K_2N_4O_{19}S_2$ (1328.90 g·mol^{-1}): C, 41.58; H, 3.64; N, 4.22. Found: C, 41.49; H, 3.39; N, 4.10. **4Ba**: Yield 40.7 mg (88.9 %) *m/z* calcd $C_{47}H_{48}Ba_2F_9Fe_2N_4O_{22}S_3^+$ 1674.9 (M-$CF_3SO_3^-$), found 1674.7 Calcd $C_{48}H_{56}Ba_2F_{12}Fe_2N_4O_{29}S_4$ (1895.54 g·mol^{-1}): C, 30.41; H, 2.98; N, 2.96. Found: C, 30.26; H, 2.99; N, 3.25.

General Procedure for NMR Experiments

An O_2 saturated solution (0.25 mL) of 1 M cyclohexene and 20 mM benzene, as an internal standard, in CD_3CN was mixed with an O_2 saturated solution (0.25 mL) of 1 mM Fe complexes (or blank solution in the control experiments) in an NMR tube. The headspace was topped off with extra O_2 and tightly capped. NMR spectra were taken 24 hours after with a long delay time (12.6 seconds).

Solid State Structures

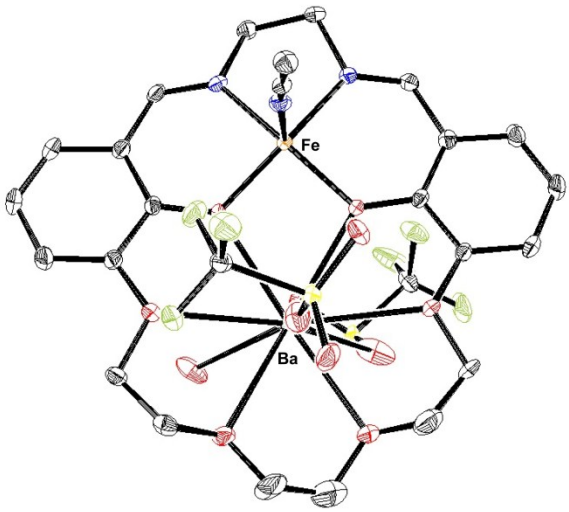

Figure S1. Solid state structure of **2Ba**. Ellipsoids were drawn at 50% probability

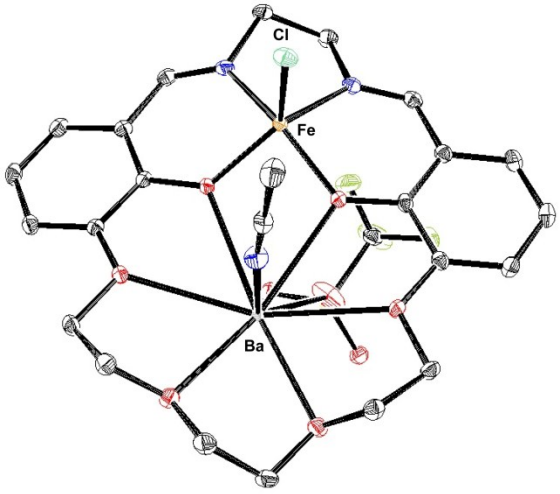

Figure S2. Solid state structure of [**3Ba**]$^{+}$. Outer sphere trifluoromethanesulfonate (OTf^{-}) anion is omitted for clarity. Ellipsoids are drawn at 50% probability.

