Supporting Information for:

Ligand mixed-valence and electrical conductivity in coordination complexes containing a redox-active phenalenol-substituted ligand.

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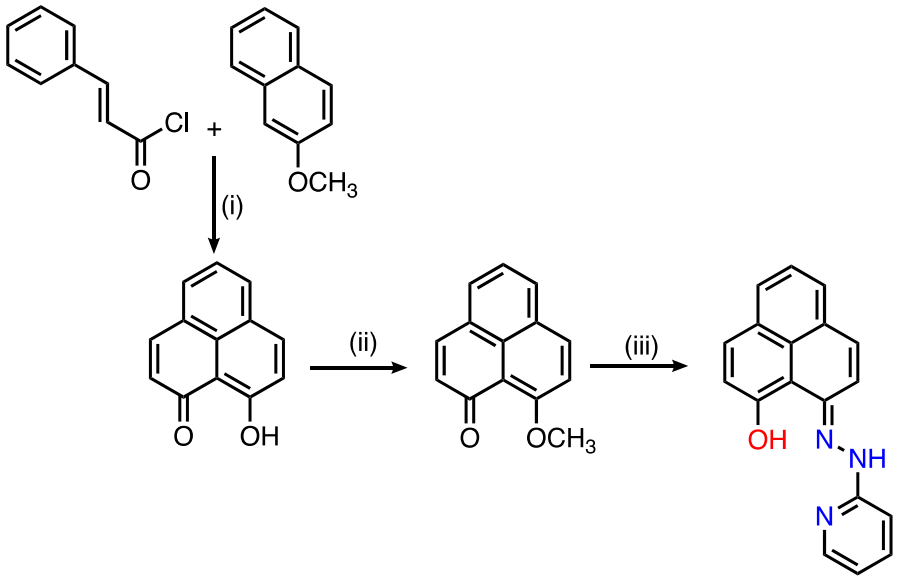
Scheme S1. Preparation of phpl. Reagents and conditions: (i) $AlCl_3$, dichloroethane and then conc HCl/H_2O (ii) MeI, Ag_2O, $CHCl_3$ and (iii) 2-hydrazinopyridine, $CHCl_3$, reflux.



Experimental section

General considerations

All reagents with the exception of 9-hydroxy-1-phenalenone[15] were commercially available and used as received. Anhydrous solvents (CH_2Cl_2) were obtained by distillation over CaH_2. $^{1}H/^{13}C$-NMR spectra were recorded with a Bruker Avance III HD 400 Digital NMR spectrometer with a 9.4 T Ascend magnet using deuterated solvents. FT-IR spectra were recorded with a Shimadzu IRAffinity spectrometer as KBr discs and UV/Vis/NIR spectra were obtained with a Shimadzu 3600 UV-Vis-NIR spectrophotometer in CH_2Cl_2 solution using quartz cuvettes. Cyclic voltammetry (CV) experiments were performed with a Bioanalytical Systems Inc. (BASI) Epsilon electrochemical workstation. Complexes **1** and **2** were dissolved in anhydrous solvent (CH_2Cl_2) and deareated by sparging with N_2 gas for 10-15 min. Solution concentrations were approximately 10^{-3} M in analyte containing approximately 0.5 M supporting electrolyte (Bu_4NPF_6). A three-electrode set-up was used including a glassy carbon working electrode, Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The scan rate for all CV experiments was 100 mV/s. High resolution EI mass spectra were recorded with a ThermoFisher high resolution double focusing magnetic sector mass spectrometer system and ESI mass spectra were obtained with a Bruker HCT Plus Proteineer LC-MS with electrospray and a syringe pump was used for direct sample infusion. A QD-MPMS SQUID magnetometer was used to record the variable temperature magnetic susceptibility properties of **2** at an external magnetic field of 2000 Oe over a temperature range of 2-300K. The sample was weighed into a gel cap and diamagnetic contributions were calculated using Pascal's constants. The electrical conductivity was measured by a HUSO HECS 994C conductometer. EPR spectra were recorded using a Bruker Elexsys E580 pulse spectrometer operating in CW mode. Microanalyses were performed by Canadian microanalytical LTD. (Delta, British Columbia, Canada).

Theoretical calculations. All theoretical calculations were performed with the programs ORCA 4.01[1] or Gaussian 09 (D.01)[2]. Geometry optimization and frequency calculations on phpl, phpl anion radical and phpl dianion were run using the BP86[3–5] functional and def2-SVP[6,7] basis set on all atoms. Broken-symmetry DFT[8-10] and TD-DFT calculations were run using the B3LYP[3,11] functional with the def2-TZVP[7] basis set on all atoms. In the TD-DFT calculations the polarized continuum model (PCM) was used to model the solvent environment (CH_2Cl_2) and 40 transitions were calculated. Tight SCF convergence criteria were used for all calculations. The program Chemissian[12] was used for the preparation of the spin density and Kohn-Sham orbital figures and the program QMForge[13] was used to analyse the TD-DFT results.

Synthesis

9-Methoxy-1-phenalenone[14]**.** 9-hydroxyphenalenone[15] (0.495 g, 2.52 mmol) and Ag_2O (0.584 g, 2.52 mmol) were combined in $CHCl_3$ (10 mL) and heated to reflux. At reflux, 26 μL of CH_3I was added and this same addition was repeated after 2, 4 and 6 h. After 7 h a grey-brown solid was filtered from the brown-yellow solution. The residue was washed several times with $CHCl_3$ and the filtrate was concentrated by rotary evaporation and pumped on under vacuum to remove excess CH_3I. A yellow-brown oil that required no further purification was obtained, Yield: Ranged between 66-94%. Spectroscopic characterization of the product was consistent with the published data.[14]

9-[2-(2-Pyridyl)hydrazono]-1-phenalenol (phpl). 9-Methoxy-1-phenalenone (0.800 g, 3.80 mmol) was added to a Schlenk flask (100 mL) and dissolved in $CHCl_3$ (50 mL) followed by rapid sparging of the solvent using N_2 for about 10 min. Then an equimolar amount of 2-hydrazinopyridine (0.416 g, 3.80 mmol) was added and the reaction mixture was refluxed under nitrogen for approximately 48 h. A color change from orange to dark red was observed as the

reaction proceeded. The solvent was removed by rotary evaporation and a dark red oil was formed which would eventually solidify to a dark red powder under reduced pressure. This material was purified by dissolution into CH_2Cl_2 (50 mL) followed by the slow addition of pentane (150 mL) with stirring. After stirring for approximately 2 h a crimson precipitate was collected by vacuum filtration and washed with pentane (3 × 50 mL). Yield, 0.425 g (yields typically ranged from 35-45%). The precipitated ligand powder is air/moisture sensitive and should be used immediately or stored under an inert atmosphere. ^{1}H NMR ($CDCl_3$): 13.01 (s, 1H), 8.22 (d, J = 4.8 Hz, 1H), 7.98 (d, J = 9.3 Hz, 1H), 7.97-7.88 (m, 3H), 7.68 (d, J = 9.3 Hz, 1H), 7.55-7.48 (m, 2H), 7.04 (d, J = 9.3 Hz, 1H), 6.82 (br dd, J = 6.3 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): 183.3, 159.1, 156.7, 148.1, 138.7, 138.6, 138.5, 131.9, 131.5, 128.0, 125.7, 125.6, 122.7, 116.4, 114.2, 108.2, 106.5 ppm. HR-MS (EI+): Calc'd for $C_{18}H_{13}N_3O$ (found) = *m/z* 287.1053 (287.1054). MS (ESI+): *m/z* 288.1 [M+H, 100%]. FT-IR (KBr): 3188 (w, br), 3155 (w, br), 3030 (w, br), 1633 (s), 1593 (m), 1438 (m), 1269 cm^{-1} (s).

[Fe(phpl)$_2$] (1): Phpl (0.180 g, 0.620 mmol) was dissolved in MeOH (25 mL) and the solution was sparged vigorously with N_2 for 5 minutes. $Fe(NO_3)_3 \cdot 9H_2O$ (0.060 g, 0.150 mmol) was added to the phpl solution resulting in a change in colour from red to brown and then an excess of triethylamine (0.4 mL) was added, resulting in a purple colored solution that was left to stir for 4 h. A brown microcrystalline precipitate was collected by vacuum filtration, washed with MeOH (3 × 25 mL) and water (2 × 10 mL), and then dried. Yield, 0.118 g (60%). Single crystals suitable for X-ray diffraction were grown by dissolving 9-10 mg of the precipitated material in 2.5 mL of $CHCl_3$, which was heated gently and passed through a cotton pipette filter into a 2 dram vial. The vial was then placed in a larger vessel for vapor diffusion with 2 mL of pentane. After approximately 2-3 d, a second batch of pentane was added (1.5 mL). After standing for an

additional week, large single crystals formed on the sides of the vial. Waiting an additional week optimized the yield of crystals. Each vial contained about 2-4 mg of crystals (approximately 30% yield). The crystals were collected via gravity filtration and washed with pentane. Anal. Calc'd for % (found) $FeC_{36}H_{22}N_6O_2$•0.55$CHCl_3$•0.05C_5H_{12}: C, 63.53 (63.62); H, 3.35 (3.27); N, 12.08 (12.09). MS (ESI+): *m/z* 627.1 [M+H, 100%]. UV-Vis (CH_2Cl_2, cm^{-1}): 29412, 18484, 11198, 5952, 3861. FT-IR (KBr, cm^{-1}): 3435 (br s), 3037 (br s), 1612 (m), 1587 (m), 1553 (m), 1475 (w), 1454 (w), 1431 (s), 1398 (w), 1325 (w), 1285 (m), 1231 (w), 1142 (m), 1024 (m), 976 (m), 839 (m), 806 (m), 756 (m), 637 (m), 594 (m).

[Co(phpl)$_2$] (2): Phpl (0.250 g, 0.870 mmol) was dissolved in MeOH (40 mL) in a 125 mL Erlenmeyer flask. An excess of triethylamine (0.4 mL) was added and the mixture was stirred for approximately 2 min. Then $Co(ClO_4)_2 \cdot 6H_2O$ (0.115 g, 0.435 mmol) was added resulting in a change in colour from red to dark blue. The mixture was left to stir in air for 1 h at room temperature. A blue precipitate was collected by vacuum filtration, washed with MeOH (3 × 25 mL) and water (2 × 10 mL), and then dried. Yield, 0.205 g (75%). Single crystals suitable for X-ray diffraction were grown by dissolving 9-10 mg of the precipitated material in 2.5 mL of $CHCl_3$, which was heated gently and passed through a cotton pipette filter into a 2 dram vial. The vial was then placed in a larger vessel for vapor diffusion with 2 mL of pentane. After approximately 2-3 d, a second batch of pentane was added (1.5 mL). After standing for an additional week, a third batch of pentane was added, (1.5 mL) and then left for 2 weeks. At this time the inside of the vial was coated in a purple crystalline material, with large single crystals rooted on the glass, growing in the direction of the solution. The single crystals were extremely brittle and were selected carefully for X-ray diffraction. The material were collected via gravity filtration and washed with pentane. Anal. Calc'd for % (found) $CoC_{36}H_{22}N_6O_2$•0.8$CHCl_3$•0.2C_5H_{12}: C, 61.40 (61.50); H, 3.43 (2.98); N,

11.36 (10.96). MS (ESI+): *m/z* 630.1 [M+H, 100%]. UV-Vis (CH_2Cl_2, cm^{-1}): 16863, 13192, 11547, 8757, 7402, 4931. FT-IR (KBr, cm^{-1}): 3040 (br s), (br s), 1618 (m), 1574 (m), 1559 (m), 1497 (m), 1474 (m), 1431 (s), 1404 (m), 1348 (m), 1335 (m), 1290 (w), 1269 (w), 1242 (w), 1182 (m), 1148 (m), 1026 (m), 976 (w), 839 (m), 814 (m), 754 (m), 682 (w).

Figure S1. ^1H NMR spectrum of phpl ($CDCl_3$).

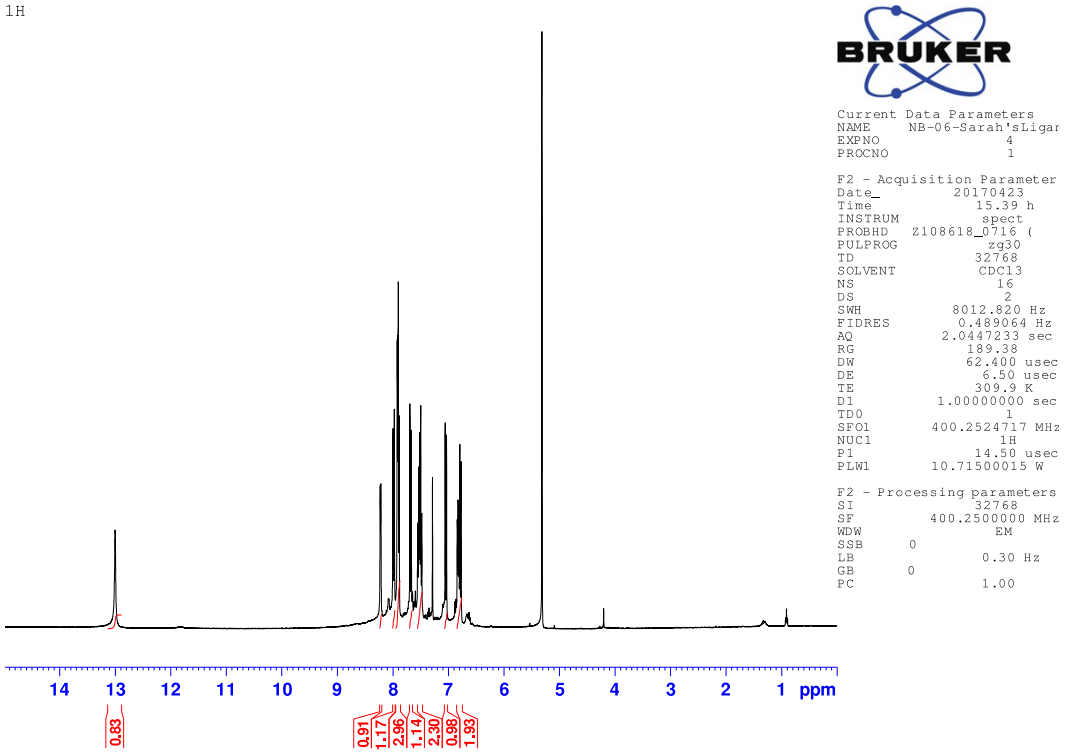


Figure S2. ^{13}C NMR spectrum of phpl ($CDCl_3$).

