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Electronic Supporting Information

Intercepting a Transient Non-Hemic Pyridine N-Oxide Fe(III) Species

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I. Materials and Instrumentation

Iron(III) chloride hexahydrate (98%) and iodosylbenzene diacetate (98 %) were purchased from Sigma-Aldrich. Sodium hypochlorite solution (5 %) was purchased from Acros Organics. Water-^{18}O (97%) was purchased from Euriso-Top. The ^{57}Fe-enriched metal (95.55%) was obtained from Chemgas (SAS JLD Instruments).

UV-visible absorption spectra were recorded on a Varian Cary 60 UV-vis spectrophotometer using 1 cm quartz cuvettes.

X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with a Bruker ER 4116DM X-band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC 503 temperature control system. Sample of typically 1 mM of complexes and intermediates were prepared in acetonitrile added with 0.1 M $TBAPF_6$ then transferred to a degassed EPR tube and frozen to 77 K before their analysis.

Electrospray ionization mass spectrometry experiments were recorded on a Thermo Scientific DSQ 2004 model under either positive or negative modes. Samples were prepared as a 100–200 µM solution in acetonitrile and were directly injected into the spectrometer. For the detection of intermediate species, the samples were frozen in liquid nitrogen following their preparation and melt to room temperature just prior to injection in the spectrometer.

The high-performance gas chromatography experiments (HPGC) were performed on a GC-2010 system from Shimadzu with a Zebron ZB Semi-Volatiles column (25 m, 0.25 mm, 0.25 mm). The Shimadzu GC software was used to perform and analyze chromatograms.

Mössbauer spectra were recorded at 4.2 and 5.8 K, either on a low field Mössbauer spectrometer equipped with a Janis SVT-400 cryostat or on a strong-field Mössbauer spectrometer equipped with an Oxford Instruments Spectromag 4000 cryostat containing an 8 T split-pair superconducting magnet. Both spectrometers were operated in a constant acceleration mode in transmission geometry. The isomer shifts are referenced against that of a room-temperature metallic iron foil. Analysis of the data was performed with a home-made program.

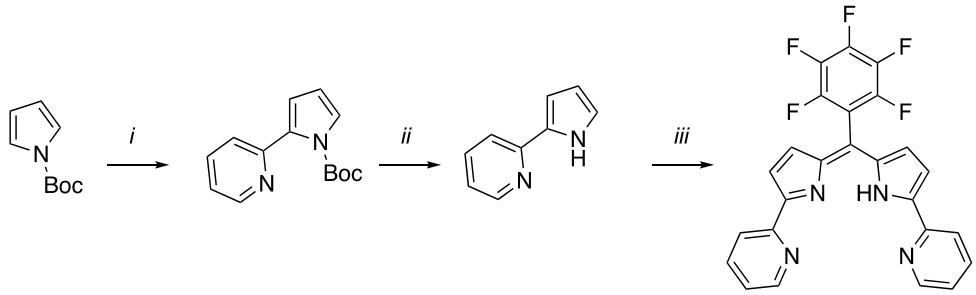
Infra-red spectra were recorded on an attenuated total reflectance-infrared (ATR-IR) Thermo-Nicole

t 6700 FTIR spectrometer, equipped with a mercury-cadmium-telluride (MCT) detector. 5 µL of the sample solution (1 mM) was deposited onto the diamond prism of the ATR-IR and the solvent was evaporated under a stream of nitrogen gas until a dry film was formed. For each spectrum, 200 sample scans were recorded with a resolution of 4 cm^{-1}, a speed of 1.8988 kHz and an aperture of 10 mm from 4000 cm^{-1} to 500 cm^{-1}.

X-ray diffraction data were collected using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo Kα radiation for crystal grown in ACN/Et_2O and Cu Kα radiation for crystal grown in acetone. Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flash-frozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected temperature by means of an N-Helix cooling device to within an accuracy of ±1K. The data were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[3]

II. Experimental procedures

The **DPPyH** ligand was synthesized in 3 steps by optimizing a previously reported[4] procedure.



i) 2-bromopyridine (2.26 mL, 23.60 mmol, 1 equiv.) was dissolved in a 2:1:1 mixture of dioxane, ethanol and water (200 mL). This solution was degassed under argon for 1h. $[Pd(PPh_3)_4]$ (2.73 g, 2.36 mmol, 0.1 equiv.) and (N- Boc-2-pyrrolyl)boronic acid (5.00 g, 23.6 mmol, 1 equiv.) were then added. The mixture was stirred for 20 min. K_2CO_3 (10.00 g, 0.24 mol, 10 equiv.) was added, and the reactional mixture was stirred vigorously at 107 °C for 2 h. After cooling to room temperature, solvents were evaporated. The obtained solid was dissolved in 200 mL of ethyl acetate then washed with 200 mL of aq. K_2CO_3 1M (3 times). The organic phase was dried over Na_2SO_4 then filtered and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 9:1) to yield 2-(N-Boc-1H-pyrrol-2-yl)pyridine as a yellow oil (3.9 g, 68%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.36 (s, 9 H, CH_3), 6.25 (t, *J* = 3.3 Hz, 1 H), 6.42 (dd, *J* = 3.3, 1.8 Hz, 1 H), 7.20 (ddd, *J* = 12, 4.8, 1.2 Hz, 1 H), 7.36–7.43 (m, 2 H), 7.68 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.60–8.64 (m, 1 H) ppm.
ii) 2-(N-Boc-1H-pyrrol-2-yl)pyridine (3.9 g, 16.05 mmol) was dissolved in CH_2Cl_2 (30 mL) and aq. HCl 3 M (30 mL) was added. The biphasic mixture was vigorously stirred at room temperature for 60 h. The solution was neutralized by addition of a a sat. aq. $NaHCO_3$ solution and extracted with 100 mL of water (3 times). The organic phase was dried over Na_2SO_4 and filtered. The solution was concentrated to yield 2-(2- Pyrrolyl)pyridine as a white solid (2.28 g, 95 %). ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 6.30 (dt, *J* = 2.6, 3.6 Hz, 1 H), 6.7 (m, 1 H), 6.9 (m, 2 H), 7.03 (dd, *J* = 2.0, 5.5 Hz, 1 H), 7.54 (d, *J* = 7.7 Hz, 2 H), 7.62 (td, *J* = 7.7, 1.6 Hz, 1 H), 8.45 (d, *J* = 5 Hz, 1 H), 9.8 (br. s, NH) ppm.
iii) *p*-toluenesulfonic acid (4.5 g, 23.7 mmol, 3 equiv.) was dissolved in toluene (50 mL). The Dean stark method was used to eliminate water in the solution. 2-(2-Pyrrolyl)pyridine (2.28 g, 15.8 mmol, 2 equiv.), pentafluorobenzaldehyde (1.55 g, 7.9 mmol, 1 equiv.) and 1,1,2,2- tetrachloroethane (50 mL) were then added. The mixture was heated at 138 °C under argon for 7 day, after which it was basified with aq. K_2CO_3 (1 M). The aqueous phase was extracted with chloroform, and the combined organic phases were concentrated and dissolved in dichloromethane (100 mL). A solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (10.5 g, 47.4 mmol, 6 equiv.) in tetrahydrofurane (80 mL) was then added dropwise. The reactional mixture was stirred overnight at room temperature. The solvents were evaporated. The obtained solid was dissolved in 200 mL chloroform, then extracted 3 times with 200 mL K_2CO_3 1 M. The organic phase was dried with Na_2SO_4 and filtered then concentrated. Precipitation in methanol (30 mL) at -20 °C followed by filtration and drying allowed the isolation of the DPPyH ligand (2 g, 54 %) as a brown solid .1H NMR ($CDCl_3$, 250 MHz): δ = 6.59 (d, *J* = 4.4 Hz, 2 H, H_{pyrrol}), 7.10 (d, *J* = 4.4 Hz, 2 H, H_{pyrrol}), 7.29 (m, 2 H), 7.82 (dd, *J* = 7.8, 1.6 Hz,2 H), 8.20 (d, *J* = 8.1 Hz, 2 H), 8.72 (d, *J* = 4.7 Hz, 2 H), 13.70 (br. s, 1 H, NH) ppm.

[FeDPPyCl$_2$]: A solution of DPPy ligand (100 mg, 215 µmol, 1 equiv.) in methanol (20 mL) was added dropwise to a solution of $FeCl_3{\cdot}6H_2O$ (58,3 mg, 215 µmol, 1 equiv.) in methanol (10 mL) at room temperature, followed by addition of diethyl ether (50 mL) in order to precipitate the solid. The brown residue was filtered and dried under vacuum to give complex [FeDPPyCl$_2$] (116 mg, 197 µmol, 91%). Single crystals were obtained by slowly diffusing diethyl ether to a saturated solution of complex [FeDPPyCl$_2$] in acetonitrile. ESI$^+$-HRMS: calcd. For $[C_{25}H_{12}ClF_5FeN_4]^+$ 554.0015; found 553.9995. UV-vis (CH_3CN): 668 nm (ε = 10 000 $M^{-1}cm^{-1}$) , 589 nm (ε = 21 600 $M^{-1}cm^{-1}$), 320 nm (ε = 27 200 $M^{-1}cm^{-1}$), 298 nm (ε = 27 700 $M^{-1}cm^{-1}$).

Iodosylbenzene[5] **(PhIO)**: 30 mL of 3 M sodium hydroxide was added over a 5 min period into iodosylbenzene diacetate (5 g., 15.5 mmol) placed in a 50 mL flask with vigorous stirring. The reaction mixture was stirred for

an additional 45 minutes to complete the reaction. The solid was filtered and washed 3 times with 100 mL water then with 50 mL chloroform (3 times). The obtained solid was dried under vacuum to yield 2.9 g PhIO (85 %).

$^{57}FeCl_3$: The ^{57}Fe-enriched $FeCl_3$ was synthesized according to the literature.[6] ^{57}Fe-enriched iron powder (100 mg) was suspended in ethanol (30 mL) and HCl was bubbled through the reaction mixture for 3 hours. The solvent was then removed by rotary evaporation and placed under high vacuum for 12 h.

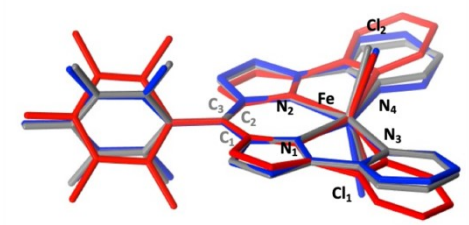
^{57}[FeDPPyCl$_2$]: The ^{57}Fe-enriched complex was prepared by metalation with the ^{57}Fe-enriched $FeCl_3$ using the procedure described above.

Stoichiometric oxidation of [FeDPPyCl$_2$] by PhIO: Solid PhIO (10eq., 1.1 mg) was added to a solution of the [Fe(DPPy)Cl$_2$] complex (10 mL, 50 µM) at room temperature. The reaction mixture was sonicated for 10 s, then the insoluble PhIO was filtered off using a syringe filter. Alternatively, a freshly prepared solution of PhIO in MeOH (1 eq., 3 µL, 50 mM) was added to the solution of the [FeDPPyCl$_2$] complex (3 mL, 50 µM). A slightly lessen conversion was observed in that case (see Fig S6). For labelling experiment, the 1st procedure was performed on a 1mL volume scale, followed by the addition of 20 µL of ^{18}O-labeled water.

III. Crystal structure determination

CCDC 1966063-1966064 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

3 Structures were obtained by X-ray analysis of single crystals grown form Et$_2$O/ACN at rt (A), acetone at 30°C (B,C). Their main features are summed up below, and crystallographic details are given in what follows. According to a CCDC search, we found that the average Fe(III)-N bond length in Fe(III) porphyrin complexes is 2.02 Å. While, the average length for Fe(III)-pyridine bonds is 2.15 Å with only 10% of reported structures showing bond distances over 2.23 Å.