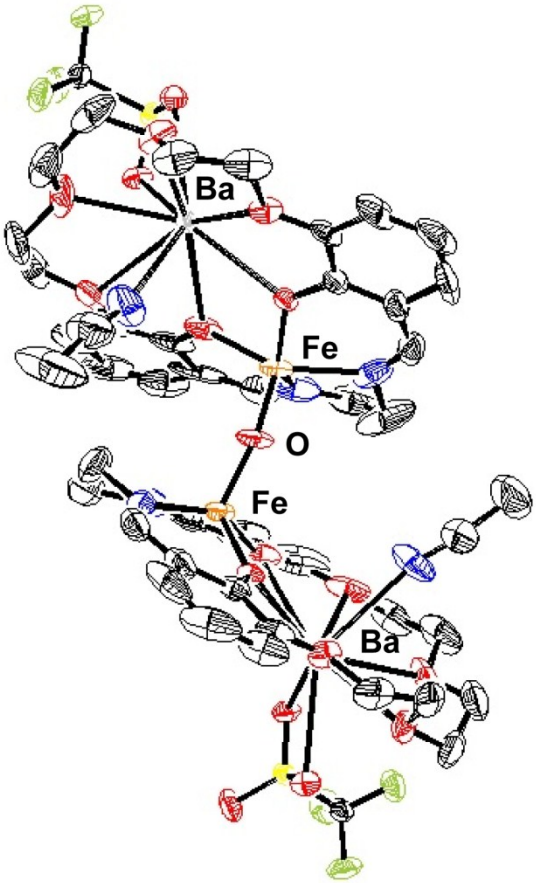

Figure S3. Solid state structure of [**4Ba**]$^{2+}$. Outer sphere trifluoromethanesulfonate (OTf^{-}) anions are omitted for clarity. Ellipsoids are drawn at 50% probability.

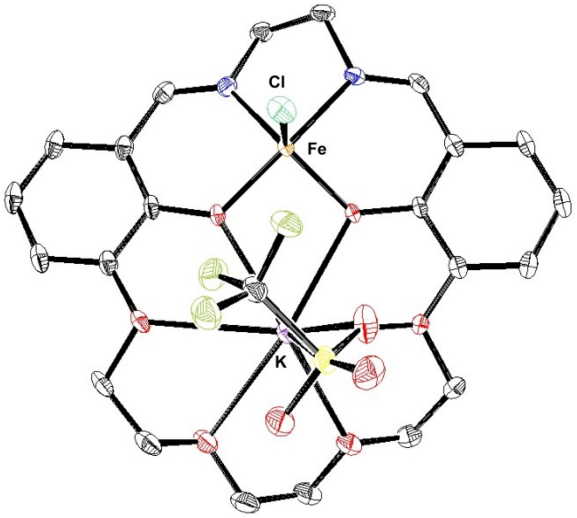

Figure S4. Solid state structure of **3K**. Ellipsoids are drawn at 50% probability.

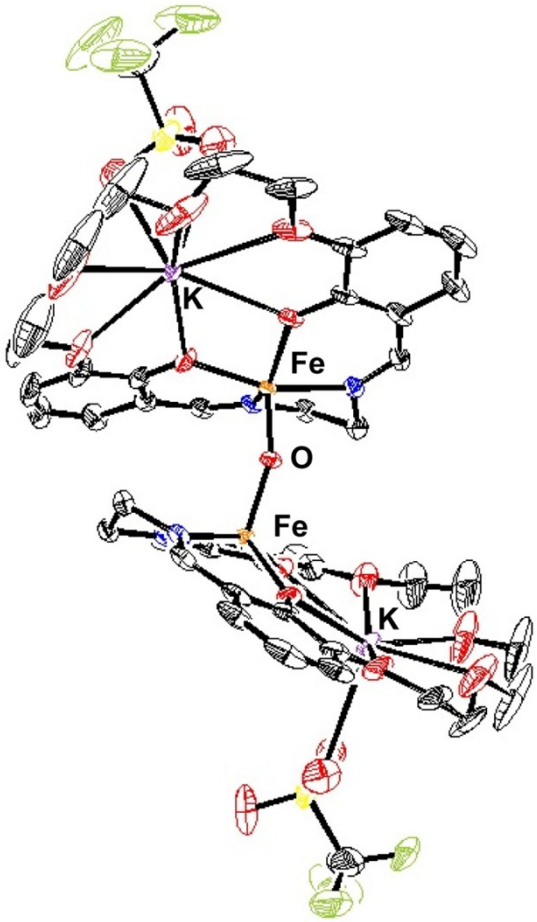

Figure S5. Solid state structure of **4K** (connectivity only). Ellipsoids are drawn at 50% probability.