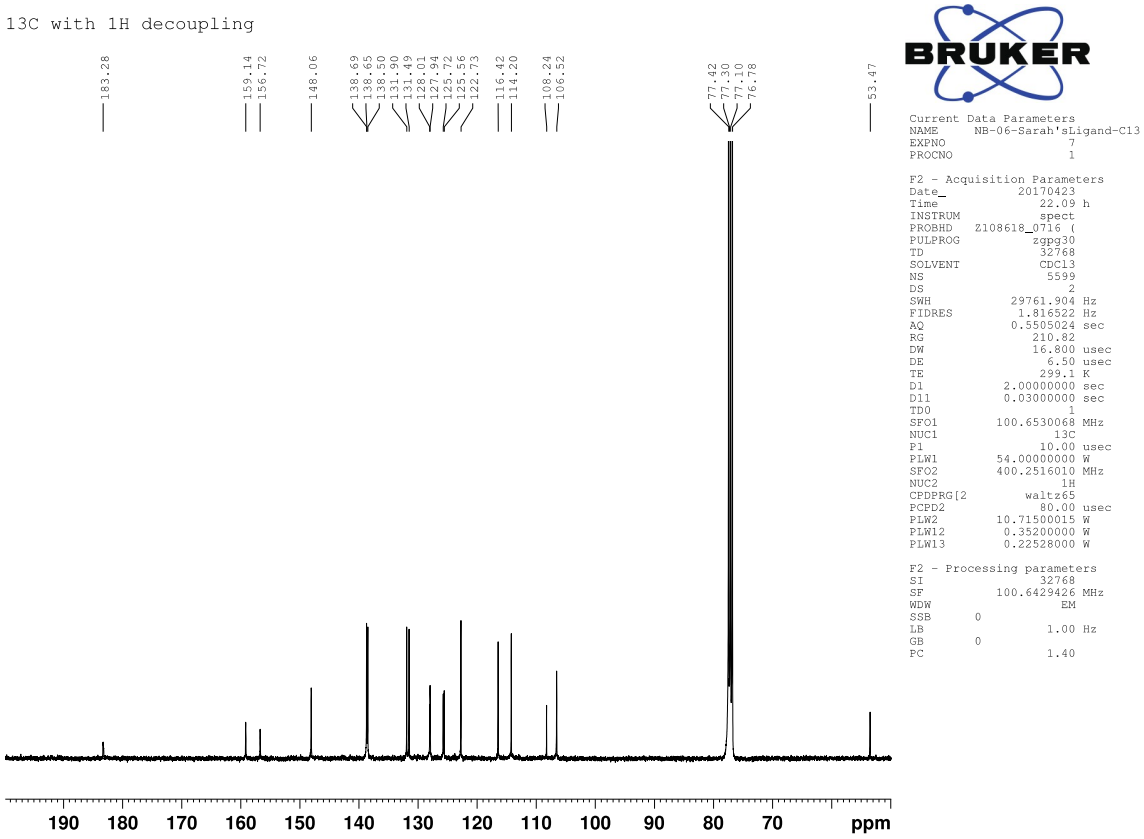


Figure S3. UV-visible spectrum of phpl (CH_2Cl_2).

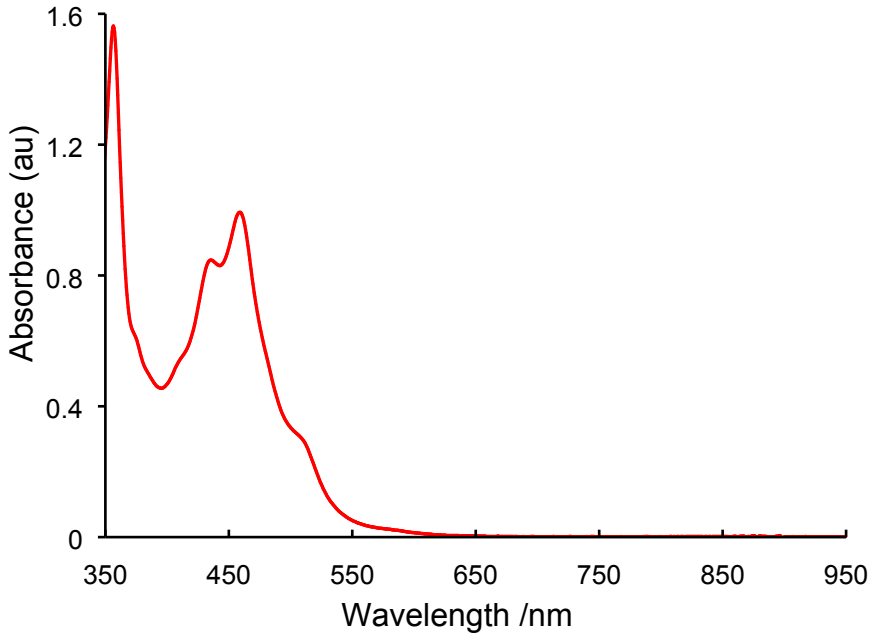


Figure S4. EI mass spectrum (positive ion mode) of phpl (top is low resolution, bottom is high resolution).

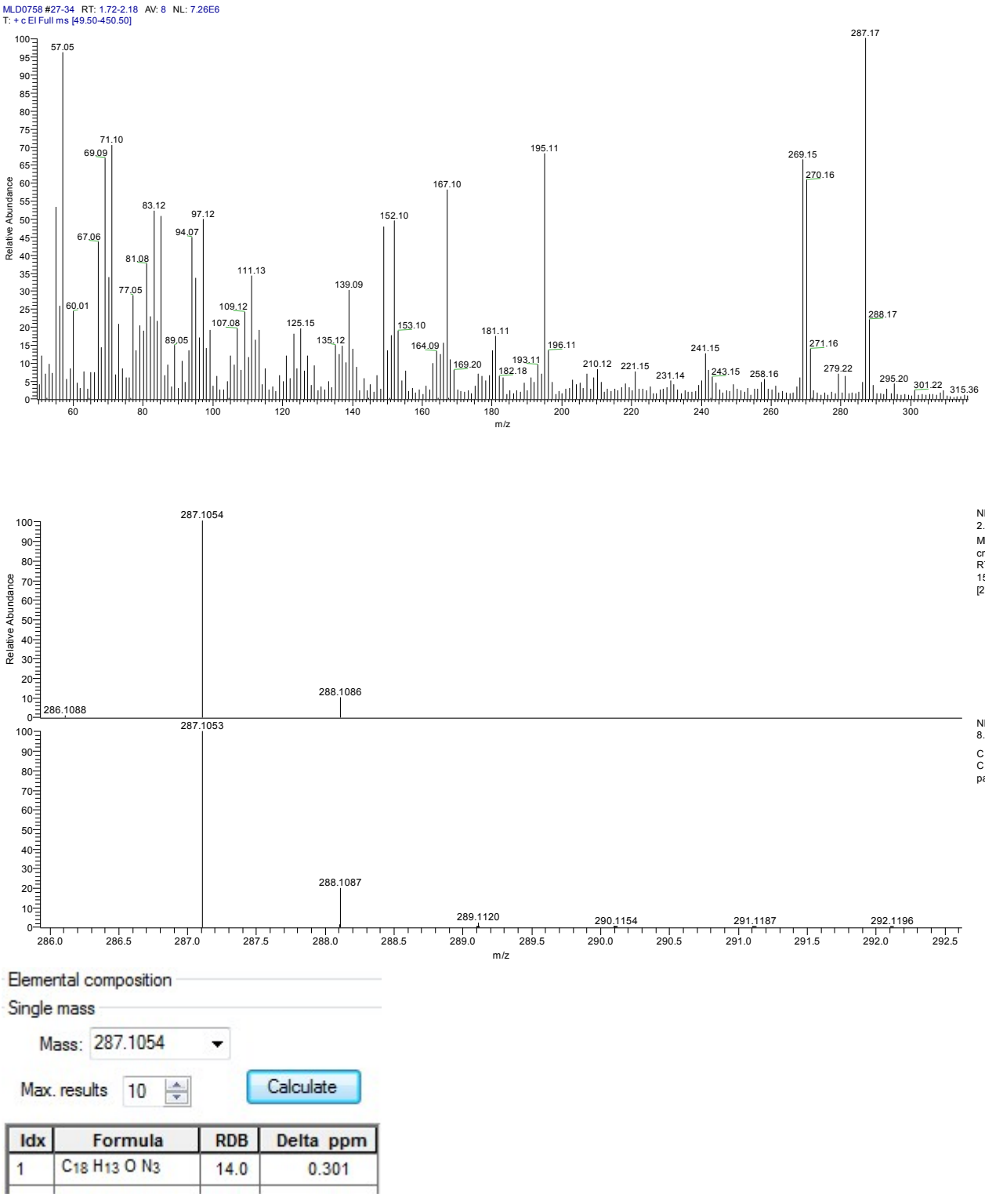


Figure S5. Calculated structures (BP86/def2-SVP) of phpl (top), phpl anion radical (middle) and phpl dianion (bottom) with selected calculated bond distances (Å).

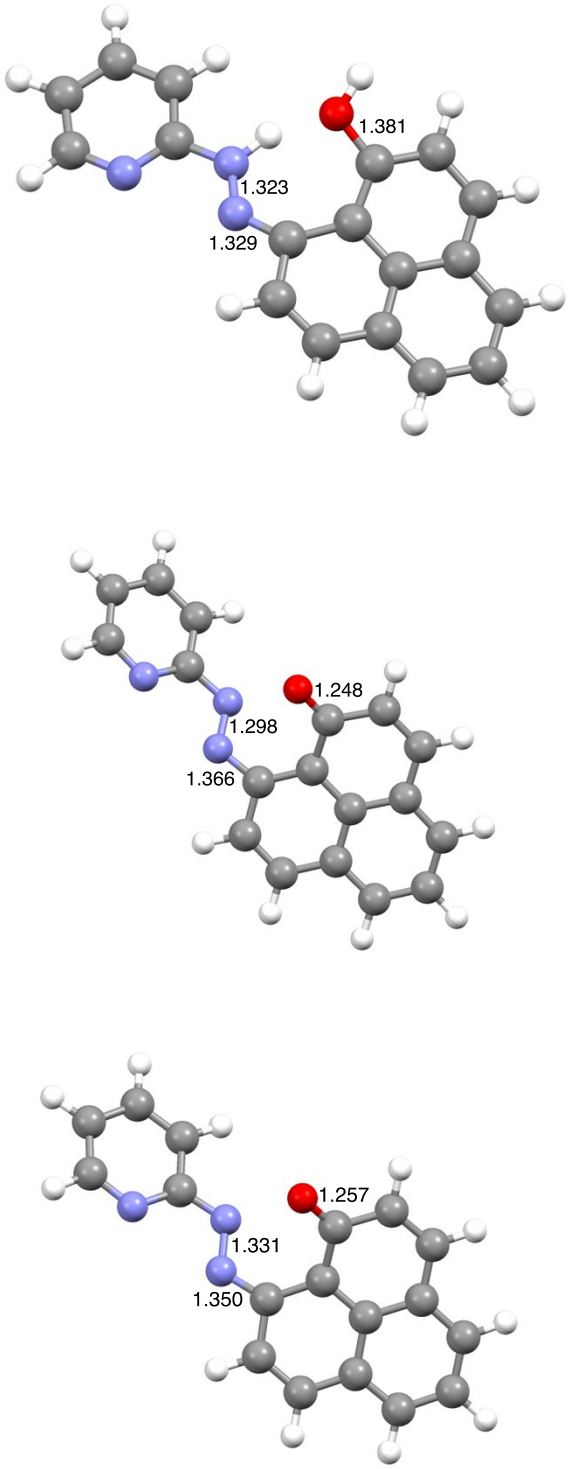


Table S1. Atomic coordinates of phpl.

C	1.06824	-0.21249	0.42161
C	2.90439	1.34051	2.01283
C	2.46838	-0.09909	0.05363
C	0.70544	0.34546	1.67007
C	1.60107	1.13836	2.43123
C	3.38170	0.70447	0.83191
H	1.24234	1.58384	3.37527
H	3.58889	1.96548	2.60677
C	0.15595	-0.93295	-0.51516
H	0.09787	-2.37786	-2.12910
C	0.78868	-1.76352	-1.53356
H	2.54765	-2.30919	-2.63049
C	2.12134	-1.70671	-1.81311
C	2.99924	-0.82227	-1.07696
C	4.74657	0.82953	0.43097
H	5.41649	1.46259	1.03374
C	5.22345	0.15036	-0.68348
H	6.27851	0.24631	-0.98289
C	4.35550	-0.68430	-1.42075
H	4.73959	-1.25034	-2.28412
O	-0.54553	0.09006	2.19711
N	-1.16029	-0.88180	-0.69061
N	-1.97515	-0.07315	-0.03265
C	-3.34062	-0.01280	-0.33330
C	-6.02800	0.16285	-0.91843
N	-3.80586	-0.69411	-1.39307
C	-4.16865	0.79357	0.49468
C	-5.52872	0.87586	0.18853
C	-5.11530	-0.60151	-1.66582
H	-3.74461	1.33829	1.35333
H	-6.19748	1.49173	0.81003
H	-5.46508	-1.17550	-2.54405
H	-7.09194	0.19936	-1.19492
H	-0.59538	0.49812	3.08277
H	-1.66868	0.37983	0.84597

Table S2. Atomic coordinates of phpl anion radical.