Structure	A	B	C
Fe-N$_1$ / Fe-N$_2$	2.048 Å	2.047 / 2.073 Å	2.076 Å
Fe-N$_3$ / Fe-N$_4$	2.238 Å	2.238 / 2.207 Å	2.240 Å
N$_1$FeN$_2$	82.5°	81.5°	81.2°
N$_3$FeN$_4$	127.1°	127.7°	131.4°
Cl$_1$FeCl$_2$	152.0°	151.1°	147.3°

Figure S1: Left : Overlay along N_1-C_1-C_2-C_3-N_2 fragment of the FeDPPy in A, B, C (right, H and C_6F_5 omitted); Right : Selected parameters showing 1st coordination sphere distortions along the 3 forms.

a. Structure obtained from crystals grown in ACN/Et$_2$O (A)

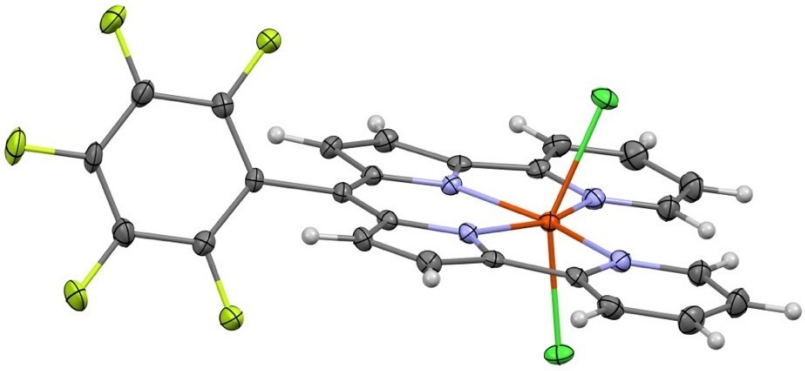


Figure S2: ORTEP representation at 30% of probability of X–Ray structure of [FeDPPyCl$_2$] complex.

The presence of solvent molecules could easily be seen by residual peaks located in closed spherical cavities (Figure S3).

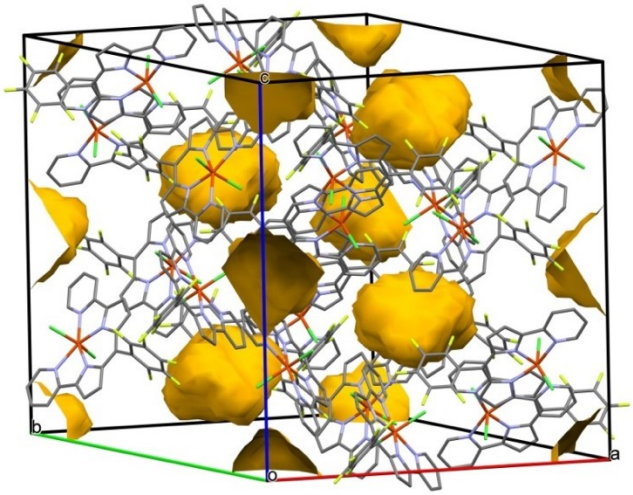


Figure S3: Crystal packing displaying space occupied by solvent molecules.

Unfortunately, they were disordered so badly that it could not be modeled even with restraints. Consequently, SQUEEZE[3] (from PLATON) was used to calculate the void space, the electron count and to get a new HKL file. According to the SQUEEZE results and the different experimental evidence, a total number 14 CH_3CN solvent molecules (308 electrons) were considered per unit cell. Without solvent molecules: R1= 0.0848 for 3835 reflections of I > 2σ(I) and wR2= 0.2502 for all data. With solvent molecules (SQUEEZE): R1= 0.0784 for 3835 reflections of I > 2σ(I) and wR2= 0.1902 for all data, the volume fraction was calculated to 1203 Å^3 which corresponds to 11% of the unit cell volume, and to 305 electrons per unit cell allocated to solvent molecules. The crystal data collection and refinement parameters are given in Table S1.

b. Structures obtained from crystals grown in acetone at 30°C (B and C)

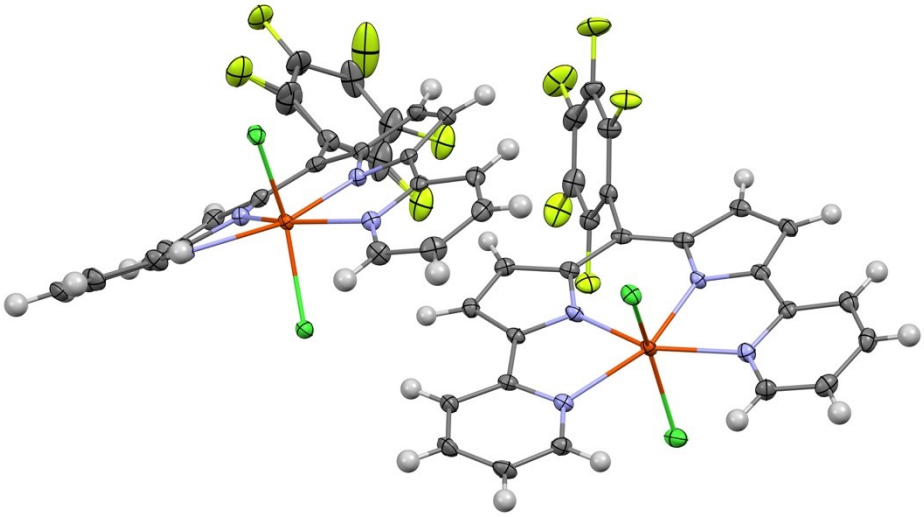


Figure S4: ORTEP representation at 30 % of probability of X–Ray structure of the two crystallographically independent molecules of [FeDPPyCl$_2$] complex.

In the crystal of the [FeDPPyCl$_2$] complex, the asymmetric unit is composed of one and a half molecules. One of [FeDPPyCl$_2$] complexes is situated on two-fold symmetry axes. The crystal data collection and refinement parameters are given in Table S2.

Table S1: Crystallographic data and structure refinement details from crystals grown in ACN/Et_2O.

Compound	**[FeDPPyCl2] (A)**
Empirical Formula	C_{25} H_{12} Cl_2 F_5 Fe N_4 [+ 7/9 (C_2 H_3 N)]
M_r	590.14
Crystal size, mm^3	0.08 x 0.08 x 0.04
Crystal system	trigonal
Space group	R -3 c
a, Å	22.4084(16)
b, Å	22.4084(16)
c, Å	25.9110(19)
α, °	90
β, °	90
γ, °	120
Cell volume, $Å^3$	11267.7(18)
Z ; Z'	18; 1/2
T, K	100 (1)
Radiation type ; wavelength Å	MoKα; 0.71073
F_{000}	5310
μ, mm^{-1}	0.868
θ range, °	2.623–30.530
Reflection collected	100 553
Reflections unique	3 835
R_{int}	0.1980
GOF	1.023
Refl. Obs. (I>2σ(I))	2 070
Parameters	170
wR_2 (all data)	0.1902
R value (I>2σ(I))	0.0784
Largest diff. peak and hole (e-.$Å^{-3}$)	0.901; -0.511

Table S2: Crystallographic data and structure refinement details from crystals grown in acetone at 30°C.

Compound	**[FeDPPyCl2] (B,C)**
Empirical Formula	C_{25} H_{12} Cl_2 F_5 Fe N_4
M_r	590.14
Crystal size, mm^3	0.26 x 0.10 x 0.05
Crystal system	monoclinic
Space group	*C* 2/*c*
a, Å	19.907(3)
b, Å	13.511(2)
c, Å	26.718(5)
α, °	90
β, °	104.497(8)
γ, °	90
Cell volume, $Å^3$	6957(2)
Z ; Z'	12 ; 3/2
T, K	100 (1)
Radiation type ; wavelength Å	CuKα; 1.54178
F_{000}	3540
μ, mm^{-1}	7.755
θ range, °	3.417 - 66.749
Reflection collected	52 122
Reflections unique	6 155
R_{int}	0.0422
GOF	1.021
Refl. Obs. (I>2σ(I))	5 818
Parameters	512
wR_2 (all data)	0.0864
R value (I>2σ(I))	0.0330
Largest diff. peak and hole (e-.$Å^{-3}$)	1.407 ; -0.593

IV. Catalysis

Catalytic experiments were carried out in a glass vial (3 mL) containing 1 mL of acetonitrile, 1 mM of [$FeDPPyCl_2$] (1 eq.) and 800 mM of substrate. The reaction was started by adding 20 eq. of PhIO to the solution. After stirring for the desired reaction time at room temperature, 3 µL of internal standard solution (2 mM final) were added to the reaction mixture. The resulting solution was filtered through a short silica gel column. 1.5 mL MeOH were used to collect all remaining organic products. The obtained solution was injected into HPGC to detect and quantify the oxidized products. Conversions were determined by GC against internal standards and calculated relatively to the PhIO as a limiting reagent.

Table S3: Catalytic oxidation activity of [$FeDPPyCl_2$]. [$FeDPPyCl_2$]/PhIO/Substrate 1:20:800 eq.

Substrate	Reaction Time	Products	Conversion rel. to PhIO	TON_{max}
PPh_3	<1min	$O=PPh_3$	100 %	20
SPhMe	2h	O=SPhMe	95 %	19
cyclooctene	2/24h	cyclooctene oxide	30 / 46 %	9.2
cyclohexene‡	2h	cyclohexene oxide	12 %	3.2
		cyclohexenol	4 %	
toluene	2h/24h	benzyl alcohol	51 % / 93 %	20
		benzaldehyde	1 % / 7 %	
diphenylmethane	24h	diphenylmethanol	15 %	6.2
		benzophenone	8 %	
cyclohexane	24h	cyclohexanol	3 %	1.4
		cyclohexanone	2 %	

‡ the solvent was degassed prior experiment

V. UV-visible Absorption spectroscopy

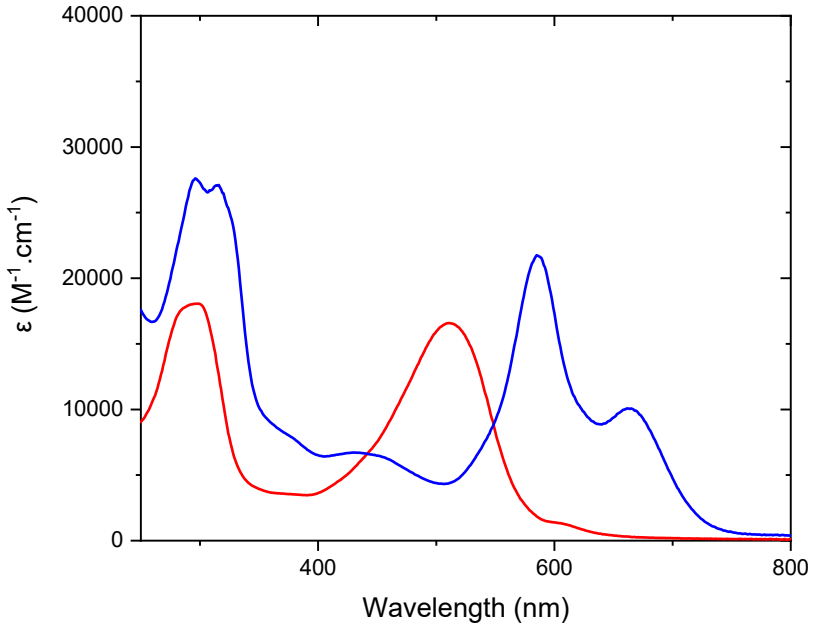


Figure S5: UV-visible spectra of DPPy ligand (red) and [FeDPPyCl$_2$] (blue) in acetonitrile.

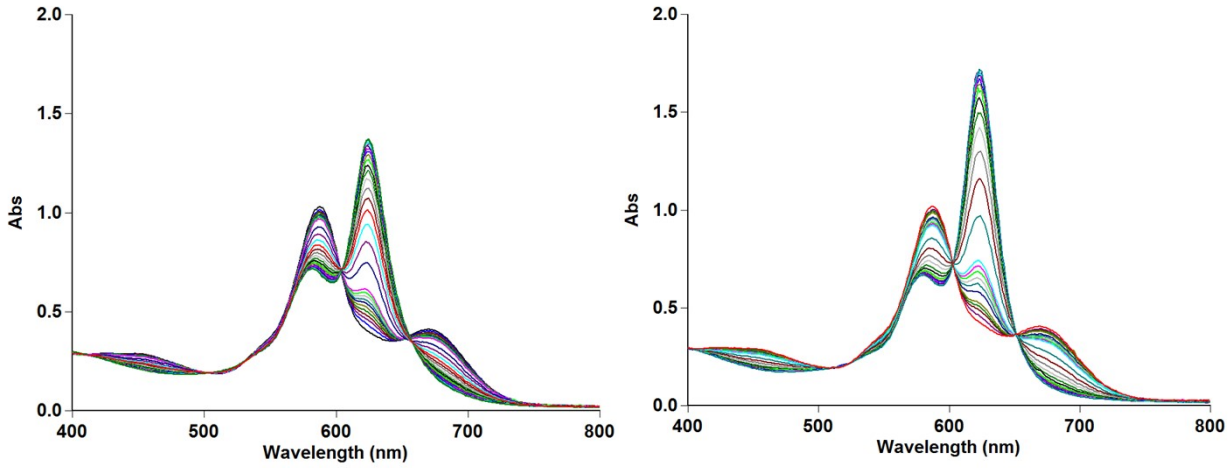


Figure S6: UV-visible spectral changes observed with a [FeDPPyCl$_2$] solution in ACN upon addition of ca. 1eq (left) or 2 eq (right) of PhIO in MeOH at -40°C. 10 spectra /min between t=0 and 1min, then 1 spectrum /min until maximum is reached.