Table S1. Oxidation catalysis under rigorously dry conditions.

Complexes	Cyclohexene Hydroperoxide (mM)	Cyclohexenol (mM)	Cyclohexenone (mM)	Turnover Number*
3K	5.0	4.6	7.5	39.2
3Ba	2.7	3.2	10.6	48.6
C	0	0.35	0	0.7
No Fe control	1	0.4	0	0.8

*-OOH was not counted toward turnover number

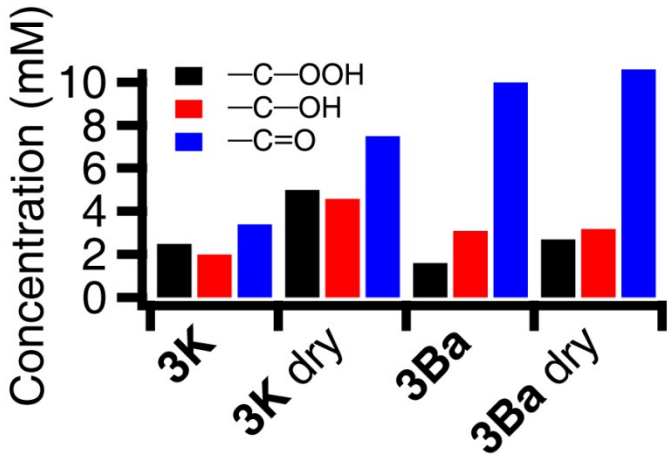

Figure S6. Comparison between oxidation reactivity in ambient and dry conditions.