C	0.97095	-0.22037	0.16570
C	2.59727	1.16980	2.08926
C	2.39531	-0.13397	-0.01302
C	0.38156	0.18126	1.47638
C	1.26155	0.98994	2.33894
C	3.22638	0.58042	0.93411
H	0.78348	1.38604	3.25009
H	3.23064	1.74541	2.78834
C	0.19055	-0.84616	-0.88464
H	0.23717	-2.09668	-2.64453
C	0.87659	-1.56266	-1.92410
H	2.74383	-2.02997	-2.90296
C	2.24617	-1.51192	-2.06578
C	3.05017	-0.75910	-1.14391
C	4.61955	0.68331	0.71765
H	5.22450	1.24547	1.44957
C	5.23501	0.08081	-0.39226
H	6.32393	0.16864	-0.53860
C	4.45395	-0.64029	-1.30748
H	4.92498	-1.13143	-2.17576
O	-0.74039	-0.17444	1.89029
N	-1.16701	-0.82361	-1.03838
N	-1.79934	0.21839	-0.59120
C	-3.18093	0.11126	-0.54202
C	-5.95535	0.08561	-0.36854
N	-3.84250	-1.06622	-0.74018
C	-3.88239	1.31906	-0.24193
C	-5.27348	1.30470	-0.15843
C	-5.17532	-1.05410	-0.65182
H	-3.28638	2.22903	-0.07806
H	-5.82945	2.22858	0.07322
H	-5.68202	-2.02809	-0.81436
H	-7.05298	0.01629	-0.30657

Table S3. Atomic coordinates of phpl dianion.

C	0.99325	-0.24603	0.23763
C	2.65539	1.22182	2.06476
C	2.40289	-0.11751	0.00182
C	0.44691	0.12666	1.56382
C	1.32534	0.99165	2.36435
C	3.26087	0.64078	0.90610
H	0.86954	1.38187	3.29283
H	3.29009	1.83487	2.73560
C	0.16550	-0.89919	-0.79739
H	0.20916	-2.21920	-2.50016
C	0.86095	-1.65992	-1.80641
H	2.71484	-2.15612	-2.80448
C	2.22659	-1.60153	-1.98148
C	3.04802	-0.77464	-1.12849
C	4.65423	0.76700	0.63402
H	5.27092	1.35612	1.33872
C	5.24143	0.15390	-0.47670
H	6.32466	0.26040	-0.66825
C	4.43617	-0.62334	-1.34523
H	4.89120	-1.13893	-2.21122
O	-0.64344	-0.28252	2.03622
N	-1.16325	-0.82279	-1.02089
N	-1.83257	0.16702	-0.43443
C	-3.18491	0.08949	-0.49134
C	-6.01012	0.13487	-0.53168
N	-3.89161	-1.04383	-0.87744
C	-3.91329	1.27633	-0.09620
C	-5.30022	1.29902	-0.11982
C	-5.22303	-0.98208	-0.88526
H	-3.31284	2.14312	0.22247
H	-5.84654	2.21214	0.18293
H	-5.74755	-1.91667	-1.19897
H	-7.11256	0.09225	-0.55641

Figure S6. Calculated HOMO (top) and LUMO (bottom) of phpl (B3LYP/def2-TZVP).

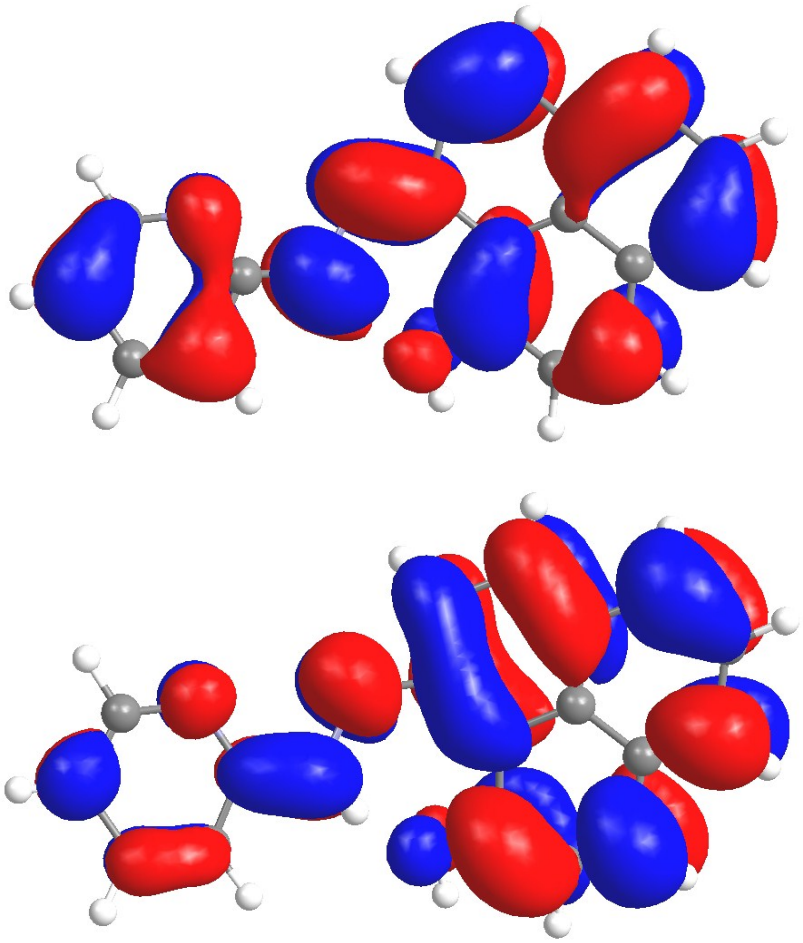


Table S4. Selected calculated electronic transitions of phpl (B3LYP/def2-TZVP/PCM(CH_2Cl_2).

Energy (cm^{-1})	λ (nm)	Oscillator strength	Contributions
23063.1	433.593	0.916	92.0% HOMO → LUMO
27195.9	367.702	0.0258	84.2% HOMO → L + 2
25208.7	396.688	0.00699	91.3% HOMO → L + 1

Table S5. Crystal data and structure refinement for **1** (CCDC 1850515).

Empirical formula	$C_{37}H_{23}Cl_3FeN_6O_2$	
Formula weight	745.81	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9198(6) Å	α = 62.430(2)°.
	b = 15.2069(10) Å	β = 84.064(2)°.
	c = 15.7177(10) Å	γ = 77.040(2)°.
Volume	1841.8(2) $Å^3$	
Z	2	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.667 mm^{-1}	
F(000)	760	
Crystal size	0.180 x 0.100 x 0.050 mm^3	
Theta range for data collection	1.462 to 27.571°.	
Index ranges	-11<=h<=11, -19<=k<=19, -20<=l<=20	
Reflections collected	45086	
Independent reflections	8520 [R(int) = 0.0679]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6765	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8520 / 0 / 455	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1214	
R indices (all data)	R1 = 0.0964, wR2 = 0.1413	
Largest diff. peak and hole	0.662 and -0.667 $e.Å^{-3}$	

Table S6. Bond lengths (Å) and angles (°) for **1**.

Fe(1)-N(1)	1.876(2)	C(9)-H(9A)	0.9500
Fe(1)-O(2)	1.8823(19)	C(10)-C(11)	1.425(4)
Fe(1)-O(1)	1.8952(18)	C(10)-H(10A)	0.9500
Fe(1)-N(4)	1.902(2)	C(11)-C(12)	1.415(4)
Fe(1)-N(3)	1.934(2)	C(12)-C(13)	1.430(4)
Fe(1)-N(6)	1.943(2)	C(14)-C(15)	1.391(4)
O(1)-C(1)	1.270(3)	C(15)-C(16)	1.380(4)
O(2)-C(19)	1.303(3)	C(15)-H(15A)	0.9500
N(1)-N(2)	1.338(3)	C(16)-C(17)	1.384(4)
N(1)-C(11)	1.387(3)	C(16)-H(16A)	0.9500
N(2)-C(14)	1.378(3)	C(17)-C(18)	1.374(4)
N(3)-C(18)	1.344(3)	C(17)-H(17A)	0.9500
N(3)-C(14)	1.352(3)	C(18)-H(18A)	0.9500
N(4)-C(29)	1.347(3)	C(19)-C(20)	1.419(4)
N(4)-N(5)	1.374(3)	C(19)-C(30)	1.422(4)
N(5)-C(32)	1.346(3)	C(20)-C(21)	1.351(4)
N(6)-C(36)	1.348(3)	C(20)-H(20A)	0.9500
N(6)-C(32)	1.364(3)	C(21)-C(22)	1.423(4)
C(1)-C(2)	1.442(4)	C(21)-H(21A)	0.9500
C(1)-C(12)	1.450(3)	C(22)-C(23)	1.409(4)
C(2)-C(3)	1.334(4)	C(22)-C(31)	1.412(4)
C(2)-H(2A)	0.9500	C(23)-C(24)	1.371(4)
C(3)-C(4)	1.430(4)	C(23)-H(23A)	0.9500
C(3)-H(3A)	0.9500	C(24)-C(25)	1.363(5)
C(4)-C(5)	1.387(4)	C(24)-H(24A)	0.9500
C(4)-C(13)	1.426(4)	C(25)-C(26)	1.398(4)
C(5)-C(6)	1.385(4)	C(25)-H(25A)	0.9500
C(5)-H(5A)	0.9500	C(26)-C(27)	1.416(4)
C(6)-C(7)	1.371(4)	C(26)-C(31)	1.421(4)
C(6)-H(6A)	0.9500	C(27)-C(28)	1.359(4)
C(7)-C(8)	1.411(4)	C(27)-H(27A)	0.9500
C(7)-H(7A)	0.9500	C(28)-C(29)	1.436(4)
C(8)-C(9)	1.398(4)	C(28)-H(28A)	0.9500
C(8)-C(13)	1.421(4)	C(29)-C(30)	1.433(4)
C(9)-C(10)	1.364(4)	C(30)-C(31)	1.440(4)

C(32)-C(33)	1.411(4)	N(1)-N(2)-C(14)	110.6(2)
C(33)-C(34)	1.363(4)	C(18)-N(3)-C(14)	118.7(2)
C(33)-H(33A)	0.9500	C(18)-N(3)-Fe(1)	129.50(17)
C(34)-C(35)	1.400(4)	C(14)-N(3)-Fe(1)	111.77(17)
C(34)-H(34A)	0.9500	C(29)-N(4)-N(5)	116.9(2)
C(35)-C(36)	1.366(4)	C(29)-N(4)-Fe(1)	127.02(19)
C(35)-H(35A)	0.9500	N(5)-N(4)-Fe(1)	115.99(16)
C(36)-H(36A)	0.9500	C(32)-N(5)-N(4)	110.0(2)
C(37)-Cl(3A)	1.561(11)	C(36)-N(6)-C(32)	119.2(2)
C(37)-Cl(2A)	1.727(10)	C(36)-N(6)-Fe(1)	129.90(19)
C(37)-Cl(1)	1.735(4)	C(32)-N(6)-Fe(1)	110.82(18)
C(37)-Cl(2)	1.738(4)	O(1)-C(1)-C(2)	116.4(2)
C(37)-Cl(3)	1.785(4)	O(1)-C(1)-C(12)	124.8(2)
C(37)-Cl(1A)	1.790(15)	C(2)-C(1)-C(12)	118.8(2)
C(37)-H(37)	1.0000	C(3)-C(2)-C(1)	121.8(2)
		C(3)-C(2)-H(2A)	119.1
N(1)-Fe(1)-O(2)	92.86(9)	C(1)-C(2)-H(2A)	119.1
N(1)-Fe(1)-O(1)	94.26(8)	C(2)-C(3)-C(4)	121.9(3)
O(2)-Fe(1)-O(1)	91.32(8)	C(2)-C(3)-H(3A)	119.1
N(1)-Fe(1)-N(4)	173.99(10)	C(4)-C(3)-H(3A)	119.1
O(2)-Fe(1)-N(4)	92.11(9)	C(5)-C(4)-C(13)	119.5(3)
O(1)-Fe(1)-N(4)	89.00(8)	C(5)-C(4)-C(3)	122.1(3)
N(1)-Fe(1)-N(3)	81.26(9)	C(13)-C(4)-C(3)	118.3(3)
O(2)-Fe(1)-N(3)	89.42(9)	C(6)-C(5)-C(4)	122.0(3)
O(1)-Fe(1)-N(3)	175.49(8)	C(6)-C(5)-H(5A)	119.0
N(4)-Fe(1)-N(3)	95.42(9)	C(4)-C(5)-H(5A)	119.0
N(1)-Fe(1)-N(6)	94.32(9)	C(7)-C(6)-C(5)	119.5(3)
O(2)-Fe(1)-N(6)	172.45(8)	C(7)-C(6)-H(6A)	120.2
O(1)-Fe(1)-N(6)	90.47(9)	C(5)-C(6)-H(6A)	120.2
N(4)-Fe(1)-N(6)	80.58(9)	C(6)-C(7)-C(8)	121.0(3)
N(3)-Fe(1)-N(6)	89.37(9)	C(6)-C(7)-H(7A)	119.5
C(1)-O(1)-Fe(1)	128.06(16)	C(8)-C(7)-H(7A)	119.5
C(19)-O(2)-Fe(1)	125.66(17)	C(9)-C(8)-C(7)	121.4(3)
N(2)-N(1)-C(11)	114.3(2)	C(9)-C(8)-C(13)	118.8(2)
N(2)-N(1)-Fe(1)	118.38(17)	C(7)-C(8)-C(13)	119.9(3)
C(11)-N(1)-Fe(1)	127.27(16)	C(10)-C(9)-C(8)	121.6(3)