The previous experiments were performed to assess the number of PhIO equivalent needed to generate the detected active species. The small conversion increase observed from addition of 1 to 2eq of PhIO is probably due to an overestimation of the concentration of the prepared PhIO solution, this reagent being known to be very difficult to purify. We can thus assume that one equivalent of PhIO only is needed to generate the active species.

VI. EPR spectroscopy

The experimental spectrum of [FeDPPyCl2] could be fitted with a 1:1 mixture of two high spin (S = 5/2) iron(III) species probably corresponding to two different geometries. The first set is characterized by three signals at g = 5.1, 3.7 and 2.0 (E/D=0.27) while the second one is characterized by three signals at g = 9.1, 4.2 and 3 (E/D=0.18).

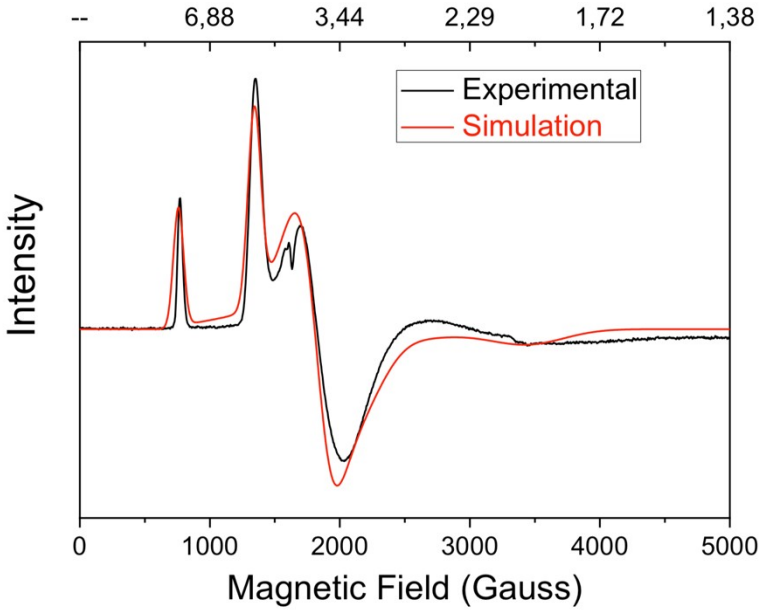


Figure S7: EPR spectrum of [FeDPPyCl$_2$] (1 mM) in acetonitrile in presence of TBAPF$_6$ (0.1 mM) (cavity signal substracted) and its simulation. Experimental conditions: Microwave power 0.250 mW, microwave freq. 9.63 GHz, modulation amplitude 8 Gauss, gain 44 dB, temperature 10 K.

The experimental spectrum of the oxidized complex could be fitted with a high spin (S = 5/2) iron(III) species with g = 4.28 (E/D=0.33).

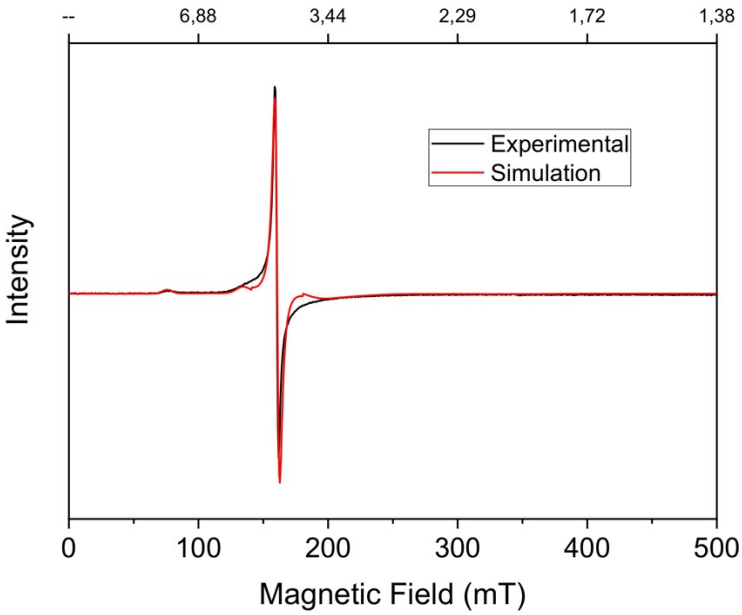


Figure S8: EPR spectrum of [FeDPPyCl$_2$] (1 mM) in acetonitrile in presence of TBAPF$_6$ (0.1 mM) at 10 K after oxidation by PhIO and its simulation (red); Microwave power 0.250 mW, microwave freq. 9.63 GHz, modulation amplitude 8 Gauss, gain 44 dB, temperature 10 K.

VII. Mössbauer spectroscopy

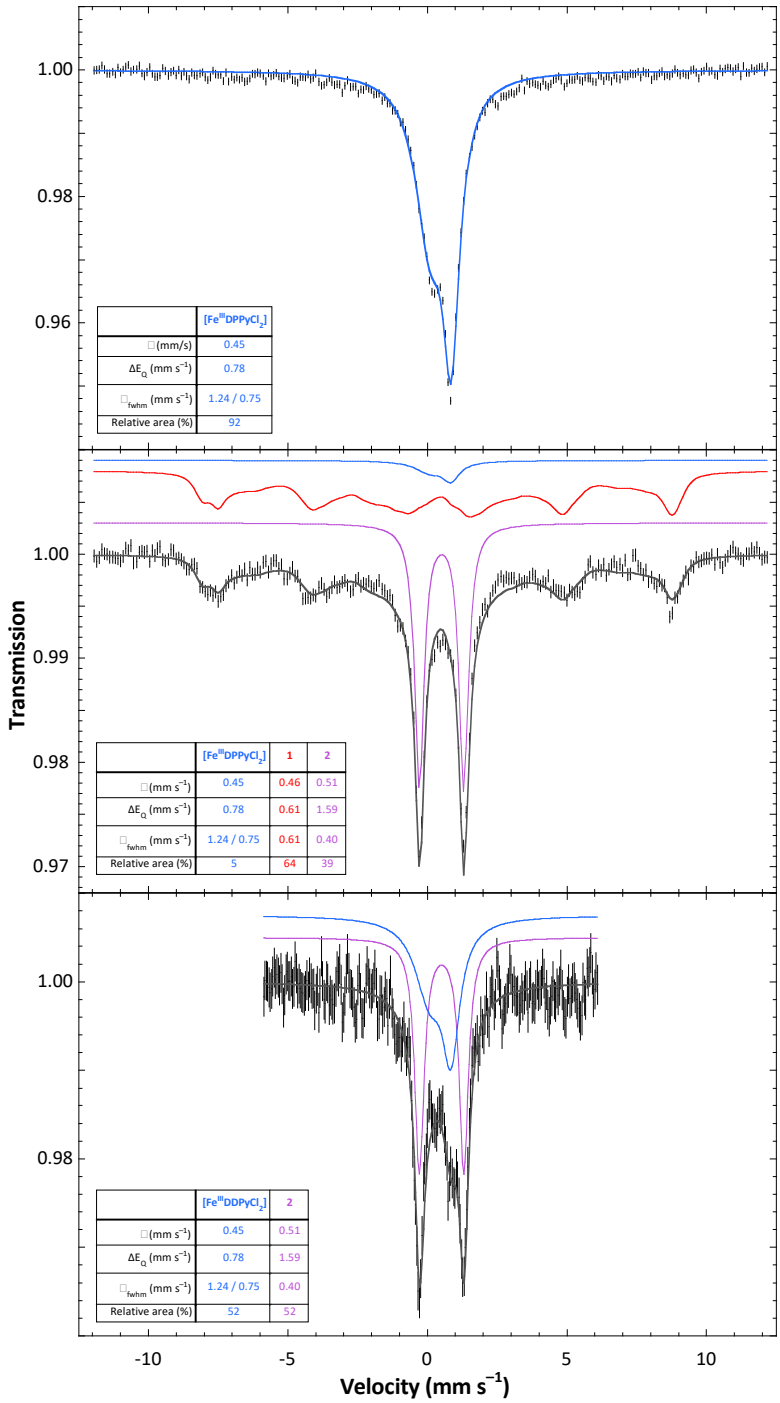


*Figure S9: Experimental Mössbauer spectra (hatched bars) recorded at 4.2 (bottom) and 5.8 K (top and middle) using a 0.06 T external magnetic field applied parallel to the γ-beam. Spectra were recorded on frozen solutions of [^{57}FeDPPyCl$_2$] in acetonitrile (2 mM) (top), 10 min after oxidation by PhIO (middle), and after additional 2 h at room temperature (bottom). A simultaneous monitoring of the reaction was performed by UV-visible in order to take samples corresponding to the green and red spectra reproduced on the left part of Figure 2. Simulations are overlaid on experimental spectra as thick solid lines and deconvolutions are displayed above. The starting species (in blue) is well-described by a doublet with two different linewidths.[7] Species **2** (in mauve) was simulated by a doublet whereas species **1** (in red) was simulated assuming a S=5/2 spin state. Species **1** is tentatively assigned to the transient species **I**.*

VIII. Mass spectrometry

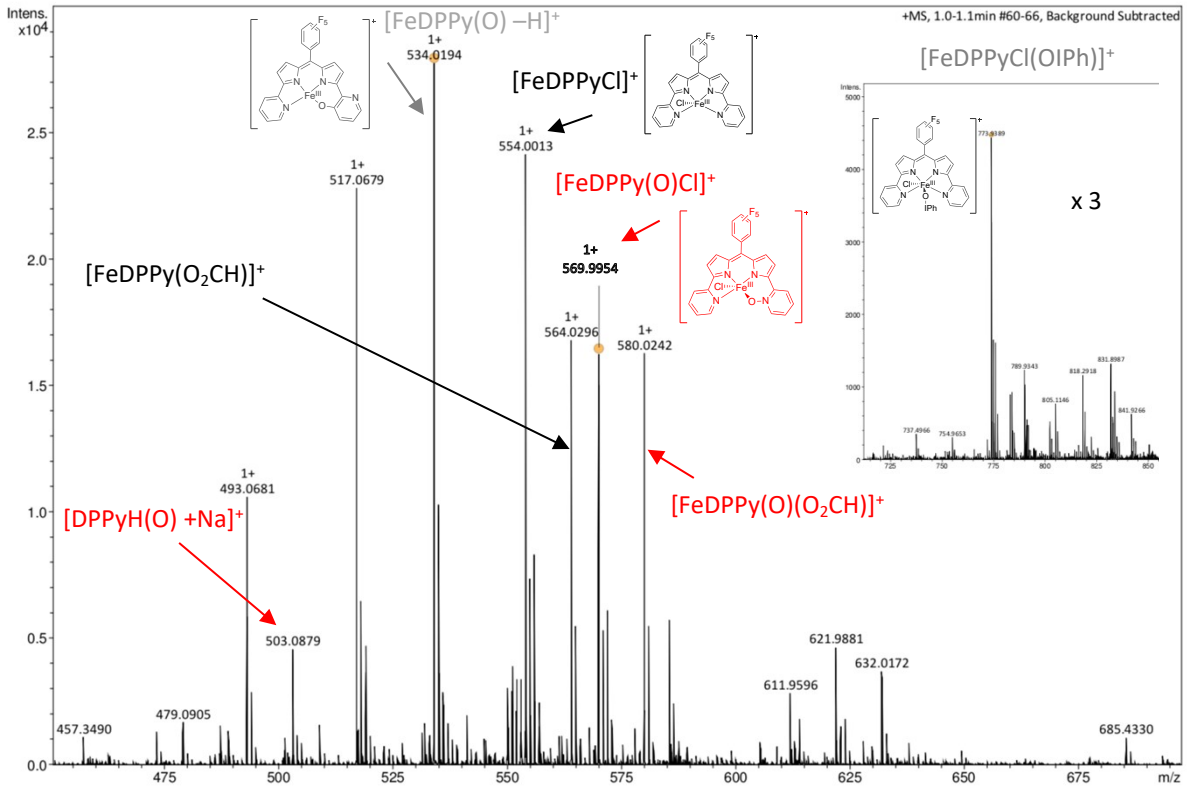


Figure S10: ESI+-HRMS analyses and possible assignment of the oxidation products obtained from the reaction of [FeDPPyCl$_2$] with PhIO in acetonitrile. Formiate adducts result from anion exchange with the calibrant, sodium formiate.