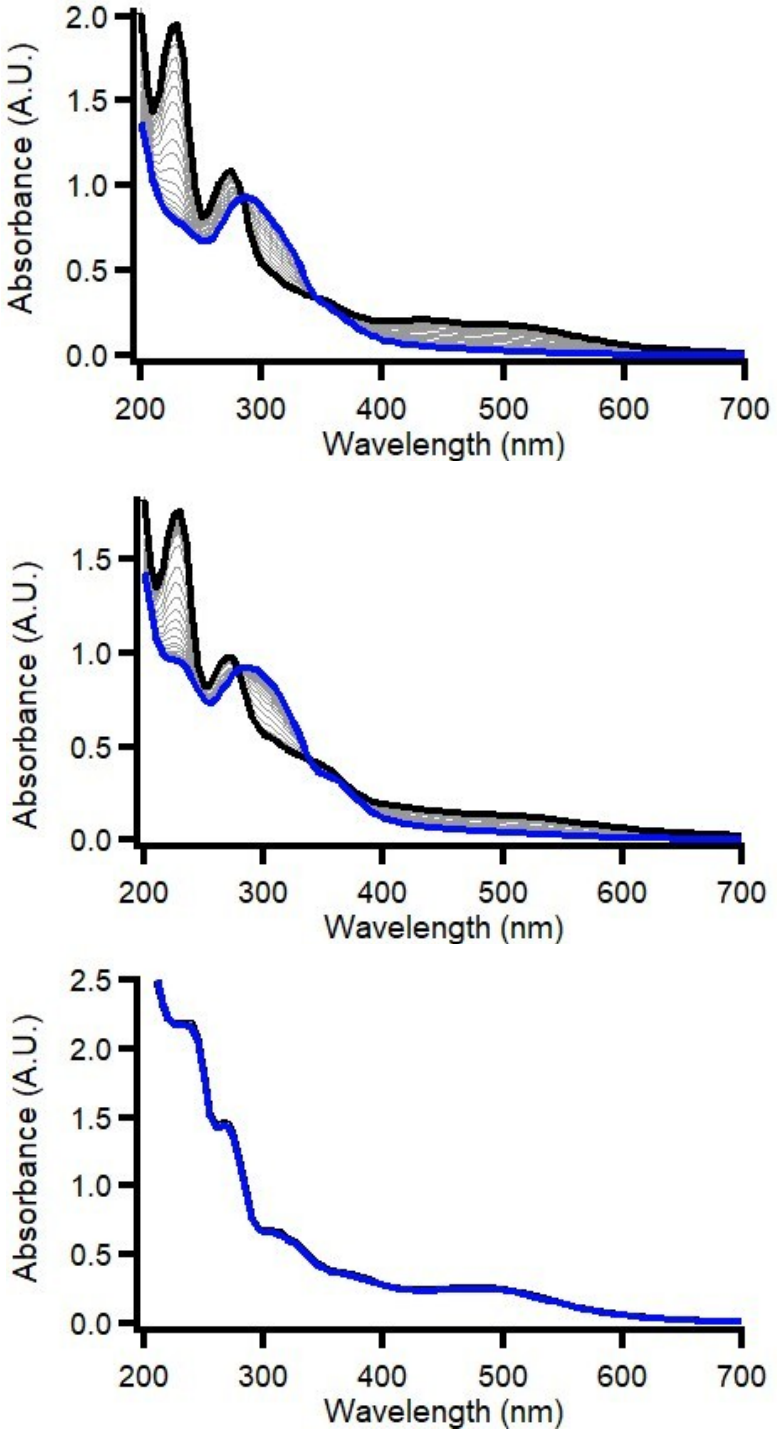

Figure S7. UV-vis spectra of **3K** (top), **3Ba** (middle), and Fe(Cl)(Ph_2salenCl_4) (**C**) (bottom) with additional 10 equivalents of *tert*-BuOOH over 12 hours. Black trace represents t = 0 time point whereas blue trace represents the end point.