C(10)-C(9)-H(9A)	119.2	C(20)-C(21)-H(21A)	119.7
C(8)-C(9)-H(9A)	119.2	C(22)-C(21)-H(21A)	119.7
C(9)-C(10)-C(11)	121.0(3)	C(23)-C(22)-C(31)	119.3(3)
C(9)-C(10)-H(10A)	119.5	C(23)-C(22)-C(21)	121.8(3)
C(11)-C(10)-H(10A)	119.5	C(31)-C(22)-C(21)	118.9(3)
N(1)-C(11)-C(12)	121.9(2)	C(24)-C(23)-C(22)	121.2(3)
N(1)-C(11)-C(10)	118.8(2)	C(24)-C(23)-H(23A)	119.4
C(12)-C(11)-C(10)	119.3(2)	C(22)-C(23)-H(23A)	119.4
C(11)-C(12)-C(13)	118.6(2)	C(25)-C(24)-C(23)	119.7(3)
C(11)-C(12)-C(1)	123.6(2)	C(25)-C(24)-H(24A)	120.1
C(13)-C(12)-C(1)	117.9(2)	C(23)-C(24)-H(24A)	120.1
C(8)-C(13)-C(4)	118.1(2)	C(24)-C(25)-C(26)	122.1(3)
C(8)-C(13)-C(12)	120.6(2)	C(24)-C(25)-H(25A)	119.0
C(4)-C(13)-C(12)	121.3(2)	C(26)-C(25)-H(25A)	119.0
N(3)-C(14)-N(2)	117.8(2)	C(25)-C(26)-C(27)	122.3(3)
N(3)-C(14)-C(15)	121.7(3)	C(25)-C(26)-C(31)	118.9(3)
N(2)-C(14)-C(15)	120.4(2)	C(27)-C(26)-C(31)	118.8(3)
C(16)-C(15)-C(14)	118.4(3)	C(28)-C(27)-C(26)	121.9(3)
C(16)-C(15)-H(15A)	120.8	C(28)-C(27)-H(27A)	119.0
C(14)-C(15)-H(15A)	120.8	C(26)-C(27)-H(27A)	119.0
C(15)-C(16)-C(17)	120.1(3)	C(27)-C(28)-C(29)	120.8(3)
C(15)-C(16)-H(16A)	120.0	C(27)-C(28)-H(28A)	119.6
C(17)-C(16)-H(16A)	120.0	C(29)-C(28)-H(28A)	119.6
C(18)-C(17)-C(16)	118.4(3)	N(4)-C(29)-C(30)	120.9(2)
C(18)-C(17)-H(17A)	120.8	N(4)-C(29)-C(28)	119.6(3)
C(16)-C(17)-H(17A)	120.8	C(30)-C(29)-C(28)	119.4(2)
N(3)-C(18)-C(17)	122.7(2)	C(19)-C(30)-C(29)	123.4(2)
N(3)-C(18)-H(18A)	118.7	C(19)-C(30)-C(31)	118.2(3)
C(17)-C(18)-H(18A)	118.7	C(29)-C(30)-C(31)	118.2(2)
O(2)-C(19)-C(20)	116.5(2)	C(22)-C(31)-C(26)	118.7(3)
O(2)-C(19)-C(30)	124.3(3)	C(22)-C(31)-C(30)	120.7(2)
C(20)-C(19)-C(30)	119.1(2)	C(26)-C(31)-C(30)	120.7(3)
C(21)-C(20)-C(19)	122.3(3)	N(5)-C(32)-N(6)	119.2(3)
C(21)-C(20)-H(20A)	118.9	N(5)-C(32)-C(33)	121.2(2)
C(19)-C(20)-H(20A)	118.9	N(6)-C(32)-C(33)	119.6(3)
C(20)-C(21)-C(22)	120.6(3)	C(34)-C(33)-C(32)	119.9(3)

C(34)-C(33)-H(33A)	120.0	C(35)-C(36)-H(36A)	118.5
C(32)-C(33)-H(33A)	120.0	Cl(3A)-C(37)-Cl(2A)	118.1(6)
C(33)-C(34)-C(35)	119.6(3)	Cl(1)-C(37)-Cl(2)	111.7(2)
C(33)-C(34)-H(34A)	120.2	Cl(1)-C(37)-Cl(3)	108.0(2)
C(35)-C(34)-H(34A)	120.2	Cl(2)-C(37)-Cl(3)	110.4(2)
C(36)-C(35)-C(34)	118.4(3)	Cl(3A)-C(37)-Cl(1A)	109.7(7)
C(36)-C(35)-H(35A)	120.8	Cl(2A)-C(37)-Cl(1A)	118.3(6)
C(34)-C(35)-H(35A)	120.8	Cl(1)-C(37)-H(37)	108.9
N(6)-C(36)-C(35)	123.0(3)	Cl(2)-C(37)-H(37)	108.9
N(6)-C(36)-H(36A)	118.5	Cl(3)-C(37)-H(37)	108.9

Figure S7. Molecular structure of **1** with data collected at 300(2) K (displacement ellipsoids at 30% probability). H atoms and solvent omitted for clarity.

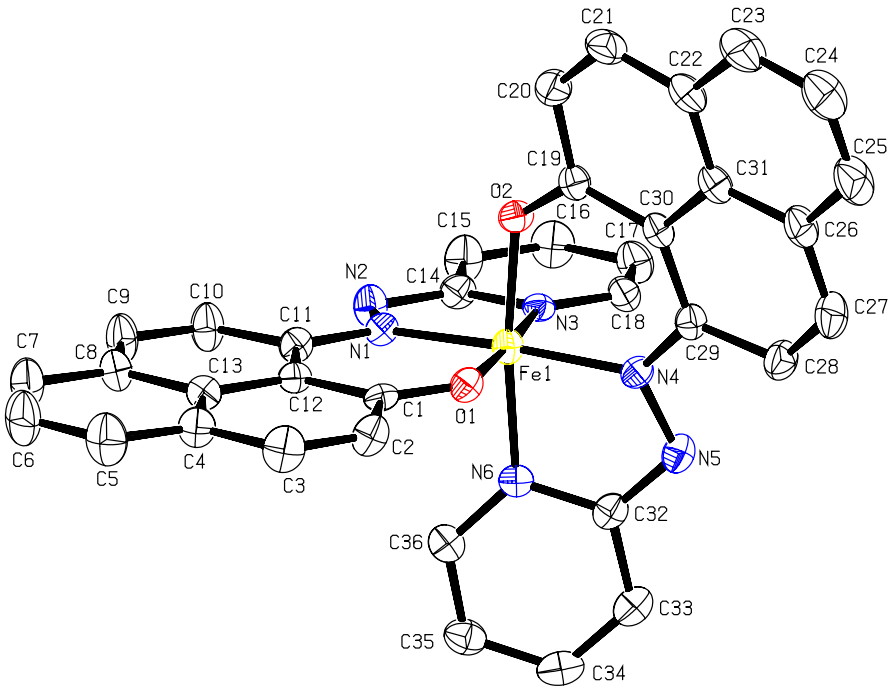


Table S7. Crystallographic parameters for **1** (300(2) K) (CCDC 1850517).

Empirical formula	$C_{37}H_{23}Cl_3FeN_6O_2$	
Formula weight	745.81	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9729(16) Å	α = 63.208(5)°.
	b = 15.308(3) Å	β = 83.982(5)°.
	c = 15.837(3) Å	γ = 77.463(5)°.
Volume	1895.4(6) $Å^3$	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.649 mm^{-1}	
F(000)	760	
Crystal size	0.180 x 0.100 x 0.050 mm^3	
Theta range for data collection	1.440 to 27.705°.	
Index ranges	-11<=h<=11, -19<=k<=19, -20<=l<=20	
Reflections collected	39529	
Independent reflections	8721 [R(int) = 0.0518]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6259	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8721 / 0 / 456	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0720, wR2 = 0.1832	
R indices (all data)	R1 = 0.1222, wR2 = 0.2273	
Largest diff. peak and hole	0.771 and -0.592 $e.Å^{-3}$	

Table S8. Bond distances (Å) and angles (°) for **1** (300(2) K).

Fe(1)-N(1)	1.881(3)	C(6)-H(6A)	0.9300
Fe(1)-O(2)	1.889(3)	C(7)-C(8)	1.407(6)
Fe(1)-O(1)	1.903(3)	C(7)-H(7A)	0.9300
Fe(1)-N(4)	1.906(3)	C(8)-C(9)	1.400(6)
Fe(1)-N(3)	1.935(3)	C(8)-C(13)	1.432(6)
Fe(1)-N(6)	1.946(3)	C(9)-C(10)	1.355(6)
O(1)-C(1)	1.264(4)	C(9)-H(9A)	0.9300
O(2)-C(19)	1.295(4)	C(10)-C(11)	1.422(5)
N(1)-N(2)	1.338(4)	C(10)-H(10A)	0.9300
N(1)-C(11)	1.387(5)	C(11)-C(12)	1.418(5)
N(2)-C(14)	1.368(5)	C(12)-C(13)	1.429(5)
N(3)-C(18)	1.330(5)	C(14)-C(15)	1.409(6)
N(3)-C(14)	1.361(5)	C(15)-C(16)	1.370(6)
N(4)-C(29)	1.353(5)	C(15)-H(15A)	0.9300
N(4)-N(5)	1.368(4)	C(16)-C(17)	1.387(6)
N(5)-C(32)	1.335(5)	C(16)-H(16A)	0.9300
N(6)-C(36)	1.339(5)	C(17)-C(18)	1.381(6)
N(6)-C(32)	1.374(5)	C(17)-H(17A)	0.9300
C(1)-C(2)	1.447(5)	C(18)-H(18A)	0.9300
C(1)-C(12)	1.455(5)	C(19)-C(30)	1.426(5)
C(2)-C(3)	1.333(6)	C(19)-C(20)	1.436(6)
C(2)-H(2A)	0.9300	C(20)-C(21)	1.359(6)
C(3)-C(4)	1.426(6)	C(20)-H(20A)	0.9300
C(3)-H(3A)	0.9300	C(21)-C(22)	1.407(7)
C(4)-C(5)	1.392(6)	C(21)-H(21A)	0.9300
C(4)-C(13)	1.421(6)	C(22)-C(23)	1.412(6)
C(5)-C(6)	1.377(7)	C(22)-C(31)	1.420(6)
C(5)-H(5A)	0.9300	C(23)-C(24)	1.380(8)
C(6)-C(7)	1.359(7)	C(23)-H(23A)	0.9300

C(24)-C(25)	1.361(8)	O(1)-Fe(1)-N(3)	175.43(12)
C(24)-H(24A)	0.9300	N(4)-Fe(1)-N(3)	95.57(13)
C(25)-C(26)	1.405(6)	N(1)-Fe(1)-N(6)	94.69(13)
C(25)-H(25A)	0.9300	O(2)-Fe(1)-N(6)	172.94(12)
C(26)-C(31)	1.413(6)	O(1)-Fe(1)-N(6)	90.07(12)
C(26)-C(27)	1.420(7)	N(4)-Fe(1)-N(6)	80.66(13)
C(27)-C(28)	1.348(6)	N(3)-Fe(1)-N(6)	89.73(12)
C(27)-H(27A)	0.9300	C(1)-O(1)-Fe(1)	127.9(2)
C(28)-C(29)	1.433(5)	C(19)-O(2)-Fe(1)	125.8(2)
C(28)-H(28A)	0.9300	N(2)-N(1)-C(11)	113.9(3)
C(29)-C(30)	1.442(6)	N(2)-N(1)-Fe(1)	118.3(2)
C(30)-C(31)	1.430(5)	C(11)-N(1)-Fe(1)	127.5(2)
C(32)-C(33)	1.423(6)	N(1)-N(2)-C(14)	110.6(3)
C(33)-C(34)	1.365(7)	C(18)-N(3)-C(14)	118.8(3)
C(33)-H(33A)	0.9300	C(18)-N(3)-Fe(1)	129.9(3)
C(34)-C(35)	1.392(7)	C(14)-N(3)-Fe(1)	111.3(2)
C(34)-H(34A)	0.9300	C(29)-N(4)-N(5)	116.3(3)
C(35)-C(36)	1.371(6)	C(29)-N(4)-Fe(1)	127.1(3)
C(35)-H(35A)	0.9300	N(5)-N(4)-Fe(1)	116.5(2)
C(36)-H(36A)	0.9300	C(32)-N(5)-N(4)	109.9(3)
C(37)-Cl(3A)	1.529(14)	C(36)-N(6)-C(32)	119.7(3)
C(37)-Cl(2)	1.646(9)	C(36)-N(6)-Fe(1)	130.0(3)
C(37)-Cl(1)	1.697(10)	C(32)-N(6)-Fe(1)	110.1(3)
C(37)-Cl(2A)	1.771(13)	O(1)-C(1)-C(2)	116.6(3)
C(37)-Cl(3)	1.807(10)	O(1)-C(1)-C(12)	125.1(3)
C(37)-Cl(1A)	1.83(2)	C(2)-C(1)-C(12)	118.4(3)
C(37)-H(37)	0.9800	C(3)-C(2)-C(1)	122.0(4)
		C(3)-C(2)-H(2A)	119.0
N(1)-Fe(1)-O(2)	92.11(12)	C(1)-C(2)-H(2A)	119.0
N(1)-Fe(1)-O(1)	94.17(12)	C(2)-C(3)-C(4)	122.1(4)
O(2)-Fe(1)-O(1)	91.31(12)	C(2)-C(3)-H(3A)	118.9
N(1)-Fe(1)-N(4)	174.44(13)	C(4)-C(3)-H(3A)	118.9
O(2)-Fe(1)-N(4)	92.44(13)	C(5)-C(4)-C(13)	119.8(4)
O(1)-Fe(1)-N(4)	88.91(12)	C(5)-C(4)-C(3)	122.3(4)
N(1)-Fe(1)-N(3)	81.29(13)	C(13)-C(4)-C(3)	117.9(4)
O(2)-Fe(1)-N(3)	89.45(12)	C(6)-C(5)-C(4)	121.7(5)