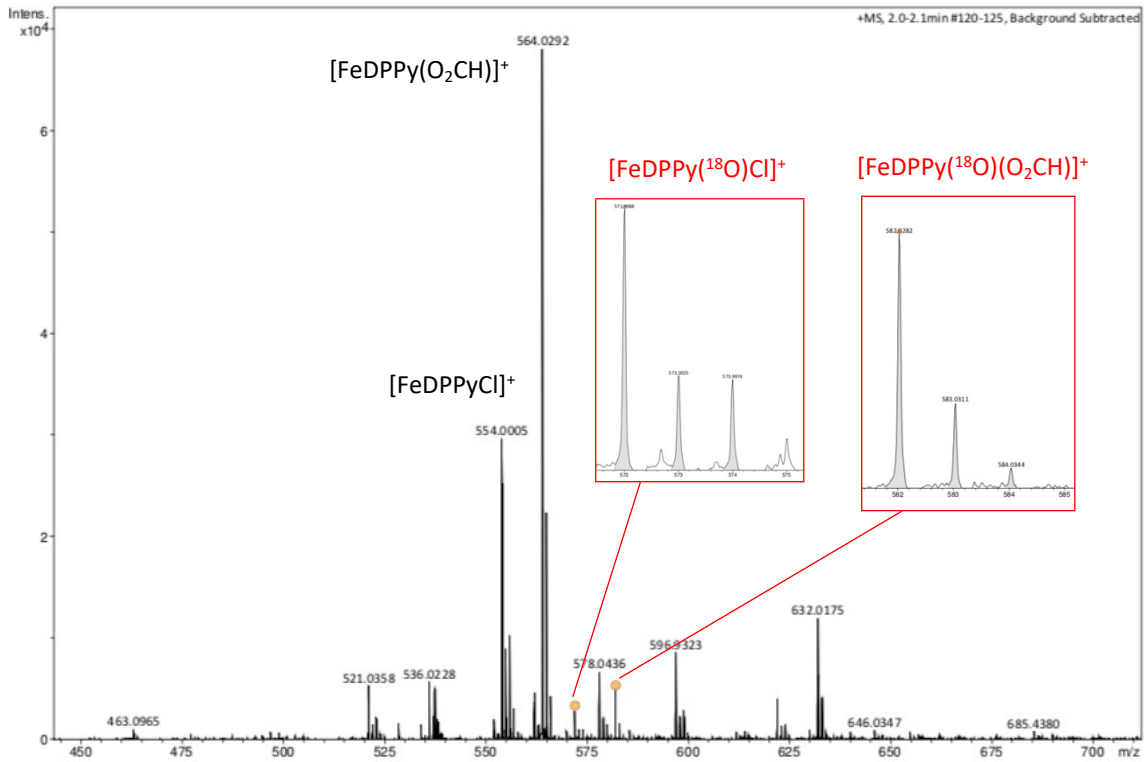


Figure S11: ESI+-HRMS analyses showing isotopic shifts upon addition of H218O to the previous sample

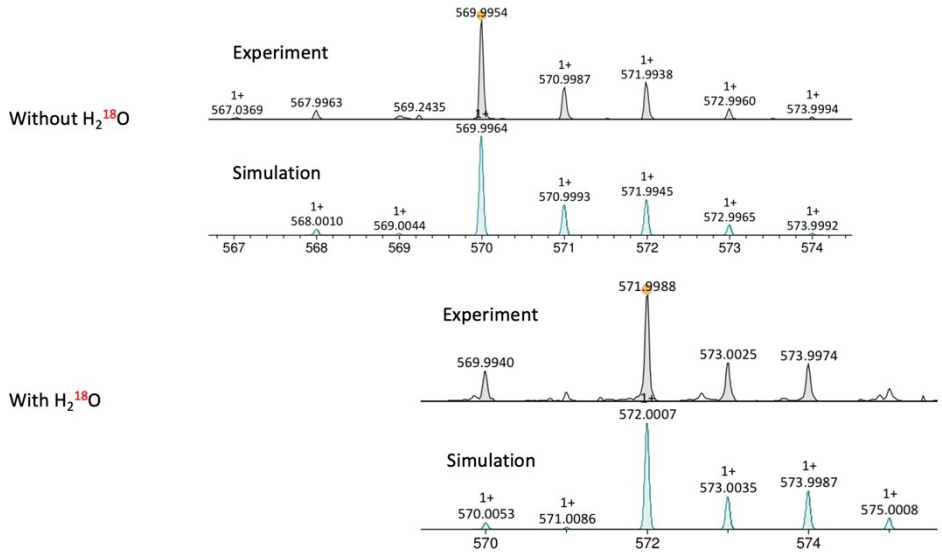


Figure S12: Zoom on the isotopic peak distribution corresponding to $[FeDPPy(O)Cl]^+$ in the absence and presence of $H_2^{18}O$.

IX. Infra-Red spectroscopy

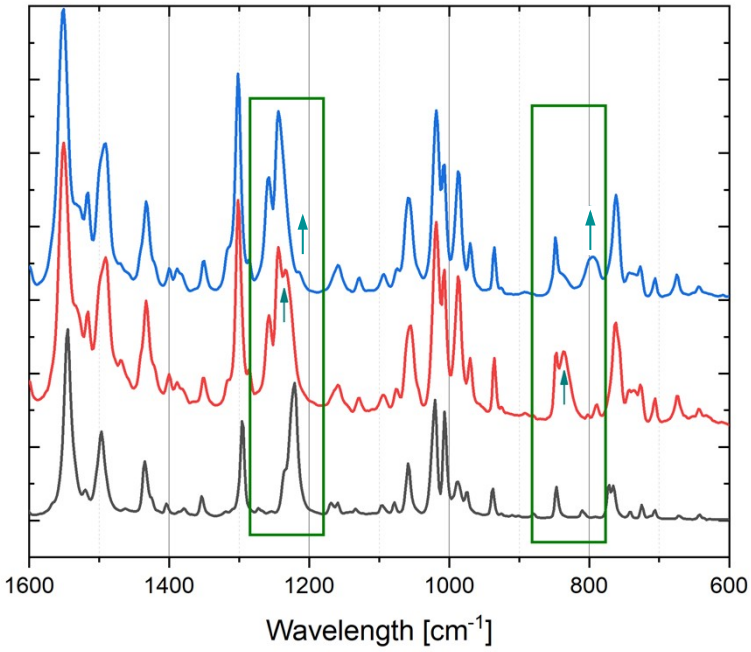


Figure S13: Infrared spectra of a solution of $[FeDPPyCl_2]$ before (black), after addition of PhIO (red), followed by addition of $H_2^{18}O$ (blue).

X. Reactivity with NaClO

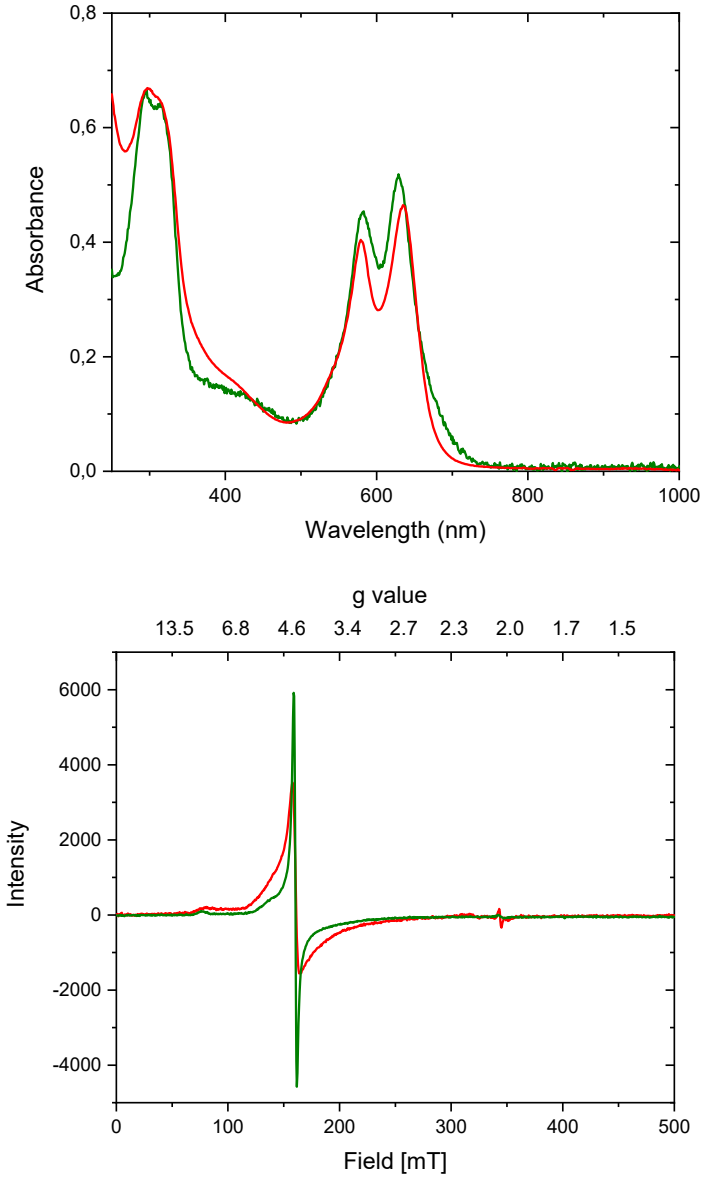


Figure S14: Comparison of the spectroscopic features of the species formed upon oxidation of [FeDPPyCl$_2$] by PhIO (red) and NaClO (green) monitored by UV-vis (top) and EPR (bottom) spectroscopies.

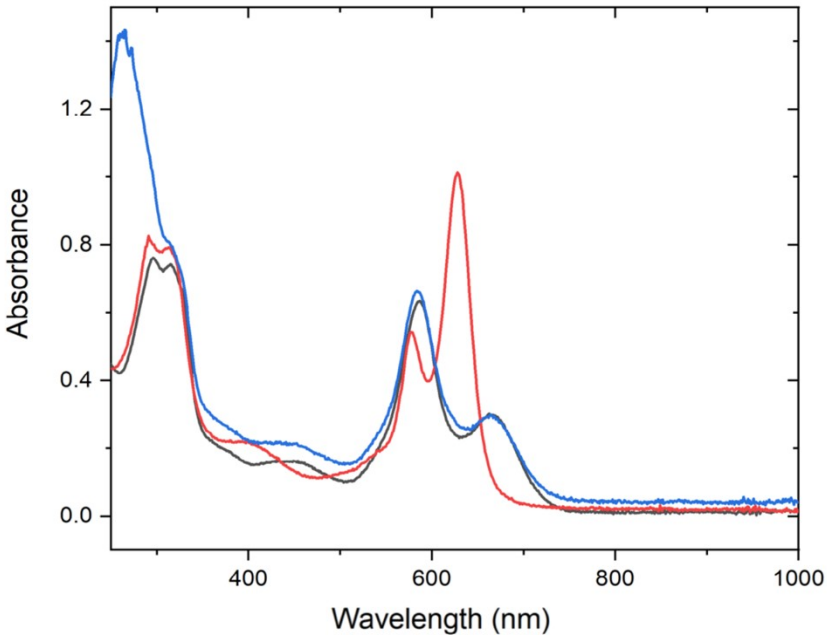


Figure S15: UV-vis spectra of a [FeDPPyCl$_2$] solution in ACN, before (blue) and after oxidation by NaClO (red) followed by its reaction with PPh$_3$ (black).