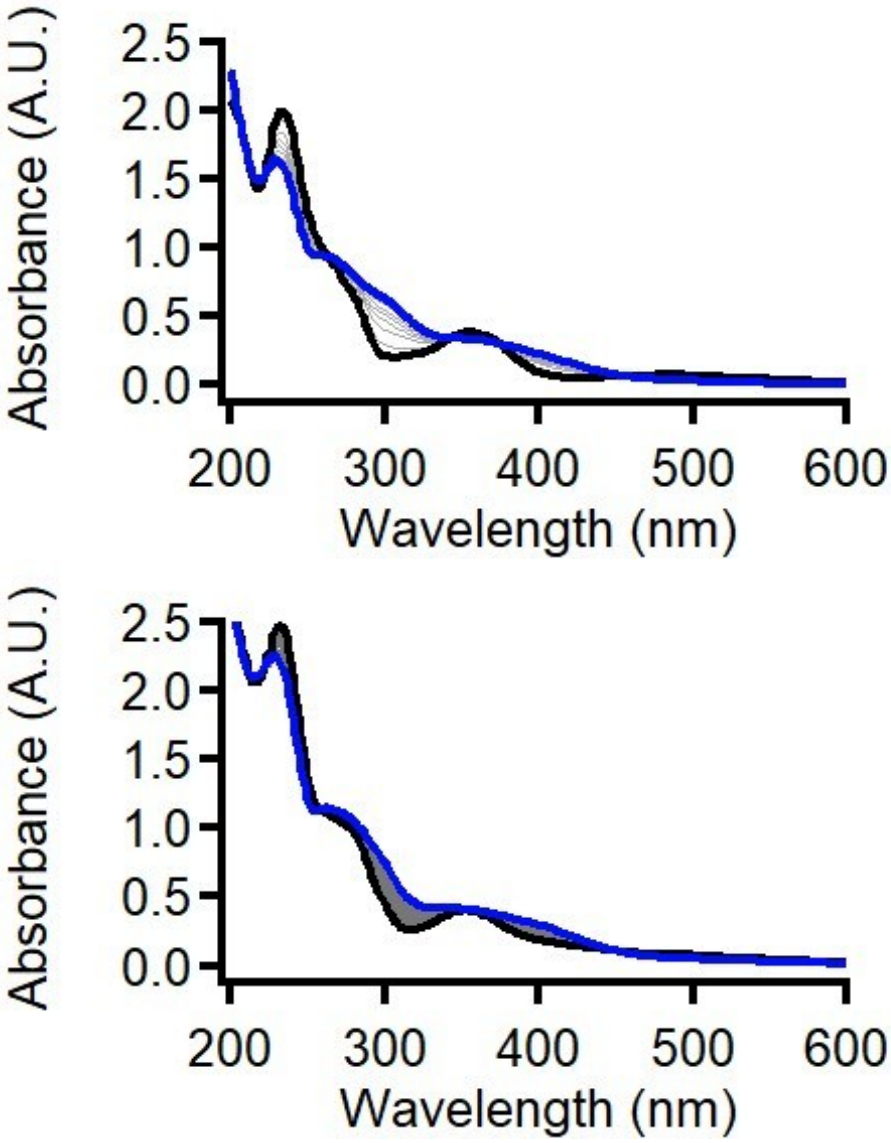

Figure S8. UV-vis spectra of aerobic oxidation of **2K** (top) and **2Ba** (bottom), under air at room temperature. Black trace represents t = 0 time point whereas blue trace represents the end point.

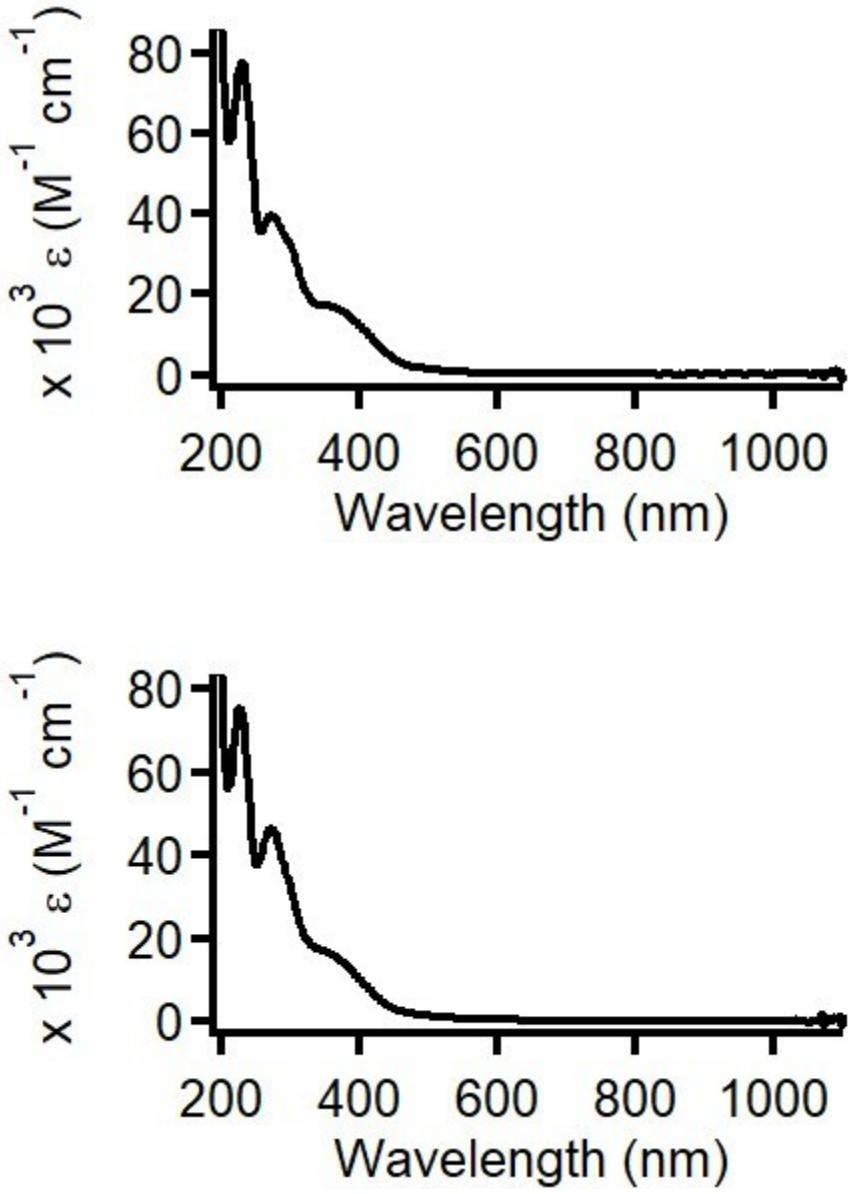

Figure S9. UV-vis spectra of **4K** (top) and **4Ba** (bottom)