C(6)-C(5)-H(5A)	119.1	C(18)-C(17)-H(17A)	120.8
C(4)-C(5)-H(5A)	119.1	C(16)-C(17)-H(17A)	120.8
C(7)-C(6)-C(5)	120.2(5)	N(3)-C(18)-C(17)	123.2(4)
C(7)-C(6)-H(6A)	119.9	N(3)-C(18)-H(18A)	118.4
C(5)-C(6)-H(6A)	119.9	C(17)-C(18)-H(18A)	118.4
C(6)-C(7)-C(8)	120.9(5)	O(2)-C(19)-C(30)	125.2(4)
C(6)-C(7)-H(7A)	119.6	O(2)-C(19)-C(20)	116.2(3)
C(8)-C(7)-H(7A)	119.6	C(30)-C(19)-C(20)	118.6(4)
C(9)-C(8)-C(7)	122.0(4)	C(21)-C(20)-C(19)	121.6(4)
C(9)-C(8)-C(13)	117.9(4)	C(21)-C(20)-H(20A)	119.2
C(7)-C(8)-C(13)	120.1(4)	C(19)-C(20)-H(20A)	119.2
C(10)-C(9)-C(8)	122.5(4)	C(20)-C(21)-C(22)	121.0(4)
C(10)-C(9)-H(9A)	118.7	C(20)-C(21)-H(21A)	119.5
C(8)-C(9)-H(9A)	118.7	C(22)-C(21)-H(21A)	119.5
C(9)-C(10)-C(11)	120.9(4)	C(21)-C(22)-C(23)	120.8(5)
C(9)-C(10)-H(10A)	119.6	C(21)-C(22)-C(31)	119.3(4)
C(11)-C(10)-H(10A)	119.6	C(23)-C(22)-C(31)	119.9(5)
N(1)-C(11)-C(12)	121.4(3)	C(24)-C(23)-C(22)	120.4(5)
N(1)-C(11)-C(10)	119.2(3)	C(24)-C(23)-H(23A)	119.8
C(12)-C(11)-C(10)	119.4(4)	C(22)-C(23)-H(23A)	119.8
C(11)-C(12)-C(13)	118.7(3)	C(25)-C(24)-C(23)	120.2(5)
C(11)-C(12)-C(1)	123.8(3)	C(25)-C(24)-H(24A)	119.9
C(13)-C(12)-C(1)	117.5(3)	C(23)-C(24)-H(24A)	119.9
C(4)-C(13)-C(12)	122.0(4)	C(24)-C(25)-C(26)	121.5(5)
C(4)-C(13)-C(8)	117.4(4)	C(24)-C(25)-H(25A)	119.2
C(12)-C(13)-C(8)	120.5(4)	C(26)-C(25)-H(25A)	119.2
N(3)-C(14)-N(2)	118.3(3)	C(25)-C(26)-C(31)	119.7(5)
N(3)-C(14)-C(15)	120.9(4)	C(25)-C(26)-C(27)	122.1(4)
N(2)-C(14)-C(15)	120.8(4)	C(31)-C(26)-C(27)	118.2(4)
C(16)-C(15)-C(14)	119.0(4)	C(28)-C(27)-C(26)	122.4(4)
C(16)-C(15)-H(15A)	120.5	C(28)-C(27)-H(27A)	118.8
C(14)-C(15)-H(15A)	120.5	C(26)-C(27)-H(27A)	118.8
C(15)-C(16)-C(17)	119.8(4)	C(27)-C(28)-C(29)	120.9(4)
C(15)-C(16)-H(16A)	120.1	C(27)-C(28)-H(28A)	119.6
C(17)-C(16)-H(16A)	120.1	C(29)-C(28)-H(28A)	119.6
C(18)-C(17)-C(16)	118.4(4)	N(4)-C(29)-C(28)	120.0(4)

N(4)-C(29)-C(30)	121.1(3)	C(35)-C(34)-H(34A)	120.1
C(28)-C(29)-C(30)	118.9(4)	C(36)-C(35)-C(34)	119.0(4)
C(19)-C(30)-C(31)	118.7(4)	C(36)-C(35)-H(35A)	120.5
C(19)-C(30)-C(29)	123.0(3)	C(34)-C(35)-H(35A)	120.5
C(31)-C(30)-C(29)	118.3(4)	N(6)-C(36)-C(35)	122.6(4)
C(26)-C(31)-C(22)	118.2(4)	N(6)-C(36)-H(36A)	118.7
C(26)-C(31)-C(30)	121.3(4)	C(35)-C(36)-H(36A)	118.7
C(22)-C(31)-C(30)	120.5(4)	Cl(2)-C(37)-Cl(1)	112.2(7)
N(5)-C(32)-N(6)	120.0(4)	Cl(3A)-C(37)-Cl(2A)	124.0(9)
N(5)-C(32)-C(33)	120.9(4)	Cl(2)-C(37)-Cl(3)	112.7(6)
N(6)-C(32)-C(33)	119.0(4)	Cl(1)-C(37)-Cl(3)	103.5(6)
C(34)-C(33)-C(32)	119.7(4)	Cl(3A)-C(37)-Cl(1A)	107.5(11)
C(34)-C(33)-H(33A)	120.2	Cl(2A)-C(37)-Cl(1A)	118.2(9)
C(32)-C(33)-H(33A)	120.2	Cl(2)-C(37)-H(37)	109.4
C(33)-C(34)-C(35)	119.7(4)	Cl(1)-C(37)-H(37)	109.4
C(33)-C(34)-H(34A)	120.1	Cl(3)-C(37)-H(37)	109.4

Figure S8. Molecular structure of **2** with data collected at 150(2) K (displacement ellipsoids at 30% probability). H atoms and solvent omitted for clarity.

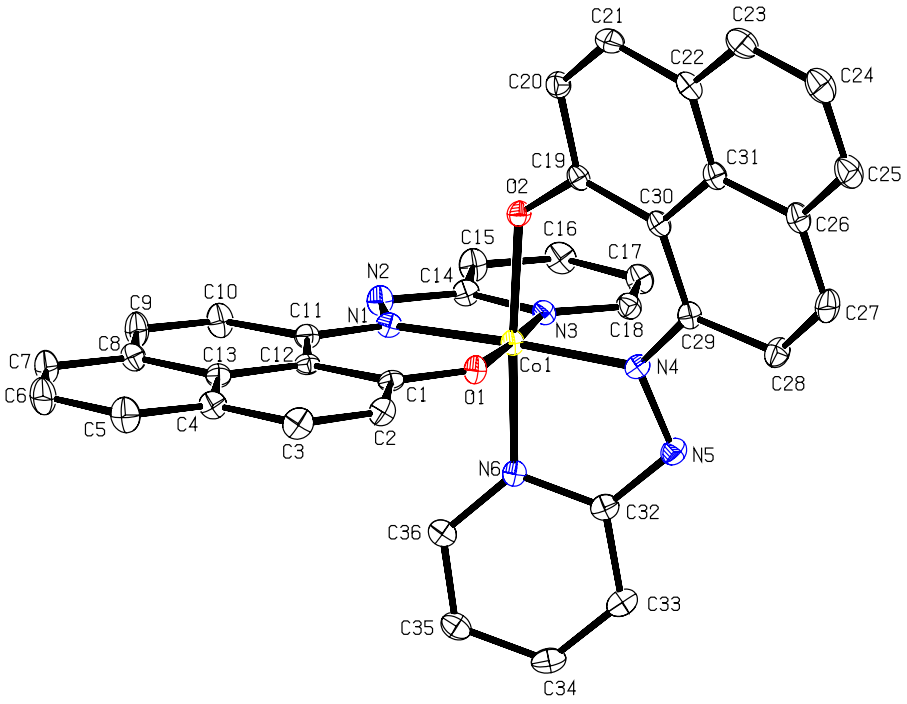


Table S9. Crystallographic parameters for **2** (150(2) K) (CCDC 1911792).

Empirical formula	$C_{37}H_{23}Cl_3CoN_6O_2$	
Formula weight	748.89	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 8.8117(4) Å	α = 63.6340(10)°.
	b = 15.1002(8) Å	β = 83.957(2)°.
	c = 15.6455(8) Å	γ = 78.009(2)°.
Volume	1824.31(16) $Å^3$	
Z	2	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	0.731 mm^{-1}	
F(000)	762	
Crystal size	0.150 x 0.140 x 0.140 mm^3	
Theta range for data collection	1.453 to 27.643°.	
Index ranges	-11<=h<=11, -19<=k<=19, -20<=l<=20	
Reflections collected	45917	
Independent reflections	8468 [R(int) = 0.0683]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6689	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8468 / 15 / 455	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1164	

R indices (all data)	R1 = 0.0848, wR2 = 0.1312
Extinction coefficient	n/a
Largest diff. peak and hole	0.630 and -0.837 e.Å^{-3}

Table S10. Bond distances (Å) and angles (°) for **2** (150(2) K).

Co(1)-N(4)	1.882(2)	C(5)-C(6)	1.384(4)
Co(1)-O(1)	1.8833(17)	C(5)-H(5A)	0.9500
Co(1)-O(2)	1.8873(18)	C(6)-C(7)	1.373(4)
Co(1)-N(1)	1.896(2)	C(6)-H(6A)	0.9500
Co(1)-N(3)	1.902(2)	C(7)-C(8)	1.410(4)
Co(1)-N(6)	1.909(2)	C(7)-H(7A)	0.9500
O(1)-C(1)	1.278(3)	C(8)-C(9)	1.412(4)
O(2)-C(19)	1.314(3)	C(8)-C(13)	1.419(4)
N(1)-N(2)	1.336(3)	C(9)-C(10)	1.355(4)
N(1)-C(11)	1.366(3)	C(9)-H(9A)	0.9500
N(2)-C(14)	1.368(3)	C(10)-C(11)	1.429(4)
N(3)-C(18)	1.343(3)	C(10)-H(10A)	0.9500
N(3)-C(14)	1.363(3)	C(11)-C(12)	1.423(3)
N(4)-C(29)	1.328(3)	C(12)-C(13)	1.436(4)
N(4)-N(5)	1.390(3)	C(14)-C(15)	1.401(4)
N(5)-C(32)	1.331(3)	C(15)-C(16)	1.373(4)
N(6)-C(36)	1.356(3)	C(15)-H(15A)	0.9500
N(6)-C(32)	1.376(3)	C(16)-C(17)	1.389(4)
C(1)-C(2)	1.437(3)	C(16)-H(16A)	0.9500
C(1)-C(12)	1.444(3)	C(17)-C(18)	1.379(4)
C(2)-C(3)	1.345(4)	C(17)-H(17A)	0.9500
C(2)-H(2A)	0.9500	C(18)-H(18A)	0.9500
C(3)-C(4)	1.428(4)	C(19)-C(20)	1.416(4)
C(3)-H(3A)	0.9500	C(19)-C(30)	1.418(4)
C(4)-C(5)	1.393(4)	C(20)-C(21)	1.360(4)
C(4)-C(13)	1.420(4)	C(20)-H(20A)	0.9500

C(21)-C(22)	1.424(4)	O(1)-Co(1)-O(2)	90.20(8)
C(21)-H(21A)	0.9500	N(4)-Co(1)-N(1)	175.01(9)
C(22)-C(23)	1.406(4)	O(1)-Co(1)-N(1)	94.84(8)
C(22)-C(31)	1.413(4)	O(2)-Co(1)-N(1)	89.64(8)
C(23)-C(24)	1.372(4)	N(4)-Co(1)-N(3)	94.41(9)
C(23)-H(23A)	0.9500	O(1)-Co(1)-N(3)	176.99(9)
C(24)-C(25)	1.381(4)	O(2)-Co(1)-N(3)	88.98(8)
C(24)-H(24A)	0.9500	N(1)-Co(1)-N(3)	82.27(9)
C(25)-C(26)	1.391(4)	N(4)-Co(1)-N(6)	82.45(9)
C(25)-H(25A)	0.9500	O(1)-Co(1)-N(6)	90.28(8)
C(26)-C(27)	1.423(4)	O(2)-Co(1)-N(6)	176.44(8)
C(26)-C(31)	1.427(4)	N(1)-Co(1)-N(6)	93.83(9)
C(27)-C(28)	1.354(4)	N(3)-Co(1)-N(6)	90.71(9)
C(27)-H(27A)	0.9500	C(1)-O(1)-Co(1)	126.66(16)
C(28)-C(29)	1.444(4)	C(19)-O(2)-Co(1)	124.03(17)
C(28)-H(28A)	0.9500	N(2)-N(1)-C(11)	115.9(2)
C(29)-C(30)	1.447(4)	N(2)-N(1)-Co(1)	116.85(16)
C(30)-C(31)	1.444(4)	C(11)-N(1)-Co(1)	127.20(17)
C(32)-C(33)	1.424(4)	N(1)-N(2)-C(14)	111.0(2)
C(33)-C(34)	1.358(4)	C(18)-N(3)-C(14)	119.1(2)
C(33)-H(33A)	0.9500	C(18)-N(3)-Co(1)	129.53(18)
C(34)-C(35)	1.407(4)	C(14)-N(3)-Co(1)	111.35(17)
C(34)-H(34A)	0.9500	C(29)-N(4)-N(5)	118.0(2)
C(35)-C(36)	1.366(4)	C(29)-N(4)-Co(1)	126.78(18)
C(35)-H(35A)	0.9500	N(5)-N(4)-Co(1)	114.95(16)
C(36)-H(36A)	0.9500	C(32)-N(5)-N(4)	110.2(2)
C(37)-Cl(3A)	1.653(6)	C(36)-N(6)-C(32)	119.7(2)
C(37)-Cl(2A)	1.710(6)	C(36)-N(6)-Co(1)	129.95(19)
C(37)-Cl(2)	1.730(3)	C(32)-N(6)-Co(1)	110.21(17)
C(37)-Cl(1)	1.731(3)	O(1)-C(1)-C(2)	115.6(2)
C(37)-Cl(1A)	1.771(7)	O(1)-C(1)-C(12)	125.6(2)
C(37)-Cl(3)	1.792(4)	C(2)-C(1)-C(12)	118.8(2)
C(37)-H(37)	1.0000	C(3)-C(2)-C(1)	122.1(2)
		C(3)-C(2)-H(2A)	118.9
N(4)-Co(1)-O(1)	88.53(8)	C(1)-C(2)-H(2A)	118.9
N(4)-Co(1)-O(2)	94.04(9)	C(2)-C(3)-C(4)	121.3(2)