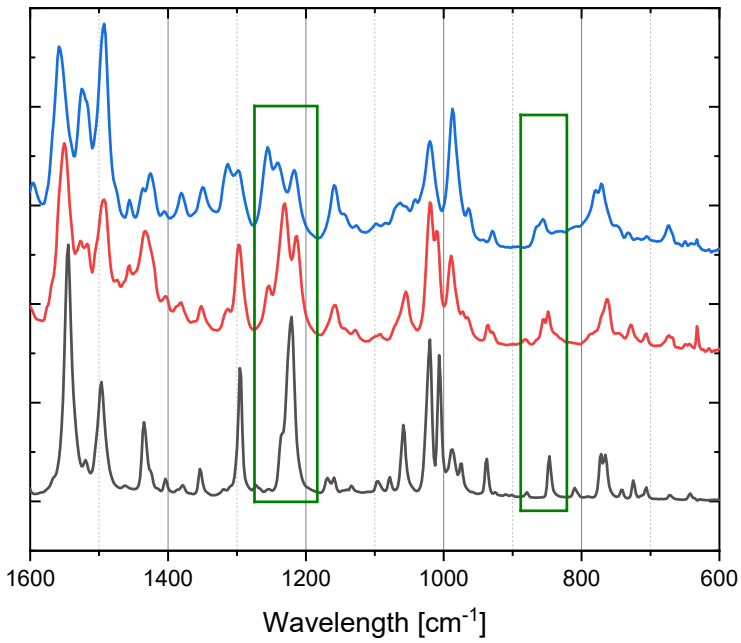
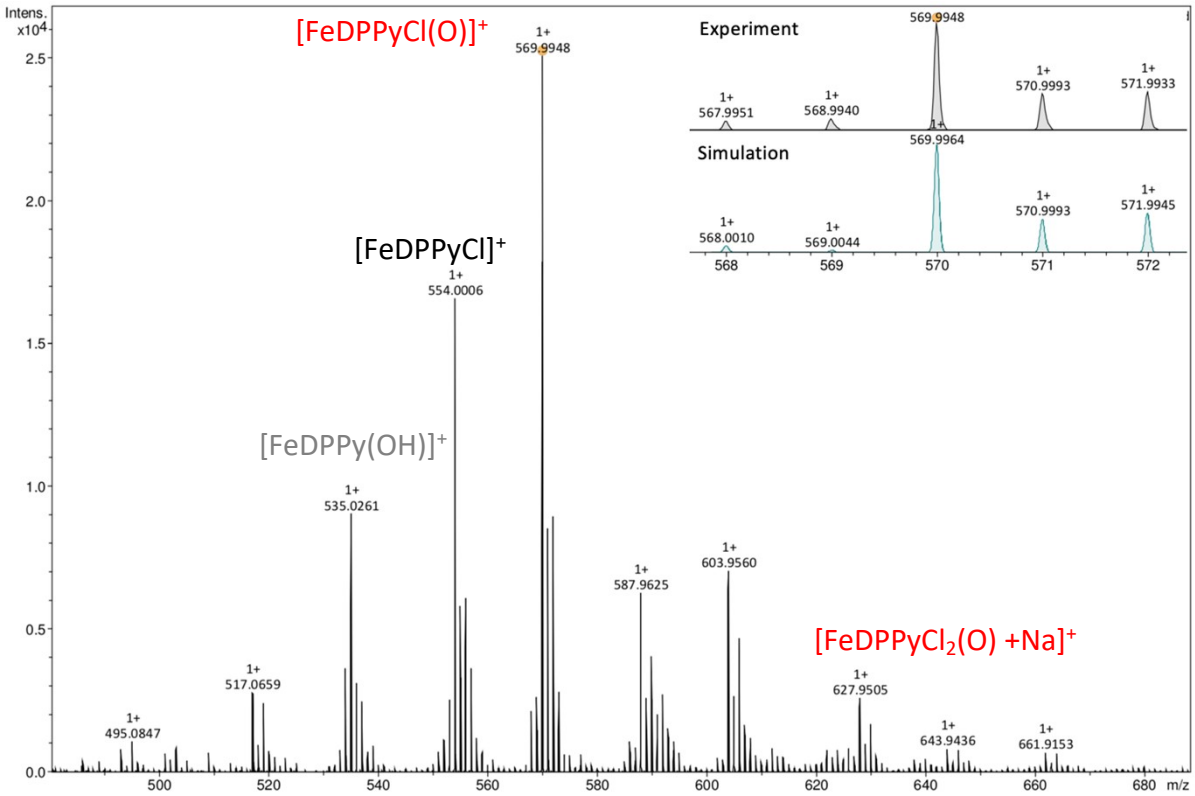


Figure S16: Infrared spectra of [FeDPPyCl$_2$] precursor (black), after adding NaClO (red) then H$_2$^{18}O (blue).



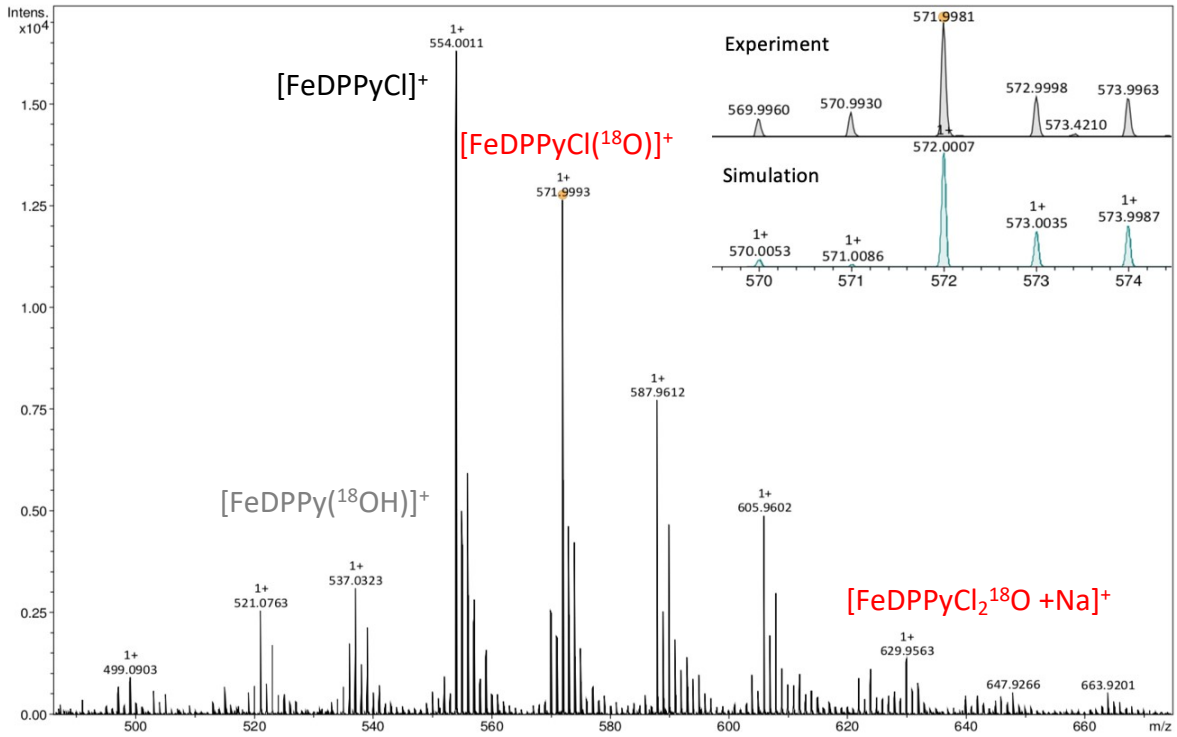


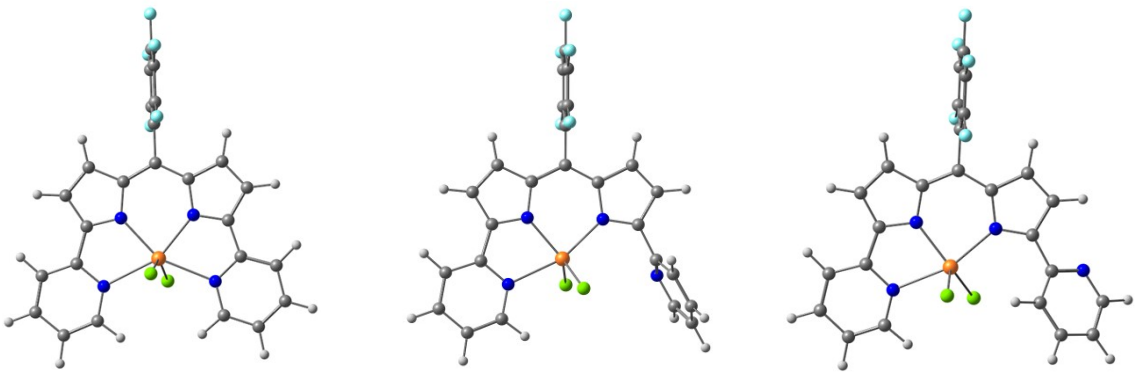
Figure S17: ESI⁺-HRMS analyses of [FeDPPyCl$_2$] + NaClO frozen solution in acetonitrile with $H_2{}^{16}O$ (Top) with $H_2{}^{16}O$ $H_2{}^{18}O$ (Bottom). Inset: Experimental and simulated isotopic distribution of detected species at m/z =569.9948 and 571.9981.

XI. DFT Calculations

Calculations are based on the density functional theory (DFT) and were performed with Gaussian 09 software package.[8] Geometries were optimized in the gas phase, using the B3LYP[9] functional which is known to perform well in IR prediction,[10] in combination with TZVP[11] (H,C,N,O,Cl,Fe) and the ECP implemented def2-SVP(I)[12] basis sets. Optimizations were followed by vibrational analysis to confirm the nature of minima or transition states and predict IR spectra. Figures of the structures were performed using ChemCraft or Mercury program. IR spectra were generated by convoluting the theoretical stick spectra with a gaussian fit available in Chemcraft.

Table S4: Comparison of some structural parameters between the geometry optimized [5][FeDPPyCl$_2$] and the X-ray characterized structures, distances in Angstrom, angles in degree.

	B3LYP/TZVP	XRD (form A)	XRD (form B)	XRD (form C)
d(Fe-N3)	2.343	2.235	2.207	2.240
d(Fe-N4)	2.343	2.235	2.238	2.240
d(Fe-N1)	2.113	2.048	2.047	2.076
d(Fe-N2)	2.113	2.048	2.073	2.076
d(Fe-Cl1)	2.299	2.317	2.326	2.302
d(Fe-Cl2)	2.299	2.317	2.308	2.302
A(N1-Fe-N2)	81.9	82.5	81.5	81.2
A(N1-Fe-N3)	72.9	75.2	74.16	75.4
A(N2-Fe-N4)	72.9	75.2	74.16	75.3
A(N3-Fe-N4)	132.2	127.1	127.2	131.4
A(Cl1-Fe-Cl1)	143.8	152	151.1	147.3



Closed form Transition state Open form

	E (H)	ΔE (kcal/mol)	G (H)	ΔG (kcal/mol)
Closed form	-3862.9833	0.0	-3862.7304	0.0
TS	-3862.9686	9.3	-3862.7159	9.1
Open form	-3862.9748	5.4	-3862.7224	5.0

Figure S18: DFT optimized structures and energies of the closed and open forms of [FeDPPyCl$_2$], as weel as the transition state associated with the decoordination of one pyridine arm.

For the decoordination of one pyridine arm, an associated rate constant of 10^7 can be expected, based on the Eyring equation at 298K.

The structure of the computed [Fe(DPPyO)Cl_2] species is given in the article (Fig. 3). Of note, isomers resulting from O insertion in one of the pyrrolic-Fe bond or oxidation of a pendant pyridine arm were calculated respectively 7 and 3 kcal/mol higher in energy.

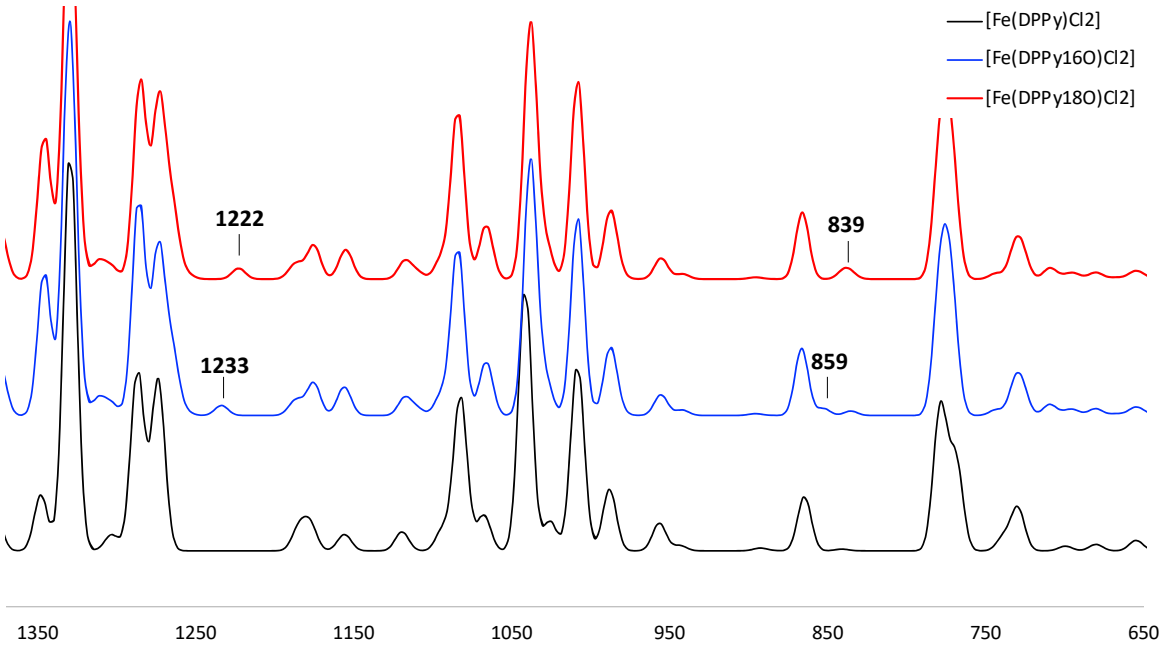
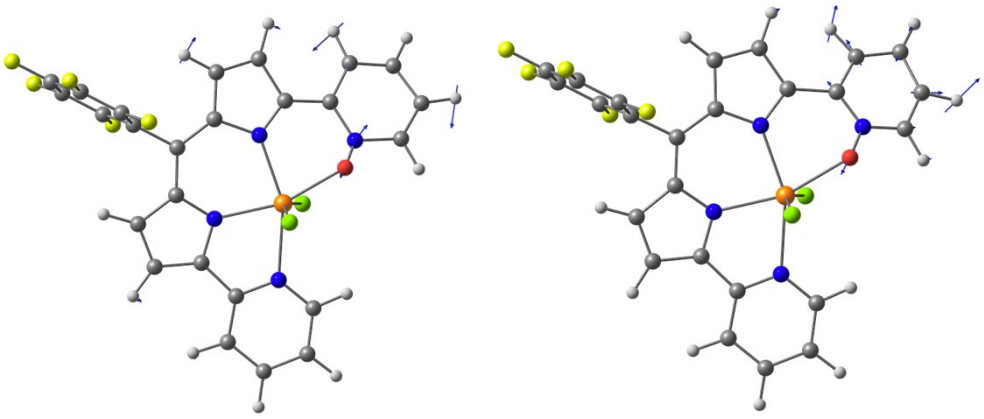


Figure S19: Comparison of the IR spectra calculated for [FeDPPyCl_2] and [Fe(DPPyO)Cl_2]. No scaling correction applied, $W_{1/2}$=10 Gaussian broadening.