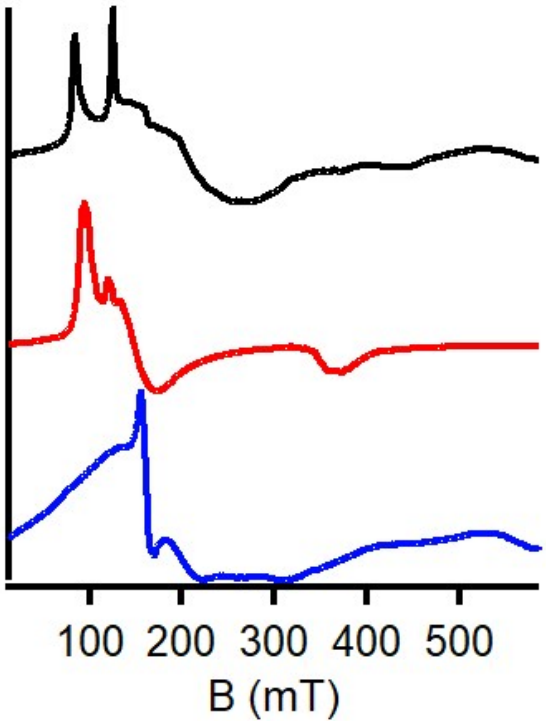

Figure S10. EPR spectra of **3K** (black), **3Ba** (red), and Fe(Cl)(Ph_2salenCl_4) (**C**) (blue), showing characteristics of S = 5/2 Fe complexes.

Table S2. Crystal data and structure refinement for **2Ba.**

Empirical formula	$C_{52}\ H_{54}\ Ba_2\ F_{12}\ Fe_2\ N_6\ O_{24}\ S_4$	
Formula weight	1889.63	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.8491(7) Å	α= 75.9118(8)°.
	b = 11.7518(8) Å	β= 86.5298(8)°.
	c = 14.5176(10) Å	γ = 71.8096(8)°.
Volume	1705.3(2) $Å^3$	
Z	1	
Density (calculated)	1.840 Mg/m^3	
Absorption coefficient	1.792 mm^{-1}	
F(000)	936	
Crystal color	orange	
Crystal size	0.399 x 0.195 x 0.100 mm^3	
Theta range for data collection	1.877 to 29.047°	
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-19 \le l \le 19$	
Reflections collected	21189	
Independent reflections	8297 [R(int) = 0.0177]	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6271	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8297 / 0 / 499	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I) = 7734 data]	R1 = 0.0221, wR2 = 0.0542	
R indices (all data, 0.73 Å)	R1 = 0.0243, wR2 = 0.0554	
Largest diff. peak and hole	1.316 and -0.511 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **3K.**

Empirical formula	C23 H24 Cl F3 Fe K N2 O9 S
Formula weight	691.90
Temperature	128(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.2530(13) Å α= 90°.
	b = 17.652(2) Å β= 90.075(2)°.
	c = 13.5982(15) Å γ = 90°.
Volume	2701.2(5) $Å^3$
Z	4
Density (calculated)	1.701 Mg/m^3
Absorption coefficient	0.965 mm^{-1}
F(000)	1412
Crystal color	red
Crystal size	0.356 x 0.218 x 0.139 mm^3
Theta range for data collection	1.890 to 28.760°
Index ranges	-15 <= h <= 15, -22 <= k <= 23, -17 <= l <= 17
Reflections collected	31457
Independent reflections	6588 [R(int) = 0.0528]
Completeness to theta = 26.000°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6588 / 0 / 370
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I) = 5410 data]	R1 = 0.0349, wR2 = 0.0849
R indices (all data, 0.73 Å)	R1 = 0.0464, wR2 = 0.0912
Extinction coefficient	n/a
Largest diff. peak and hole	0.455 and -0.902 $e.Å^{-3}$