C(2)-C(3)-H(3A)	119.4	C(16)-C(15)-H(15A)	120.4
C(4)-C(3)-H(3A)	119.4	C(14)-C(15)-H(15A)	120.4
C(5)-C(4)-C(13)	119.7(3)	C(15)-C(16)-C(17)	119.7(2)
C(5)-C(4)-C(3)	121.7(2)	C(15)-C(16)-H(16A)	120.2
C(13)-C(4)-C(3)	118.5(2)	C(17)-C(16)-H(16A)	120.2
C(6)-C(5)-C(4)	121.5(3)	C(18)-C(17)-C(16)	118.9(3)
C(6)-C(5)-H(5A)	119.3	C(18)-C(17)-H(17A)	120.5
C(4)-C(5)-H(5A)	119.3	C(16)-C(17)-H(17A)	120.5
C(7)-C(6)-C(5)	119.9(3)	N(3)-C(18)-C(17)	122.3(2)
C(7)-C(6)-H(6A)	120.0	N(3)-C(18)-H(18A)	118.9
C(5)-C(6)-H(6A)	120.0	C(17)-C(18)-H(18A)	118.9
C(6)-C(7)-C(8)	120.6(3)	O(2)-C(19)-C(20)	115.6(2)
C(6)-C(7)-H(7A)	119.7	O(2)-C(19)-C(30)	125.0(2)
C(8)-C(7)-H(7A)	119.7	C(20)-C(19)-C(30)	119.4(2)
C(7)-C(8)-C(9)	120.7(3)	C(21)-C(20)-C(19)	122.1(3)
C(7)-C(8)-C(13)	120.1(2)	C(21)-C(20)-H(20A)	118.9
C(9)-C(8)-C(13)	119.2(2)	C(19)-C(20)-H(20A)	118.9
C(10)-C(9)-C(8)	121.2(3)	C(20)-C(21)-C(22)	120.6(3)
C(10)-C(9)-H(9A)	119.4	C(20)-C(21)-H(21A)	119.7
C(8)-C(9)-H(9A)	119.4	C(22)-C(21)-H(21A)	119.7
C(9)-C(10)-C(11)	121.3(2)	C(23)-C(22)-C(31)	119.7(3)
C(9)-C(10)-H(10A)	119.3	C(23)-C(22)-C(21)	121.8(3)
C(11)-C(10)-H(10A)	119.3	C(31)-C(22)-C(21)	118.6(2)
N(1)-C(11)-C(12)	121.3(2)	C(24)-C(23)-C(22)	121.2(3)
N(1)-C(11)-C(10)	119.1(2)	C(24)-C(23)-H(23A)	119.4
C(12)-C(11)-C(10)	119.5(2)	C(22)-C(23)-H(23A)	119.4
C(11)-C(12)-C(13)	118.3(2)	C(23)-C(24)-C(25)	119.6(3)
C(11)-C(12)-C(1)	124.0(2)	C(23)-C(24)-H(24A)	120.2
C(13)-C(12)-C(1)	117.8(2)	C(25)-C(24)-H(24A)	120.2
C(8)-C(13)-C(4)	118.1(2)	C(24)-C(25)-C(26)	121.7(3)
C(8)-C(13)-C(12)	120.4(2)	C(24)-C(25)-H(25A)	119.2
C(4)-C(13)-C(12)	121.5(2)	C(26)-C(25)-H(25A)	119.2
N(3)-C(14)-N(2)	118.5(2)	C(25)-C(26)-C(27)	122.0(3)
N(3)-C(14)-C(15)	120.9(2)	C(25)-C(26)-C(31)	119.4(3)
N(2)-C(14)-C(15)	120.6(2)	C(27)-C(26)-C(31)	118.6(2)
C(16)-C(15)-C(14)	119.1(3)	C(28)-C(27)-C(26)	122.4(3)

C(28)-C(27)-H(27A)	118.8	C(32)-C(33)-H(33A)	120.3
C(26)-C(27)-H(27A)	118.8	C(33)-C(34)-C(35)	120.5(3)
C(27)-C(28)-C(29)	120.9(3)	C(33)-C(34)-H(34A)	119.8
C(27)-C(28)-H(28A)	119.5	C(35)-C(34)-H(34A)	119.8
C(29)-C(28)-H(28A)	119.5	C(36)-C(35)-C(34)	118.4(3)
N(4)-C(29)-C(28)	119.7(2)	C(36)-C(35)-H(35A)	120.8
N(4)-C(29)-C(30)	121.4(2)	C(34)-C(35)-H(35A)	120.8
C(28)-C(29)-C(30)	118.9(2)	N(6)-C(36)-C(35)	122.5(3)
C(19)-C(30)-C(31)	118.0(2)	N(6)-C(36)-H(36A)	118.8
C(19)-C(30)-C(29)	123.5(2)	C(35)-C(36)-H(36A)	118.8
C(31)-C(30)-C(29)	118.5(2)	Cl(3A)-C(37)-Cl(2A)	124.4(5)
C(22)-C(31)-C(26)	118.4(2)	Cl(2)-C(37)-Cl(1)	113.1(2)
C(22)-C(31)-C(30)	121.0(2)	Cl(3A)-C(37)-Cl(1A)	107.0(6)
C(26)-C(31)-C(30)	120.5(3)	Cl(2A)-C(37)-Cl(1A)	113.4(6)
N(5)-C(32)-N(6)	119.7(2)	Cl(2)-C(37)-Cl(3)	109.2(2)
N(5)-C(32)-C(33)	121.1(3)	Cl(1)-C(37)-Cl(3)	107.28(19)
N(6)-C(32)-C(33)	119.1(2)	Cl(2)-C(37)-H(37)	109.1
C(34)-C(33)-C(32)	119.5(3)	Cl(1)-C(37)-H(37)	109.1
C(34)-C(33)-H(33A)	120.3	Cl(3)-C(37)-H(37)	109.1

Figure S9. ESI mass spectrum (positive ion mode) of **1**.

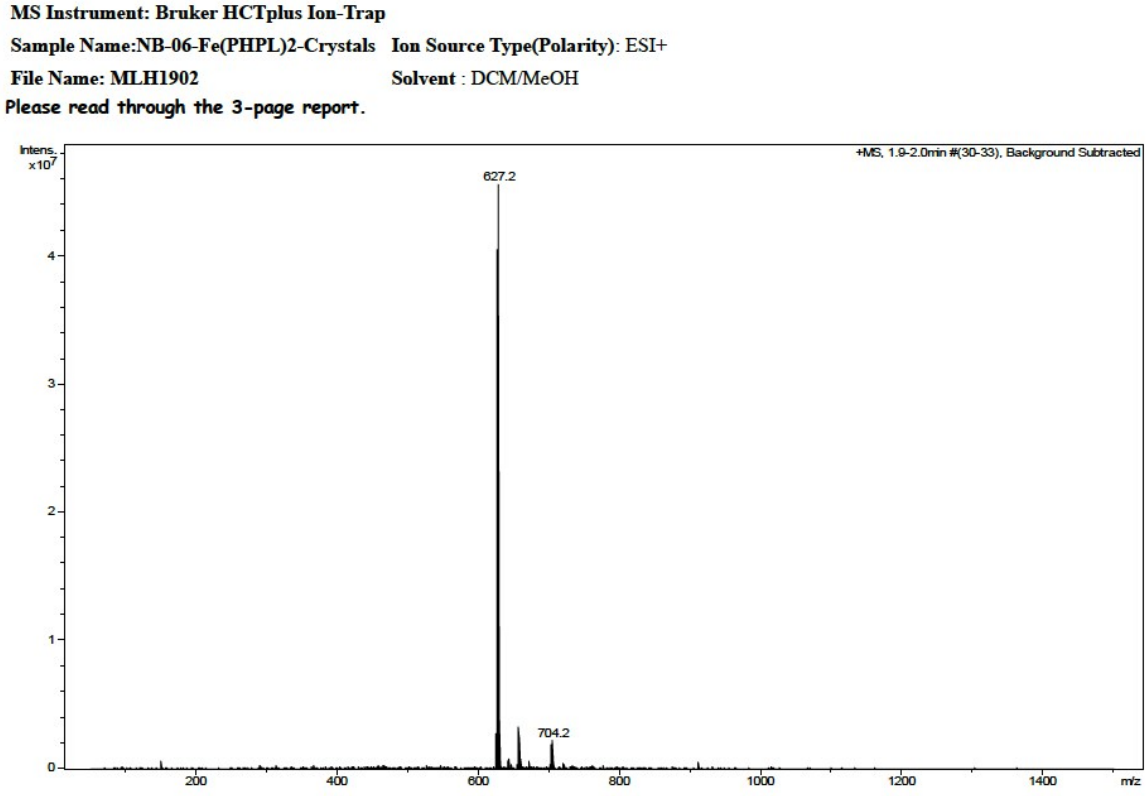


Table S11. Calculated electronic transitions of **1** (B3LYP/def2-TZVP/PCM(CH_2Cl_2).

Index	E / cm^{-1}	λ / nm	ϕ	Contributions (>/= 10%)
0	2851.17	3507.332	1.00E-04	87.4% HOMO(B) => LUMO(B)
1	3255.254	3071.957	4.70E-03	25.3% HOMO(A) => LUMO(A), 12.2% HOMO(B) => LUMO(B)
2	4269.899	2341.976	2.40E-03	22.0% H-5(A) => LUMO(A), 14.6% H-1(A) => LUMO(A), 13.8% H-5(A) => L+1(A)
3	8239.76	1213.628	1.49E-02	37.1% HOMO(A) => LUMO(A), 14.4% HOMO(A) => L+2(A), 11.0% HOMO(B) => L+2(B)
4	9108.419	1097.885	3.70E-03	42.7% HOMO(B) => L+2(B), 30.6% HOMO(A) => L+2(A), 11.5% HOMO(A) => LUMO(A)
5	10990.917	909.842	6.90E-03	78.3% HOMO(A) => L+1(A), 15.6% HOMO(A) => LUMO(A)
6	13110.542	762.745	2.00E-03	94.8% HOMO(B) => L+1(B)
7	13462.2	742.821	3.02E-02	52.9% H-1(A) => LUMO(A)
8	14090.506	709.698	8.10E-03	12.3% H-1(B) => LUMO(B)
9	14320.374	698.306	5.00E-04	37.2% H-1(B) => LUMO(B), 14.8% H-2(B) => LUMO(B), 14.4% H-1(A) => L+1(A), 13.1% H-3(B) => LUMO(B)
10	14580.084	685.867	3.29E-02	52.7% H-1(A) => L+1(A), 17.2% H-1(B) => LUMO(B)
11	15475.36	646.189	4.21E-02	22.3% H-2(B) => LUMO(B), 18.3% H-1(B) => LUMO(B), 12.2% H-3(B) => LUMO(B)
12	15604.409	640.845	1.70E-02	10.6% H-1(B) => LUMO(B)
13	15978.65	625.835	3.08E-01	47.5% HOMO(A) => L+2(A), 40.6% HOMO(B) => L+2(B)
14	17708.709	564.694	1.25E-02	8.43% H-8(B) => L+7(B), 7.89% H-5(A) => L+12(A)
15	18146.668	551.065	1.23E-02	32.4% H-2(B) => LUMO(B), 31.7% H-3(B) => LUMO(B)

16	18685.446	535.176	1.57E-01	61.5% H-4(B) => LUMO(B)
17	19036.298	525.312	3.70E-03	12.5% H-1(A) => L+2(A), 11.2% H-7(B) => L+7(B)
18	19433.122	514.585	5.19E-02	12.5% H-1(A) => L+2(A), 10.8% HOMO(B) => L+4(B), 10.6% H-2(A) => LUMO(A)
19	19536.361	511.866	7.07E-02	44.5% H-5(B) => LUMO(B)
20	19861.403	503.489	3.60E-03	28.6% H-1(A) => L+2(A), 10.4% HOMO(B) => L+6(B)
21	20024.327	499.393	1.72E-02	15.4% H-2(A) => LUMO(A), 14.2% HOMO(B) => L+4(B)
22	20409.053	489.979	8.50E-03	68.7% HOMO(A) => L+3(A)
23	20545.361	486.728	1.00E-01	20.6% H-2(A) => LUMO(A), 19.6% H-1(A) => L+2(A), 16.5% HOMO(A) => L+3(A)
24	20944.605	477.45	3.79E-02	27.4% H-7(B) => LUMO(B)
25	21249.483	470.6	4.20E-03	13.5% HOMO(B) => L+3(B), 13.1% HOMO(B) => L+5(B), 10.3% HOMO(B) => L+4(B)
26	21278.519	469.958	1.88E-02	75.4% HOMO(B) => L+3(B)
27	21962.477	455.322	5.00E-03	13.7% H-1(B) => L+2(B)
28	22098.785	452.514	3.40E-03	37.0% HOMO(B) => L+7(B)
29	22217.348	450.099	1.21E-02	57.6% H-8(B) => LUMO(B)
30	22730.317	439.941	2.92E-02	28.4% H-7(B) => LUMO(B)
31	22876.303	437.134	8.10E-03	13.3% H-1(B) => L+2(B)
32	23216.669	430.725	1.51E-02	38.1% H-2(A) => L+1(A), 12.2% H-5(A) => LUMO(A), 11.5% H-3(A) => L+1(A)
33	23354.59	428.181	7.30E-03	26.6% H-3(A) => LUMO(A), 20.8% H-4(A) => LUMO(A), 12.4% H-2(A) => L+2(A)
34	23924.017	417.99	1.51E-02	57.6% H-1(A) => L+3(A)
35	24010.319	416.488	5.10E-03	23.8% HOMO(A) => L+5(A), 12.1% HOMO(B) => L+6(B)
36	24097.427	414.982	2.00E-02	15.9% H-9(B) => LUMO(B)
37	24387.786	410.041	2.48E-02	16.6% H-9(B) => LUMO(B), 16.2% HOMO(A) => L+8(A), 13.0% HOMO(A) => L+4(A)
38	24476.507	408.555	4.00E-03	26.8% H-9(B) => LUMO(B)
39	24778.159	403.581	1.90E-03	71.7% H-6(B) => LUMO(B)

Figure S10. Frontier molecular orbitals in the broken symmetry singlet state of **1** calculated at the B3LYP/def2-TZVP level of theory (Top: α-HOMO/LUMO, bottom: β-HOMO/LUMO). Isovalue 0.03.