1233.7443 cm^{-1}
(N-O stretching)

852.7361 cm^{-1}
(C-N-O bending)

Figure S20: Scaled displacement vectors related to the main vibration modes of the N-O bond calculated for Fe(DPPy^{16}O)Cl_2.

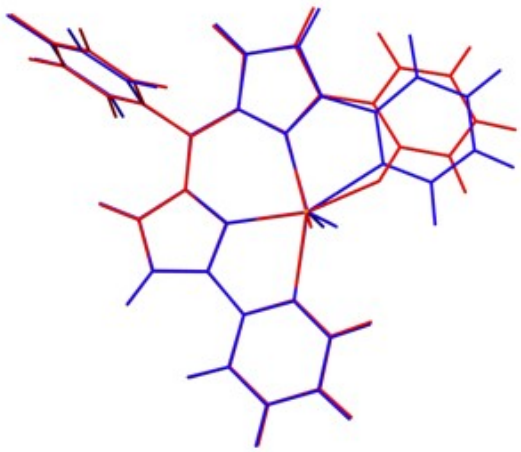
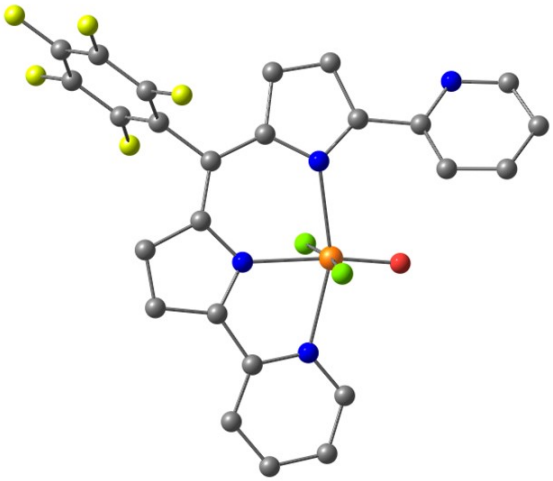
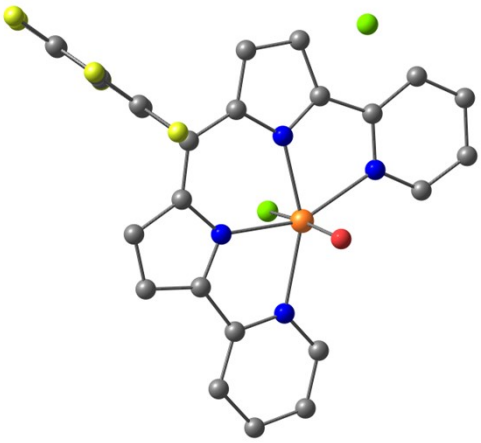


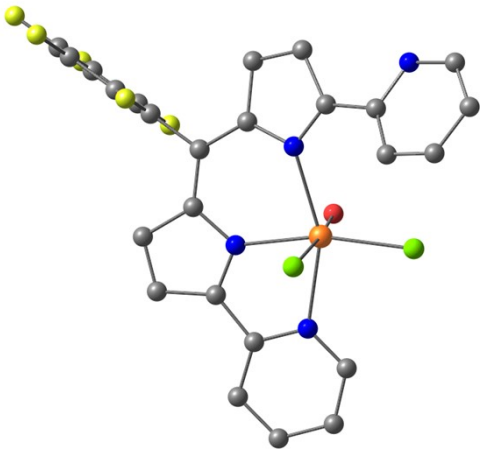
Figure S21: Overlay of the computed structures of [FeDPPyCl2] (blue) and [Fe(DPPyO)Cl_2] (red).



0.0 kcal/mol

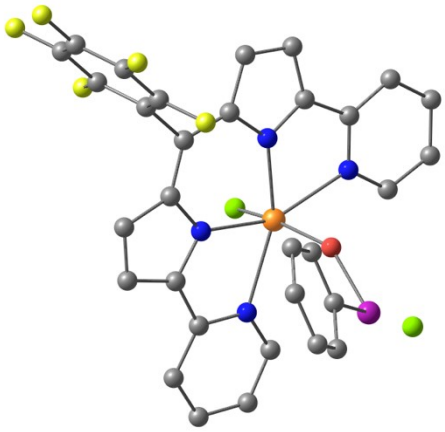


4.5 kcal/mol

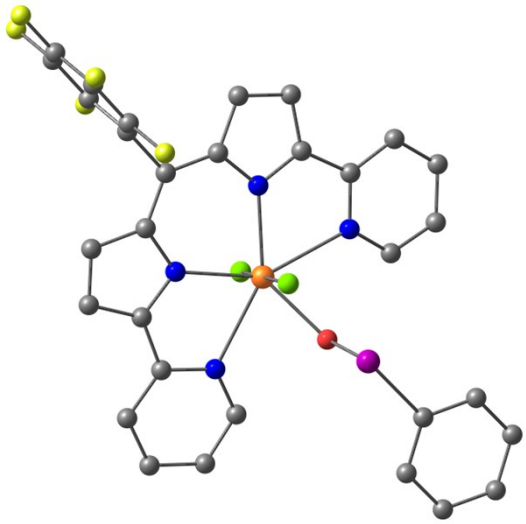


5.1 kcal/mol

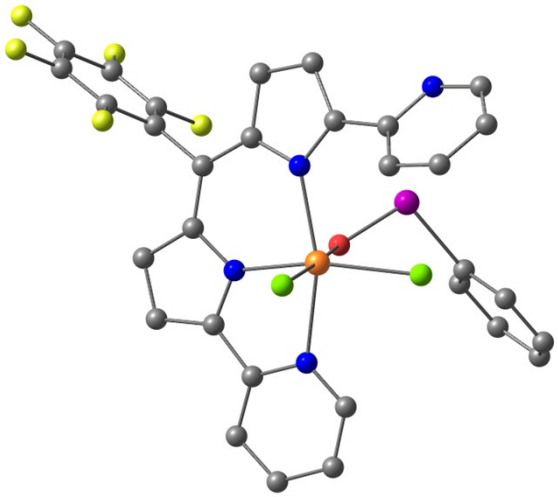
Figure S22 Computed structures for the notional [Fe^{V}=O(DPPy)Cl_2], S=5/2 structures. H omitted, C grey, O red, N blue, F yellow, Cl green, Fe orange, I purple.



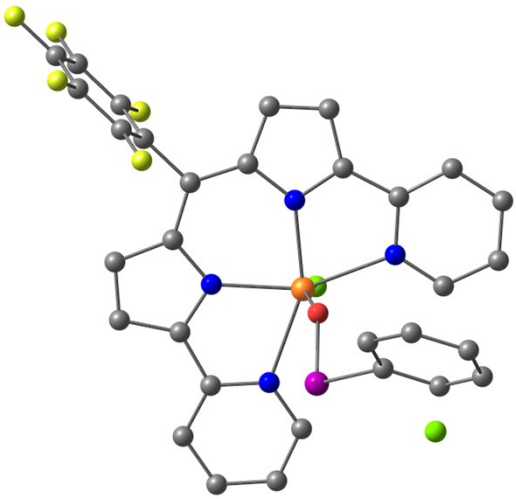
0.0 kcal/mol



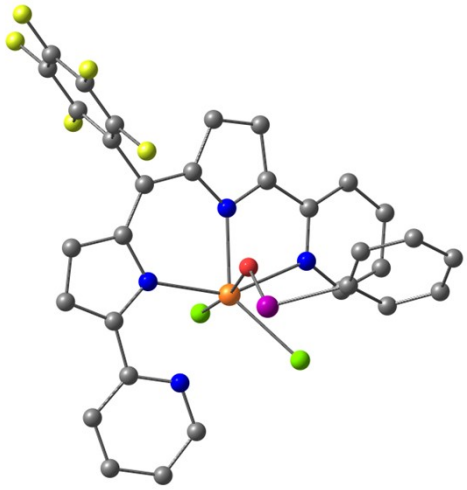
6.9 kcal/mol



7.8 kcal/mol



11.7 kcal/mol



12.1 kcal/mol

Figure S23 Computed structures for the notional [FeDPPyCl$_2$(OIPh)], S=5/2 structures with their relative free energies. H omitted, C grey, O red, N blue, F yellow, Cl green, Fe orange.

Table S5 Coordinates of the most stable optimized geometries in their lower spin state, UB3LYP energies and thermal free energy at 298K.

[FeDPPyCl$_2$]

Sextet
E(UB3LYP) = -3862.98334247 H
G = -3862.730383 H

26	-2.020274000	0.000008000	0.000023000
6	5.898701000	-0.000001000	-0.000005000
17	-2.733317000	0.000899000	2.185805000
9	7.231582000	-0.000001000	-0.000006000
9	5.872946000	0.000733000	-2.357362000
6	5.203605000	0.000368000	-1.201874000
9	3.173539000	0.000728000	-2.362350000
6	3.814999000	0.000352000	-1.189501000
7	-0.423879000	1.384597000	0.000376000
6	0.948617000	1.238040000	0.000514000
6	1.595158000	0.000002000	-0.000004000
6	3.091138000	0.000001000	-0.000005000
7	-2.968858000	2.142132000	-0.000708000
6	1.548744000	2.535699000	0.000875000
1	2.606873000	2.742055000	0.001048000
6	-0.679855000	2.699293000	0.000623000
6	0.525853000	3.452997000	0.001038000
1	0.614849000	4.527207000	0.001289000
6	-2.064321000	3.137416000	0.000158000
6	-2.458857000	4.478075000	0.000420000
1	-1.715231000	5.262984000	0.001161000
6	-3.811402000	4.778581000	-0.000282000
1	-4.141315000	5.809898000	-0.000084000
6	-4.737162000	3.740453000	-0.001271000
1	-5.801384000	3.932533000	-0.001891000
6	-4.265584000	2.434102000	-0.001448000
1	-4.947749000	1.593435000	-0.002293000
9	5.872947000	-0.000734000	2.357351000
6	5.203606000	-0.000370000	1.201863000
9	3.173541000	-0.000726000	2.362340000
6	3.815000000	-0.000352000	1.189491000
7	-0.423882000	-1.384591000	-0.000365000
6	0.948615000	-1.238035000	-0.000518000
7	-2.968864000	-2.142155000	0.000678000
6	1.548743000	-2.535693000	-0.000875000
1	2.606872000	-2.742048000	-0.001048000
6	-0.679855000	-2.699289000	-0.000628000
6	0.525854000	-3.452991000	-0.001053000
1	0.614852000	-4.527201000	-0.001317000
6	-2.064316000	-3.137428000	-0.000172000
6	-2.458835000	-4.478091000	-0.000435000
1	-1.715200000	-5.262991000	-0.001167000
6	-3.811377000	-4.778614000	0.000255000
1	-4.141277000	-5.809935000	0.000058000
6	-4.737149000	-3.740498000	0.001233000
1	-5.801369000	-3.932589000	0.001843000
6	-4.265586000	-2.434140000	0.001407000
1	-4.947760000	-1.593481000	0.002241000
17	-2.733369000	-0.000854000	-2.185740000