Table S4. Crystal data and structure refinement for **3Ba.**

Empirical formula	C26 H27 Ba Cl F6 Fe N3 O12 S2	
Formula weight	980.26	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7023(6) Å	α= 106.9710(10)°.
	b = 12.7853(7) Å	β= 104.4130(10)°.
	c = 15.6368(9) Å	γ = 98.1780(10)°.
Volume	1747.81(18) $Å^3$	
Z	2	
Density (calculated)	1.863 Mg/m^3	
Absorption coefficient	1.826 mm^{-1}	
F(000)	970	
Crystal color	black	
Crystal size	0.478 x 0.213 x 0.194 mm^3	
Theta range for data collection	1.431 to 29.074°	
Index ranges	-13 <= h <= 12, -17 <= k <= 16, 0 <= l <= 21	
Reflections collected	8424	
Independent reflections	8424 [R(int) = ?]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745802 and 0.606257	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8424 / 0 / 471	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I) = 7898 data]	R1 = 0.0209, wR2 = 0.0571	
R indices (all data, 0.73 Å)	R1 = 0.0232, wR2 = 0.0582	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.561 and -0.418 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for **4K.** Connectivity ONLY

Empirical formula	$C_{46}\ H_{48}\ F_6\ Fe_2\ K_2\ N_4\ O_{19}\ S_2$	
Formula weight	1328.90	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 32.941(2) Å	α= 90°.
	b = 8.2524(6) Å	β= 108.3022(8)°.
	c = 21.7664(15) Å	γ = 90°.
Volume	5617.7(7) $Å^3$	
Z	4	
Density (calculated)	1.571 Mg/m^3	
Absorption coefficient	0.834 mm^{-1}	
F(000)	2720	
Crystal color	red	
Crystal size	0.429 x 0.312 x 0.185 mm^3	
Theta range for data collection	1.302 to 28.779°	
Index ranges	$-42 \le h \le 44$, $-10 \le k \le 11$, $-29 \le l \le 29$	
Reflections collected	32509	
Independent reflections	6863 [R(int) = 0.0198]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6629	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6863 / 0 / 337	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I) = 6128 data]	R1 = 0.0931, wR2 = 0.2677	
R indices (all data, 0.74 Å)	R1 = 0.0990, wR2 = 0.2740	
Largest diff. peak and hole	2.931 and -1.625 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for **4Ba.**

Empirical formula	$[C_{26}\ H_{27}\ Ba\ F_6\ Fe\ N_3\ O_{12.5}\ S_2]_\infty$
Formula weight	952.81
Temperature	88(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcm*
Unit cell dimensions	a = 9.5075(4) Å α= 90°.
	b = 27.3543(12) Å β= 90°.
	c = 28.8412(12) Å γ = 90°.
Volume	7500.8(6) $Å^3$
Z	8
Density (calculated)	1.687 Mg/m^3
Absorption coefficient	1.631 mm^{-1}
F(000)	3776
Crystal color	orange
Crystal size	0.284 x 0.190 x 0.098 mm^3
Theta range for data collection	1.489 to 29.033°
Index ranges	$-12 \le h \le 12$, $-36 \le k \le 35$, $-37 \le l \le 39$
Reflections collected	89405
Independent reflections	9791 [R(int) = 0.0457]
Completeness to theta = 25.500°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.6566 and 0.4943
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9791 / 11 / 439
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I) = 7734 data]	R1 = 0.0680, wR2 = 0.1813
R indices (all data, 0.73 Å)	R1 = 0.0849, wR2 = 0.1950
Largest diff. peak and hole	3.301 and -2.011 $e.Å^{-3}$