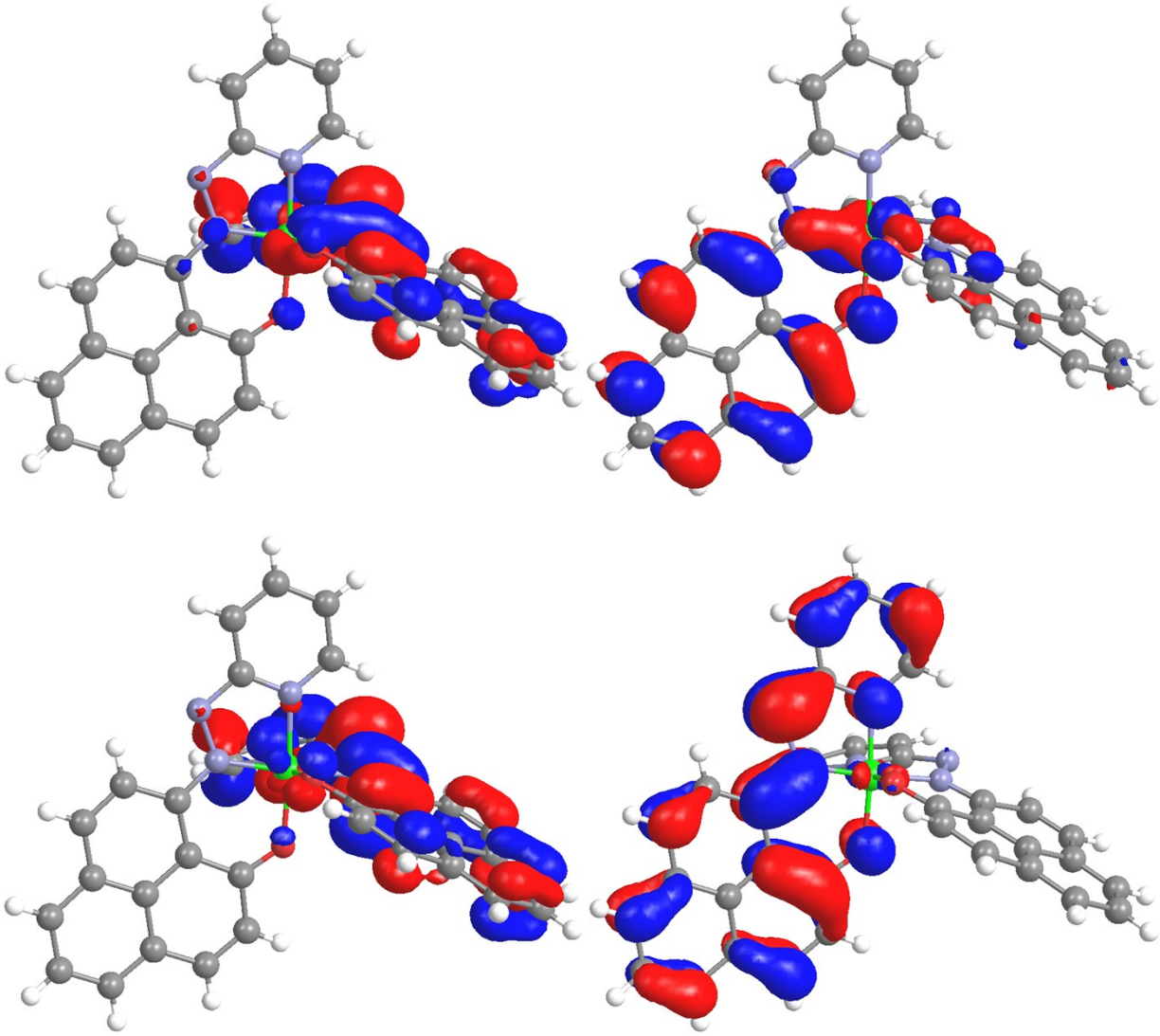


Figure S11. Cyclic voltammogram (top) and differential pulse voltammogram (bottom) of **1** in CH_2Cl_2 containing ~0.5 M $^nBu_4NPF_6$.

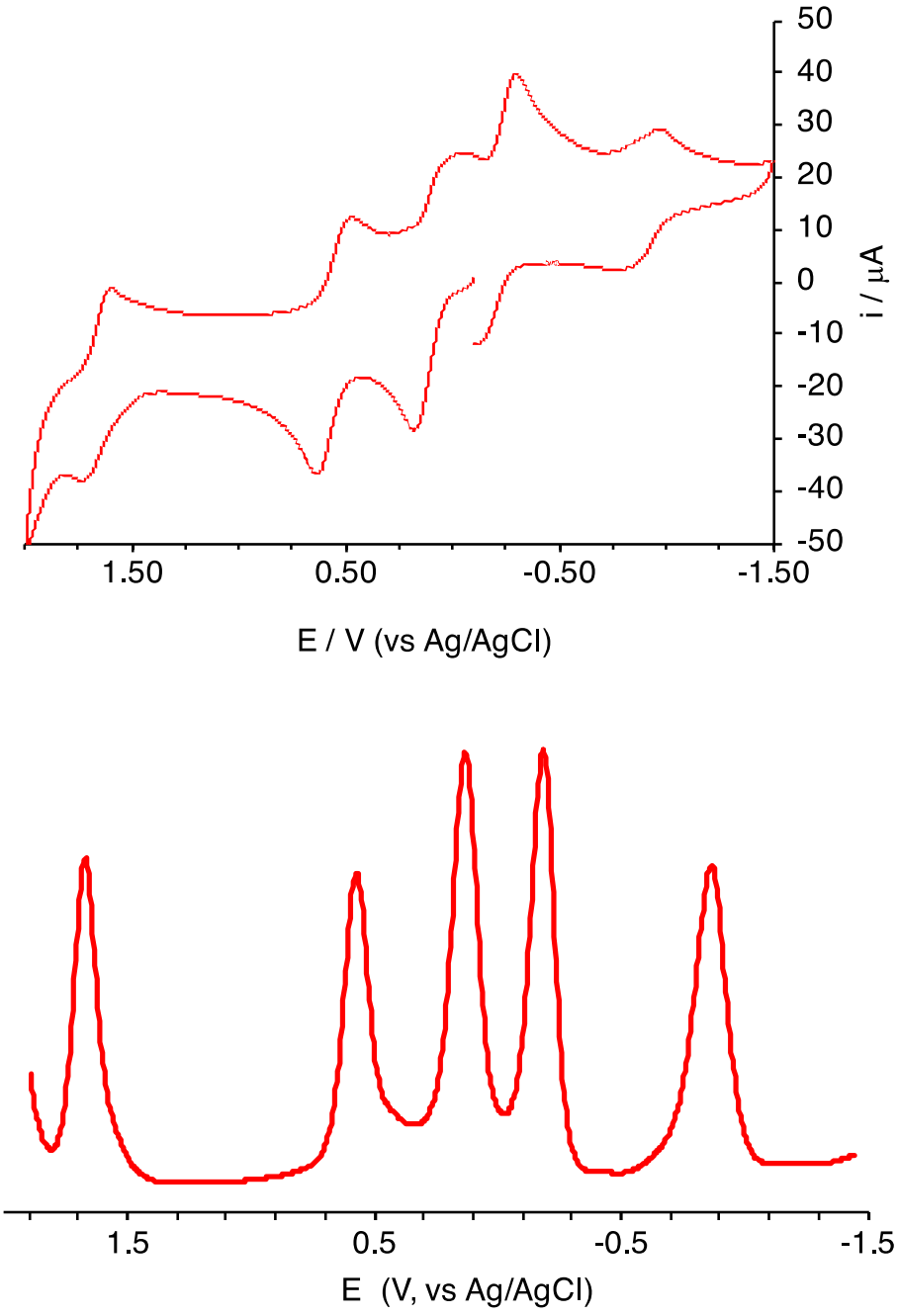


Figure S12. ESI mass spectrum (positive ion mode) of **2**.

Sample Name: NB-06-Co(PHDHPL) Crystals **Ion Source Type(Polarity)**: ESI+
File Name:MLH1187 Solvent:DCM/MeOH

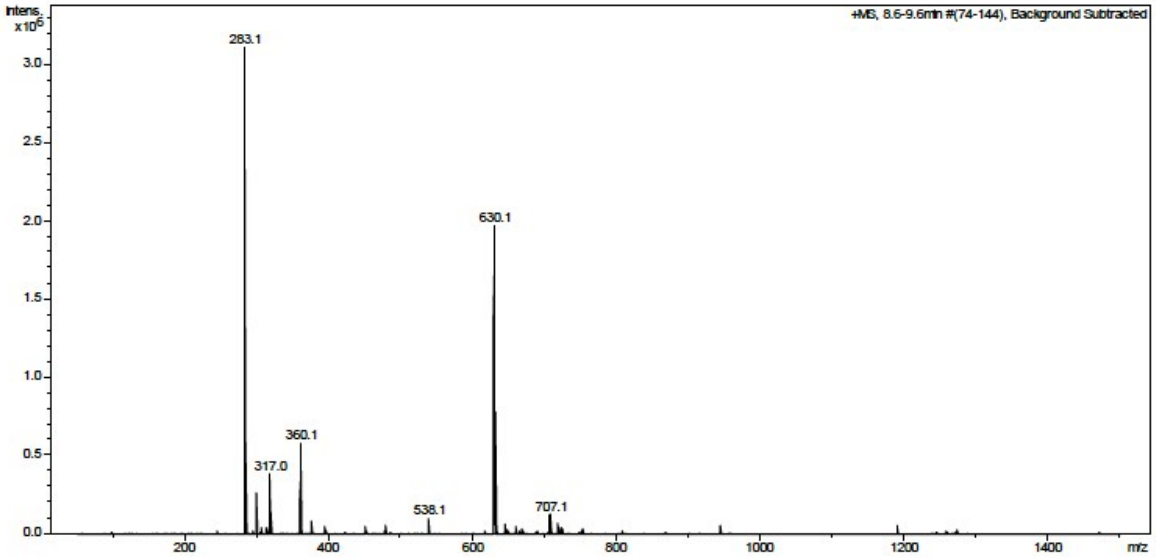


Figure S13. FTIR spectrum of **2** (KBr).

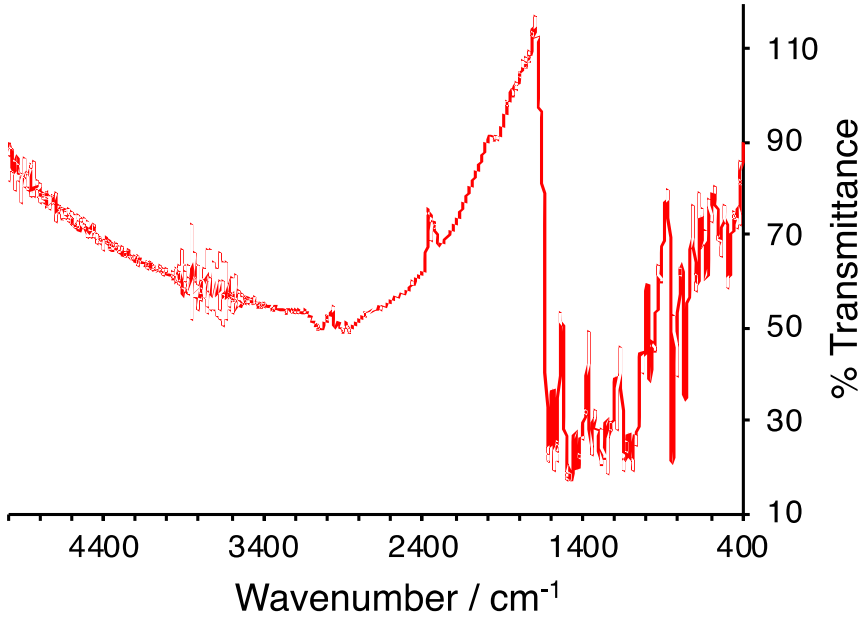


Figure S14. UV/VIS/NIR spectrum of **2** in CH_2Cl_2 at 298 K (left).

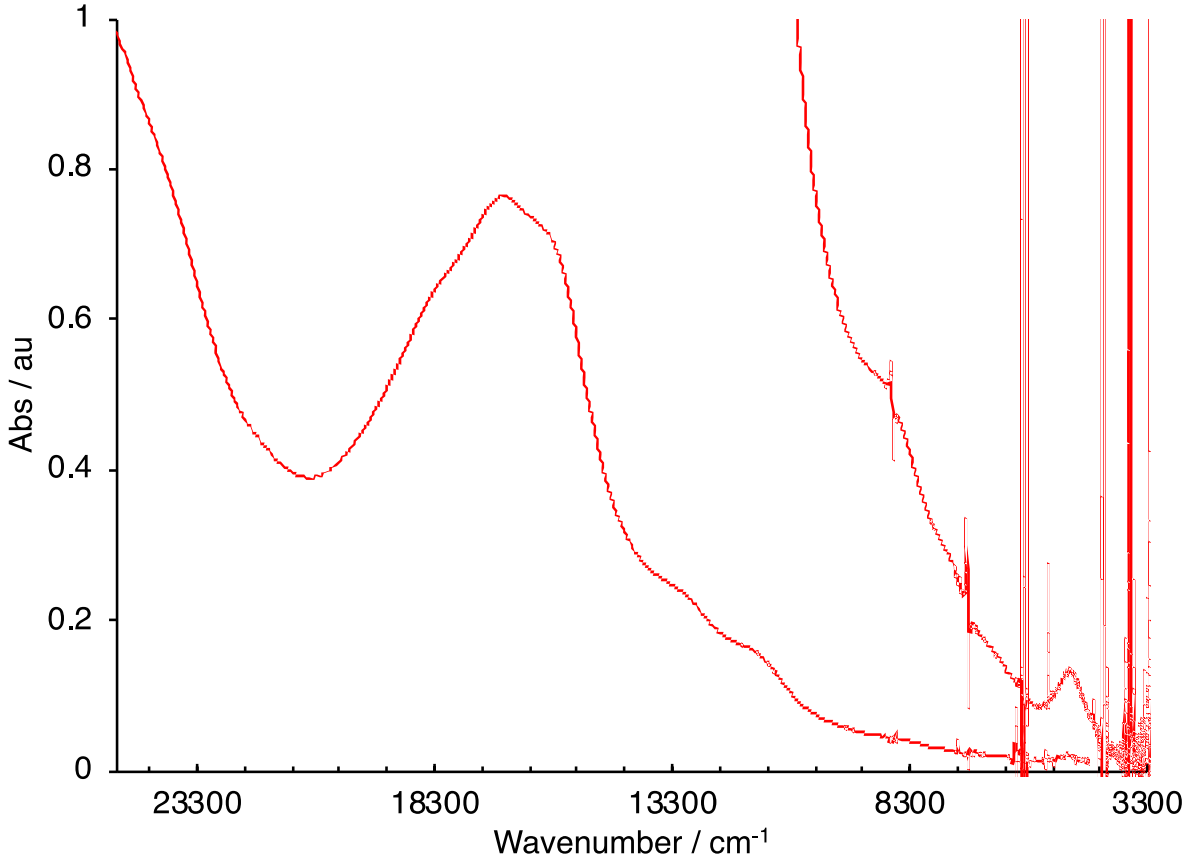


Table S12. Calculated electronic transitions of **2** (B3LYP/def2-TZVP/PCM(CH_2Cl_2).