{[FeDPPyCl$_2$]}$^{\neq}$ pyridine decoordination

Sextet
E(UB3LYP) = -3862.96855747 H
G = -3862.715939 H
One imaginary frequency : -40.7654 cm^{-1}

26	-1.957715000	0.335111367	-0.039375532
6	5.869862000	-0.216284000	0.003704000
17	-3.120514165	-0.197770798	1.798793936
9	7.200426000	-0.289729000	0.007628000
9	5.846079000	-0.290118633	-2.352218000
6	5.176939000	-0.218140000	-1.199476000
9	3.150886000	-0.140815633	-2.364802000
6	3.790294000	-0.139085633	-1.191010000
7	-0.327111000	1.572251000	0.008326367
6	1.025104000	1.326787000	-0.014585266
6	1.571707000	0.029230000	-0.006696633
6	3.066662000	-0.063293000	-0.004174000
7	-2.792313000	2.454852000	0.066022266
6	1.713875000	2.568441000	-0.024910899
1	2.783632000	2.699749000	-0.041817532
6	-0.492664000	2.912404000	0.013627367
6	0.755951000	3.566793000	-0.005731899
1	0.927747000	4.631013000	-0.006544899
6	-1.851076000	3.418208000	0.048377000
6	-2.200329000	4.770619000	0.065317000
1	-1.430964000	5.530202000	0.049252367
6	-3.542494000	5.112648000	0.100117266
1	-3.838068000	6.154325000	0.112906266
6	-4.504717000	4.107009000	0.121528899
1	-5.560760000	4.336802000	0.148504165
6	-4.081722000	2.785071000	0.102749899
1	-4.784268000	1.961934000	0.116523165
9	5.841394000	-0.138740367	2.359913000
6	5.174599000	-0.137710000	1.203068000
9	3.146015000	0.012191633	2.357083000
6	3.788366000	-0.060452000	1.186320000
7	-0.541056000	-1.273058633	-0.009091633
6	0.858791000	-1.158244000	0.007779633
7	-2.736932330	-3.345209074	-1.181520303
6	1.427223000	-2.471066000	0.062955330
1	2.480700000	-2.699627367	0.083768596
6	-0.809935000	-2.582605000	0.033594431
6	0.387508000	-3.355790000	0.089610862
1	0.426399633	-4.434227367	0.122587293
6	-2.170704367	-3.186378633	0.018078798
6	-2.756388037	-3.635012558	1.204721633
1	-2.262306340	-3.477052952	2.153507367
6	-3.994656670	-4.257537293	1.134650633
1	-4.482946606	-4.608444420	2.037010734
6	-4.597547633	-4.412720734	-0.106947468
1	-5.566791633	-4.888905468	-0.207895468
6	-3.929986330	-3.940220442	-1.231379936
1	-4.364493027	-4.042573048	-2.221270037
17	-2.961371835	0.037502697	-1.997061431

[FeDPPyCl$_2$] open form

Sextet
E(UB3LYP) = -3862.97476391 H
G = -3862.722350 H

26	1.957438000	0.366005000	-0.096090000
6	-5.839614000	-0.185619000	-0.000549000
17	2.723403000	0.284047000	-2.205161000
9	-7.170254000	-0.256015000	0.002335000
9	-5.830385000	0.232186000	2.319730000
6	-5.154095000	0.065209000	1.180704000
9	-3.136157000	0.375187000	2.319677000
6	-3.767741000	0.138598000	1.164905000
7	0.351327000	1.598832000	0.043015000
6	-0.997706000	1.353882000	-0.023097000
6	-1.540363000	0.052284000	-0.012490000
6	-3.034834000	-0.038883000	-0.006050000
7	2.817392000	2.474295000	0.112397000
6	-1.683605000	2.593827000	-0.068112000
1	-2.751860000	2.726013000	-0.124034000
6	0.520766000	2.941614000	0.040317000
6	-0.724541000	3.593589000	-0.027117000
1	-0.896521000	4.657670000	-0.043760000

6	1.879050000	3.441728000	0.098734000
6	2.233484000	4.792294000	0.145785000
1	1.466755000	5.554708000	0.136660000
6	3.576118000	5.128655000	0.204231000
1	3.874967000	6.168859000	0.239963000
6	4.534881000	4.119279000	0.220600000
1	5.591259000	4.344539000	0.268669000
6	4.107416000	2.799683000	0.173937000
1	4.806827000	1.973887000	0.191146000
9	-5.795904000	-0.599500000	-2.320797000
6	-5.136404000	-0.362134000	-1.184565000
9	-3.102148000	-0.457434000	-2.332307000
6	-3.749664000	-0.288117000	-1.174970000
7	0.569659000	-1.279413000	-0.039034000
6	-0.829346000	-1.135403000	0.020151000
7	2.199388000	-4.332453000	0.914411000
6	-1.418658000	-2.431220000	0.202992000
1	-2.474748000	-2.631371000	0.279683000
6	0.813442000	-2.592633000	0.112300000
6	-0.400484000	-3.328889000	0.285897000
1	-0.447750000	-4.392942000	0.441242000
6	2.118869000	-3.275894000	0.086218000
6	3.156354000	-2.926797000	-0.779726000
1	3.046633000	-2.103080000	-1.468513000
6	4.327672000	-3.670663000	-0.750768000
1	5.146006000	-3.418783000	-1.413821000
6	4.429141000	-4.736093000	0.132358000
1	5.325987000	-5.339343000	0.190802000
6	3.331525000	-5.027119000	0.939051000
1	3.362277000	-5.862692000	1.631029000
17	3.294013000	-0.295771000	1.568198000

Fe(DPPy^{16}O)Cl_2

Sextet

E(UB3LYP) = -3938.17018177 H

G = -3937.912925 H

26	1.943173000	-0.243611000	0.302443000
6	-5.909878000	0.157789000	-0.026818772
17	1.895763000	-0.863121000	2.527138000
9	-7.241506000	0.217247000	-0.031358000
9	-5.886743000	0.096251000	-2.392647228
6	-5.221377228	0.094187000	-1.228128772
9	-3.191560000	-0.023255000	-2.394116000
6	-3.829874000	0.035085228	-1.220116000
7	0.312373087	-1.500901228	-0.196459000
6	-1.040591456	-1.281819315	-0.189877228
6	-1.605234772	-0.008549402	-0.014957315
6	-3.099918772	0.013463087	-0.035875228
7	2.833722000	-2.335238772	-0.027070000
6	-1.672375544	-2.564347000	-0.351336000
1	-2.732436315	-2.749110913	-0.385455000
6	0.538567772	-2.812546456	-0.343570000
6	-0.684308544	-3.522502685	-0.457619000
1	-0.824364228	-4.585262685	-0.590829228
6	1.914395000	-3.284744000	-0.303961000
6	2.283641000	-4.617980228	-0.521401000
1	1.530371000	-5.360026228	-0.747689000
6	3.624223000	-4.958105000	-0.444853000
1	3.938879228	-5.982537000	-0.608378000
6	4.562928000	-3.973133000	-0.158719000
1	5.613344772	-4.201417000	-0.091194000
6	4.123334228	-2.667133772	0.039404000
1	4.819871456	-1.867737000	0.256473000
9	-5.881121000	0.217776000	2.324784000
6	-5.209243772	0.159280000	1.174340228
9	-3.185760000	0.098227000	2.330005000
6	-3.817323544	0.103019228	1.153520772
7	0.478190685	1.313575141	0.126577228
6	-0.923244685	1.196485141	0.084987544
7	3.188623456	2.499392000	0.393615772
6	-1.535551282	2.468405544	0.080515000
1	-2.589636282	2.705556228	0.087089685
6	0.780273826	2.607055000	0.070685772
6	-0.468837685	3.335433946	0.054671000
1	-0.564782826	4.406129718	0.052802228
6	2.156556108	3.137410174	-0.026075631
6	2.379427021	4.347763120	-0.607901946
1	1.421896228	4.774425099	-0.889221925
6	3.552394456	5.030886424	-0.815289598
1	3.700323141	5.986275967	-1.290634826
6	4.505225153	4.175883033	-0.299030631
1	5.565654663	4.402155729	-0.390170402
6	4.370390033	2.971745174	0.272032913
1	5.173066402	2.338197631	0.607815402
8	3.090541141	1.484569619	0.976686033
17	2.917583000	0.174871000	-1.792316000

[FeDPPy(O)Cl_2]

Quartet

E(UB3LYP) = -3938.11094925 H

G = -3937.857327 H

26	2.088669000	-0.307154000	-0.172854000
17	2.364505000	-0.234102000	2.179385000
7	0.454913000	-1.522529000	0.203292000
7	2.917914000	-2.392655000	-0.066100000
7	0.560217000	1.380926000	-0.040051000
8	3.480751000	0.485228000	-0.484979000
17	1.551785000	-0.585889000	-2.420002000
6	-0.890313000	-1.288094000	0.290350000
6	0.653819000	-2.820036000	0.381628000
6	-1.482382000	-0.042814000	0.063475000
6	-1.564251000	-2.547790000	0.579990000
6	-2.978524000	0.001019000	0.058916000
6	-3.719292000	-0.497762000	-1.011300000
6	-5.107590000	-0.462484000	-1.020084000
6	-5.786092000	0.077211000	0.064815000
9	-7.116853000	0.112852000	0.067665000
6	-5.075219000	0.578226000	1.147698000
9	-5.791757000	-0.941512000	-2.060172000
9	-3.095050000	-1.020054000	-2.069907000
6	-0.804014000	1.163603000	-0.171348000
6	-3.687726000	0.536703000	1.132666000
6	2.003441000	-3.332551000	0.252033000
6	4.185835000	-2.736029000	-0.232716000
1	-2.624642000	-2.675916000	0.720819000
6	-0.603741000	-3.501963000	0.635372000
1	-0.733850000	-4.554787000	0.826237000
6	2.357731000	-4.671751000	0.412983000
1	1.610238000	-5.410366000	0.668316000
6	3.688254000	-5.032173000	0.239571000
1	3.993571000	-6.063848000	0.359223000
6	4.617738000	-4.054943000	-0.089668000
1	5.661606000	-4.298743000	-0.233515000
1	4.863794000	-1.930192000	-0.485418000
9	-5.727853000	1.091730000	2.191647000
9	-3.030606000	1.021628000	2.190639000
6	0.751336000	2.675464000	-0.279106000
6	-1.465153000	2.404503000	-0.554991000
7	2.035856000	4.580349000	-0.806655000
6	1.991424000	3.418288000	-0.118303000
6	3.128133000	5.320407000	-0.706304000
1	-2.520477000	2.522763000	-0.735480000
6	-0.501552000	3.339300000	-0.651758000
1	-0.579159000	4.379364000	-0.917772000
6	3.019470000	3.005225000	0.739664000
1	2.927775000	2.093794000	1.312168000
6	4.147472000	3.808049000	0.845408000
1	4.958923000	3.515400000	1.499320000
6	4.215885000	4.976691000	0.102878000
1	5.080601000	5.626243000	0.152521000
1	3.141914000	6.238081000	-1.285355000

[FeDPPyCl(OIPh)]Cl

Sextet

E(UB3LYP) = -4467.66812150 H

G = -4467.336103 H

26	-1.132646000	-1.096511000	-0.628789000
6	6.652109000	0.241294000	0.105099000
17	-5.174804000	-0.317469000	0.395991000
9	7.961026000	0.461443000	0.222824000
9	7.029529000	-1.183080000	-1.734172000
6	6.174455000	-0.596688000	-0.893599000
9	4.380307000	-1.632661000	-1.976121000
6	4.808073000	-0.817948000	-1.007488000
7	0.362327000	0.171492000	-1.428050000
6	1.715293000	0.309534000	-1.196297000
6	2.423297000	-0.467857000	-0.275610000
6	3.892509000	-0.221906000	-0.143439000
7	-2.188913000	0.261164000	-2.188369000
6	2.223390000	1.335867000	-2.052314000
1	3.246520000	1.672975000	-2.096145000
6	0.031533000	1.048807000	-2.383215000
6	1.166882000	1.797977000	-2.799599000
1	1.189492000	2.571987000	-3.549441000
6	-1.345609000	1.087022000	-2.842770000
6	-1.785308000	1.888058000	-3.897647000
1	-1.090434000	2.540594000	-4.407868000
6	-3.116377000	1.822917000	-4.281513000
1	-3.478484000	2.433632000	-5.099228000
6	-3.973324000	0.962161000	-3.608039000
1	-5.019053000	0.881456000	-3.870684000
6	-3.466314000	0.195507000	-2.564776000
1	-4.107318000	-0.461882000	-1.992195000
9	6.221094000	1.657864000	1.940778000
6	5.763165000	0.849888000	0.980941000
9	3.570648000	1.215799000	1.707496000
6	4.402179000	0.611506000	0.848118000
7	0.516732000	-1.790054000	0.498532000
6	1.858473000	-1.466169000	0.520694000
7	-1.945609000	-2.735879000	0.768687000
6	2.519452000	-2.324742000	1.454119000
1	3.571894000	-2.312669000	1.687910000
6	0.336276000	-2.797037000	1.361250000
6	1.564099000	-3.160375000	1.980946000
1	1.711255000	-3.937374000	2.713344000
6	-1.002935000	-3.336170000	1.522230000
6	-1.319949000	-4.387094000	2.382765000
1	-0.546471000	-4.855603000	2.975555000
6	-2.637714000	-4.814274000	2.461379000
1	-2.908350000	-5.627939000	3.122744000
6	-3.601267000	-4.181429000	1.687706000
1	-4.641832000	-4.472420000	1.727438000
6	-3.210188000	-3.142369000	0.849191000
1	-3.934831000	-2.599648000	0.256542000
17	-1.285009000	-2.683101000	-2.267583000
6	-1.899878000	4.209717000	1.594944000
6	-0.939771000	5.147038000	1.968190000
6	-1.562128000	2.860929000	1.570511000
1	-1.195794000	6.199525000	1.987606000
6	0.344954000	4.731419000	2.305317000
6	-0.286087000	2.432503000	1.908241000
1	1.092235000	5.461422000	2.590964000
1	-0.041171000	1.379332000	1.878204000
6	0.670402000	3.378519000	2.271299000
1	1.670570000	3.052416000	2.528817000
1	-2.895911000	4.542760000	1.320797000
53	-3.139486000	1.457335000	1.065573000
8	-1.879663000	0.076339000	0.744151000

Table S6 Calculated frequencies (cm^{-1}) with their IR intensities at 298K.

[FeDPPyCl_2] closed form

10.5208	0
24.998	0.0709
30.88	0
34.334	0.0975
41.9139	3.1387
53.3409	3.507
60.7047	0
65.1986	0.1785
81.5071	0.8487
86.5492	0.5098
111.3106	0.2257
112.017	0
123.5303	0.5468
128.5594	4.9692
131.1056	1.472
131.6355	0
144.307	1.7417
172.3002	0.0014
185.1391	0
197.9609	0.5276
201.127	1.6161
210.3295	0.0252
213.4923	0
229.6654	0.0007
239.562	5.8269
255.2482	5.2817
281.1087	0.0522
283.7431	0.0339
289.4331	14.3709
289.8872	24.9264
297.9634	0
302.7783	0.0038
313.6707	1.2666
343.783	0.5647
352.414	122.7091
382.2636	0.7568
383.9931	0
404.7876	10.3705
422.2005	7.38
429.2602	0
432.0852	6.0876
442.0094	0.6509
448.8335	0.1807
484.2863	2.7777
485.084	0.0005
486.6201	0.4107
527.6344	0.0227
534.8475	1.6506
561.6856	0.4491
586.6799	0.582
648.7162	0.2639
651.2475	0
652.2897	1.1712
655.4785	10.8131
664.7501	0
678.3515	0
680.5614	7.2926
699.9319	5.316
723.896	0.174
729.5397	28.2453
730.82	21.2683
733.9762	0
739.1427	15.49
766.4145	0.0002
769.015	100.0657
772.9742	0.0005
776.804	29.6756
779.4587	137.7033
841.3345	1.939
865.0581	61.7417
881.1302	0
884.5133	0.2029
890.5744	0
893.0336	3.1166
944.0226	6.0784
954.0501	0
956.8788	31.3877
960.6608	0.1794
988.3647	69.5065
991.106	0
991.2131	0.632
1008.6787	212.9742
1026.0365	33.5929
1027.9791	0.2873
1041.7669	299.6442
1067.6802	38.8122
1070.0207	0.1088
1073.2559	4.2272
1082.8322	176.4822
1094.0341	24.5004
1116.9585	0.4998
1119.8006	21.1685
1155.3563	5.8165
1155.9491	9.4379

1157.9439	3.7202
1177.8853	29.9388
1184.5488	4.3909
1185.2075	21.1531
1268.785	2.6355
1274.0786	193.0948
1287.1176	205.7738
1298.8349	0.2448
1302.5206	10.3838
1304.5547	8.5119
1315.5782	0.2241
1327.7954	19.5477
1329.745	439.7045
1348.1714	63.8076
1377.1157	44.226
1414.5069	77.3089
1435.0456	14.4474
1454.936	121.7036
1458.6043	12.0283
1471.2193	56.4383
1474.7773	60.2135
1498.0379	7.9772
1512.961	347.0393
1516.7897	21.6285
1528.3431	80.4422
1529.4345	164.6245
1533.9572	136.6171
1563.4676	10.3506
1587.2239	804.6111
1610.7747	1.4047
1612.8881	15.0246
1637.5463	48.1201
1639.1455	9.1992
1646.0687	4.2084
1668.4972	28.0048
3186.1311	11.4282
3186.3212	6.3982
3192.4007	2.7684
3193.1093	2.1768
3208.6885	2.0108
3208.7474	9.4918
3213.8702	7.3952
3214.0022	7.7682
3241.2043	1.5509
3241.3717	4.9207
3257.3525	5.9596
3257.5502	3.704

[Fe(DPPy^{16}O)Cl$_2$]

12.811	0.0157
24.9943	0.2251
34.1666	0.1906
37.1237	0.174
39.7424	3.7138
55.3018	3.5604
62.0738	0.3589
69.5462	0.3923
79.7112	0.8958
98.0132	0.9134
104.1278	0.0324
114.3632	1.017
123.2013	0.5059
128.4177	5.4157
131.8364	0.0497
142.2174	0.5081
147.6684	1.4448
171.9623	0.0465
179.9327	0.4856
197.5476	0.3954
200.2718	1.3327
217.4064	0.6452
222.0924	9.9899
229.1616	0.2754
238.9051	7.3537
247.2677	1.8221
260.7734	7.1603
281.359	0.1295
283.8352	0.1621
289.68	14.7265
302.4323	7.8629
304.473	1.499
313.0269	1.3734
328.9926	36.7017
336.8338	96.4464
343.699	9.3231
374.7476	6.5706
384.2397	0.0258
396.6387	1.5413
420.1912	7.0858
423.279	4.8887
432.2557	3.2517
448.8757	0.1453
455.2878	1.3564
487.2349	0.7793
490.5674	0.5976
507.9633	1.9405
521.0751	1.6576
529.977	0.8935
565.3941	0.8576
572.5897	12.9141
586.4968	0.244
603.3387	7.607
650.6501	3.0623
655.2611	5.8085
657.9572	1.5166
667.6676	1.7501
679.0465	3.8282
681.7444	3.6149
693.8842	4.7286
699.2289	3.2933
709.4032	11.421
726.659	23.1666
731.3101	29.1016
743.3828	5.9599
770.0006	36.8681
772.6612	92.8987
776.5817	33.8173
777.6289	26.4426
779.5138	85.8724
835.3531	4.5809
852.7361	7.3012
866.4474	69.5468
869.2371	0.0747
888.0655	0.1014
894.254	0.133
895.8109	1.7054
941.9721	5.5236
948.9892	0.5856
955.5909	21.3176
967.6453	0.0456
980.908	2.8949
987.4916	70.6051
993.0342	0.4657
1008.2849	205.7318
1028.3278	35.5462
1038.1091	264.4597
1066.0539	54.6303
1071.067	2.8141
1074.624	0.7556
1084.1626	176.6909
1094.6325	21.1867
1109.8656	7.1597
1117.664	18.3878
1154.1073	8.4975
1156.4268	17.9782
1158.0408	4.5026
1175.3397	33.6158
1184.779	10.7536
1188.6409	7.5286
1233.7443	10.3578
1256.6137	3.786
1265.0198	65.1066
1273.6662	172.4919
1286.0388	226.9717
1298.5211	0.8389
1303.7196	12.1288
1311.676	17.9746
1327.3404	72.4027
1330.2913	350.684
1345.8866	150.5518
1374.1155	52.1876
1405.8922	100.9799
1434.2809	0.4629
1453.1065	90.1075
1454.8363	19.01
1464.8827	11.7854
1474.5831	49.5601
1490.4567	22.8009
1512.1451	335.0696
1518.2867	121.6547
1524.7198	66.4552
1527.3296	216.369
1533.6111	179.861
1556.7875	45.4611
1587.1575	566.7677
1596.123	94.1523
1612.1398	16.2895
1639.7524	21.7255
1645.9088	5.2872
1652.8182	5.2005
1667.8554	29.5528
3186.6571	8.9124
3193.3797	1.2776
3202.0058	3.4632
3208.1206	5.2899
3213.8367	8.1344
3218.118	1.0684
3228.9435	0.1528
3240.6488	2.5339
3243.5644	2.8693
3254.9728	1.6783
3257.1105	5.0389
3260.2012	4.2949

[Fe(DPPy^{18}O)Cl$_2$]

12.8091	0.0156
24.9781	0.2218
34.1558	0.1875
37.0883	0.1779
39.6274	3.7135
55.1999	3.5207
61.9656	0.3691
69.5386	0.3915
79.7091	0.8947
97.8719	0.9157
104.0454	0.0299
114.3383	1.0309
123.1673	0.5044
128.3572	5.4001
131.8326	0.0502
141.274	0.2816
147.0411	1.6715
171.9253	0.0491

179.3591	0.501
197.276	0.2527
199.8393	1.4834
217.0419	1.2083
220.9042	9.6199
228.8516	0.3226
238.6734	7.1943
246.0968	1.2532
260.1805	6.2826
281.3571	0.1397
283.8151	0.1988
289.3957	15.1164
297.8494	10.3279
304.2777	0.3311
312.8824	1.2928
327.5958	25.5703
336.2581	107.8077
343.2555	8.307
370.2241	6.7481
384.239	0.0277
395.3538	1.1968
418.4127	6.5994
422.8778	5.774
432.2469	3.2428
448.8747	0.1437
454.4391	1.3386
486.2547	0.8765
490.3672	0.5019
505.6997	2.237
518.6859	2.0204
529.865	0.8547
563.8062	8.0663
565.704	4.3227
586.1053	0.6413
593.5837	7.0812
650.6118	2.9664
655.2439	5.678
657.943	1.5306
667.6256	1.6839
678.7326	3.6861
681.7433	3.6362
693.588	4.9211

699.0001	3.1991
709.1719	11.4775
726.65	23.083
731.283	29.0819
743.3784	5.9259
769.9873	35.0298
772.3356	94.0739
776.5672	34.8513
777.6106	27.7294
779.4523	83.3535
835.3145	5.0187
839.612	8.2109
865.9626	68.7655
869.1672	0.125
888.0652	0.1026
894.2537	0.1335
895.8107	1.7097
941.774	5.1796
948.9387	0.5353
955.4443	21.4838
967.6453	0.0454
980.8969	3.0022
987.4252	70.8277
993.0338	0.4615
1008.2848	205.7364
1028.3265	35.6048
1038.0982	264.2649
1066.0304	54.5059
1071.0297	2.6299
1074.4825	0.9812
1084.1379	176.4037
1094.6154	21.2587
1109.8466	7.2532
1117.6565	18.539
1153.7848	8.6755
1155.0464	18.7455
1158.0343	4.2267
1175.2259	34.6598
1184.7761	10.716
1188.6174	7.6751
1222.8435	11.0955
1255.6808	5.3597

1264.9248	71.9119
1273.3094	181.9731
1285.2761	205.0748
1298.5201	0.8631
1303.7087	12.289
1311.626	18.1794
1327.307	72.8735
1330.2654	346.6245
1345.8207	149.1953
1374.113	52.1809
1405.8785	100.9168
1434.2596	0.4756
1453.1052	89.8643
1454.7953	19.3702
1464.7837	11.9646
1474.5641	49.4043
1490.431	22.6369
1512.1444	335.0233
1518.2497	122.7871
1524.7186	66.3704
1527.2326	213.9701
1533.6003	180.5715
1556.7035	45.5064
1587.1313	564.265
1596.0231	94.6947
1612.1395	16.2492
1639.7523	21.7382
1645.9087	5.2789
1652.8117	5.1948
1667.8554	29.5529
3186.6571	8.9121
3193.3796	1.2776
3202.0055	3.4581
3208.1206	5.2899
3213.8367	8.1347
3218.1179	1.0691
3228.9435	0.1531
3240.6488	2.5339
3243.5644	2.8692
3254.9728	1.6784
3257.1105	5.0388
3260.2012	4.2946

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