Index	E / cm^{-1}	λ / nm	ϕ	Contributions (>/= 10%)
0	2666.469	3750.278	1.20E-03	99.6% HOMO(B) => LUMO(B)
1	9469.756	1055.993	0.00E+00	48.5% HOMO(A) => L+1(A), 48.1% HOMO(B) => L+2(B)
2	10914.295	916.23	8.00E-04	98.6% HOMO(A) => LUMO(A)
3	12810.504	780.609	8.00E-04	21.4% H-1(B) => LUMO(B), 12.3% H-9(A) => L+3(A), 10.6% H-9(B) => L+3(B)
4	13225.073	756.139	9.70E-03	54.6% HOMO(B) => L+1(B), 30.5% H-1(A) => LUMO(A)
5	13415.42	745.411	2.20E-03	61.3% H-1(B) => LUMO(B)
6	13573.504	736.729	2.12E-02	32.0% HOMO(B) => L+1(B), 31.9% H-1(A) => LUMO(A), 15.8% H-3(B) => LUMO(B), 13.7% H-1(B) => LUMO(B),
7	14041.306	712.184	1.40E-03	24.4% HOMO(A) => L+3(A), 18.4% HOMO(B) => L+3(B)
8	15106.764	661.955	1.08E-01	47.2% H-3(B) => LUMO(B), 24.3% H-1(A) => LUMO(A)
9	15551.982	643.005	1.00E-03	14.7% HOMO(A) => L+4(A), 10.8% HOMO(B) => L+5(B)
10	16376.281	610.639	2.83E-01	42.6% HOMO(B) => L+2(B), 42.2% HOMO(A) => L+1(A)
11	16749.716	597.025	1.50E-03	12.9% HOMO(A) => L+4(A), 10.1% H-1(A) => L+3(A)
12	17398.992	574.746	2.80E-03	84.7% H-2(B) => LUMO(B), 10.9% H-3(B) => LUMO(B)
13	17565.142	569.309	6.27E-02	36.0% HOMO(B) => L+3(B), 31.9% HOMO(A) => L+3(A), 10.1% H-4(B) => LUMO(B)
14	18300.72	546.427	1.55E-01	38.0% H-4(B) => LUMO(B), 6.58% HOMO(B) => L+3(B)
15	18417.67	542.957	1.20E-01	28.9% H-4(B) => LUMO(B), 11.5% HOMO(B) => L+5(B)
16	19029.845	525.49	5.60E-03	20.6% HOMO(A) => L+4(A), 14.6% HOMO(B) => L+5(B)
17	19344.401	516.945	9.60E-03	18.5% HOMO(A) => L+4(A), 18.4% HOMO(B) => L+5(B)

18	19657.345	508.716	1.90E-03	31.5% H-5(B) => LUMO(B), 10.3% H-6(B) => LUMO(B)
19	19754.938	506.203	7.00E-03	16.0% HOMO(A) => L+6(A), 13.2% HOMO(B) => L+7(B), 12.2% H-5(B) => LUMO(B)
20	19767.843	505.872	1.36E-02	14.1% H-5(B) => LUMO(B), 13.3% HOMO(A) => L+6(A), 10.8% HOMO(B) => L+7(B)
21	20298.555	492.646	8.00E-04	88.0% H-1(A) => L+1(A)
22	20605.046	485.318	1.16E-02	78.9% HOMO(A) => L+2(A)
23	20839.753	479.852	2.00E-04	18.7% HOMO(A) => L+3(A), 17.7% HOMO(B) => L+3(B), 10.0% H-1(A) => L+3(A)
24	21073.654	474.526	1.10E-03	32.0% H-1(B) => L+2(B), 31.9% H-2(A) => L+1(A)
25	21639.855	462.11	6.20E-03	83.5% HOMO(B) => L+4(B)
26	21701.96	460.788	5.70E-03	81.4% H-2(A) => LUMO(A)
27	22390.758	446.613	1.83E-02	28.4% H-4(A) => LUMO(A), 20.9% H-3(B) => L+1(B)
28	22464.154	445.154	1.20E-03	13.0% H-3(A) => L+1(A), 12.3% H-2(B) => L+2(B)
29	23045.68	433.921	1.71E-02	65.3% H-1(A) => L+2(A)
30	23170.696	431.58	1.08E-02	40.0% H-1(A) => L+3(A), 11.6% H-7(B) => LUMO(B), 10.7% H-1(A) => L+2(A)
31	23494.124	425.638	1.20E-03	10.1% H-1(A) => L+4(A)
32	23534.452	424.909	9.00E-04	60.5% H-6(B) => LUMO(B), 19.5% H-5(B) => LUMO(B)
33	23690.117	422.117	8.30E-03	47.8% H-7(B) => LUMO(B), 12.7% H-8(B) => LUMO(B)
34	23857.88	419.149	2.36E-02	46.9% H-8(B) => LUMO(B)
35	24007.899	416.53	1.23E-02	14.7% H-7(B) => LUMO(B), 12.3% H-1(A) => L+4(A)
36	24206.312	413.115	3.50E-03	85.1% H-1(B) => L+1(B)
37	24720.087	404.529	5.00E-03	27.6% HOMO(A) => L+6(A), 20.9% HOMO(B) => L+7(B), 19.6% HOMO(B) => L+6(B), 14.4% HOMO(A) => L+5(A)
38	24757.995	403.91	4.90E-03	26.3% H-10(B) => LUMO(B)
39	24996.735	400.052	2.34E-02	38.0% H-10(B) => LUMO(B)

Figure S15. Mulliken spin density in the doublet state (S = ½) of **2** (B3LYP/def2-TZVP). Red and blue correspond to α and β spin densities, respectively. Isovalue 0.004.

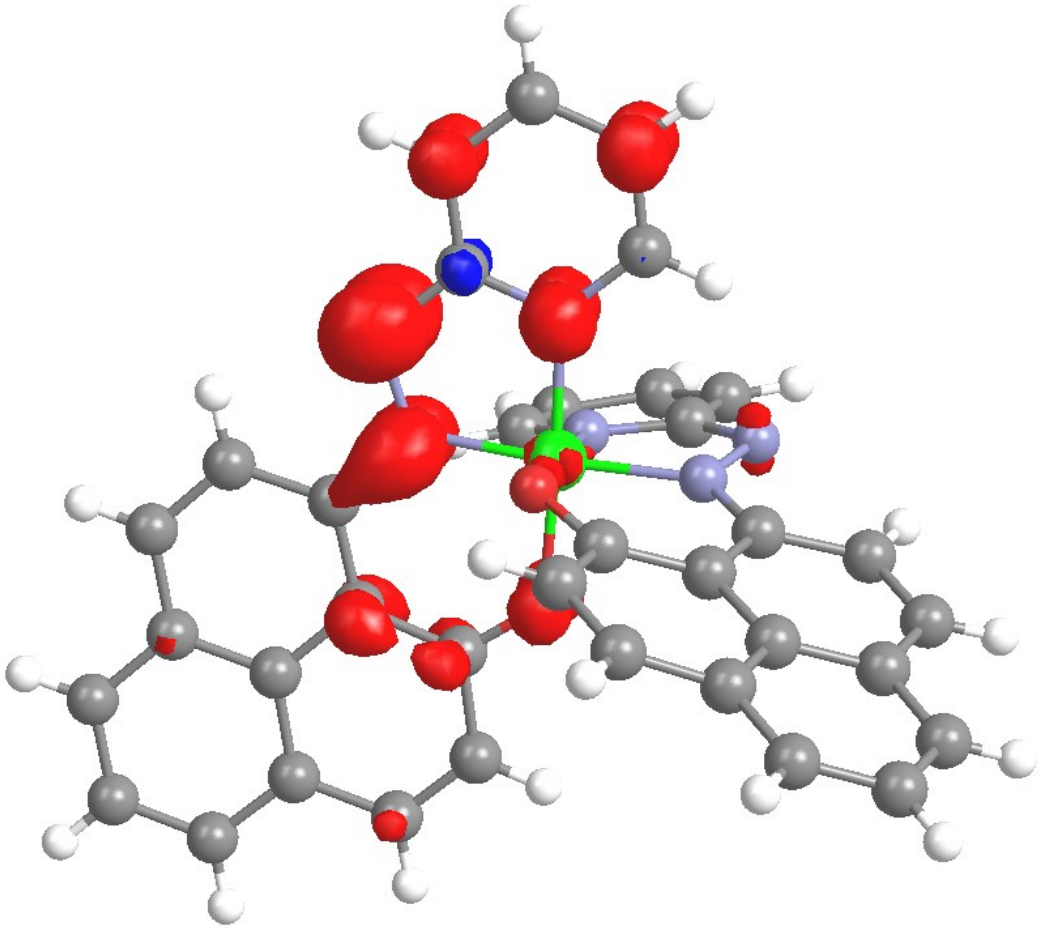


Figure S16. Frontier molecular orbitals in the doublet state (S = ½) of **2** calculated at the B3LYP/def2-TZVP level of theory (Top: α-HOMO/LUMO, bottom: β-HOMO/LUMO). Isovalue 0.03.

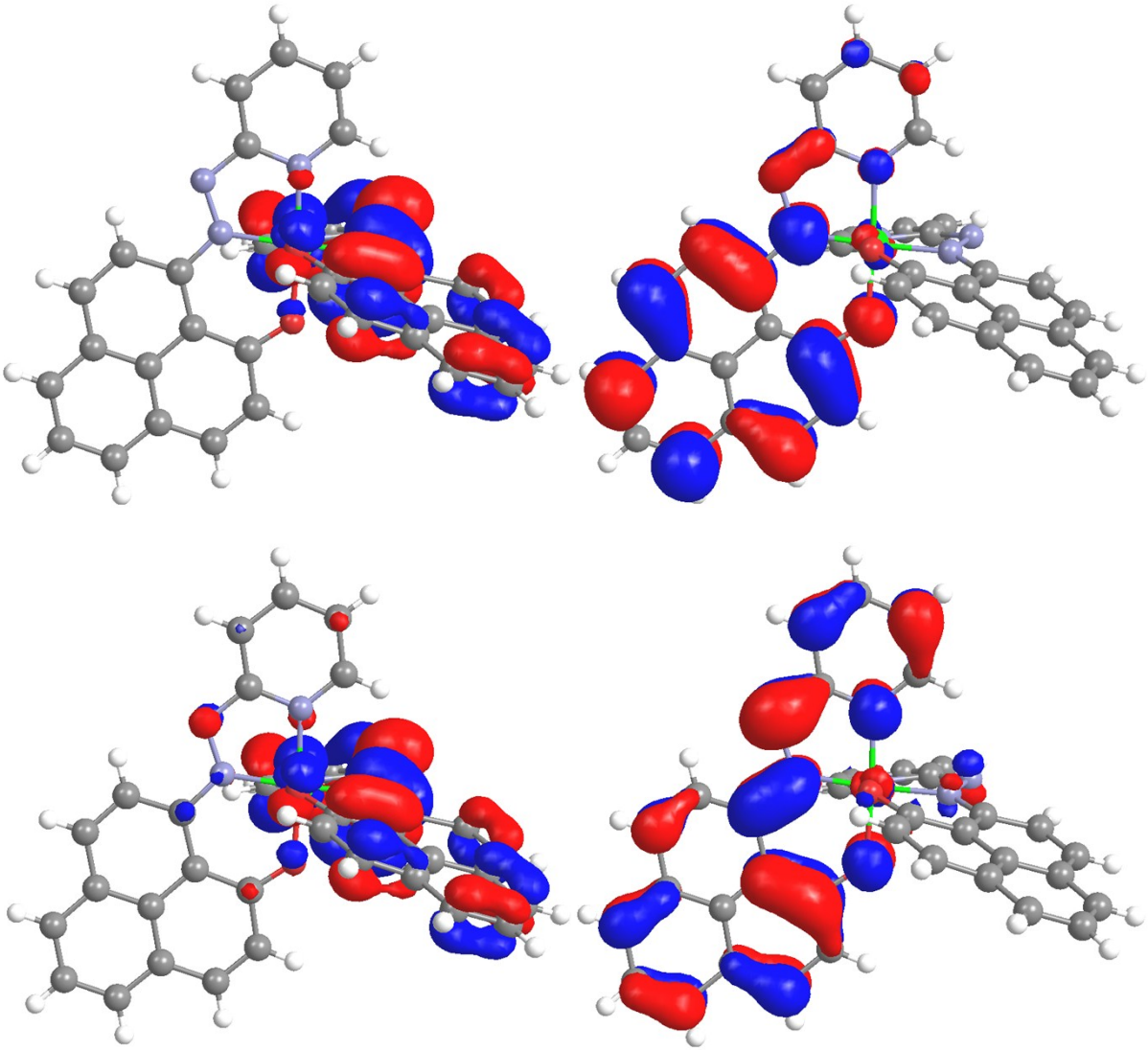


Figure S17. Cyclic voltammogram of **2** (top) and differential pulse voltammogram (bottom) of **2** in CH_2Cl_2 containing ~0.5 M $^nBu_4NPF_6$.

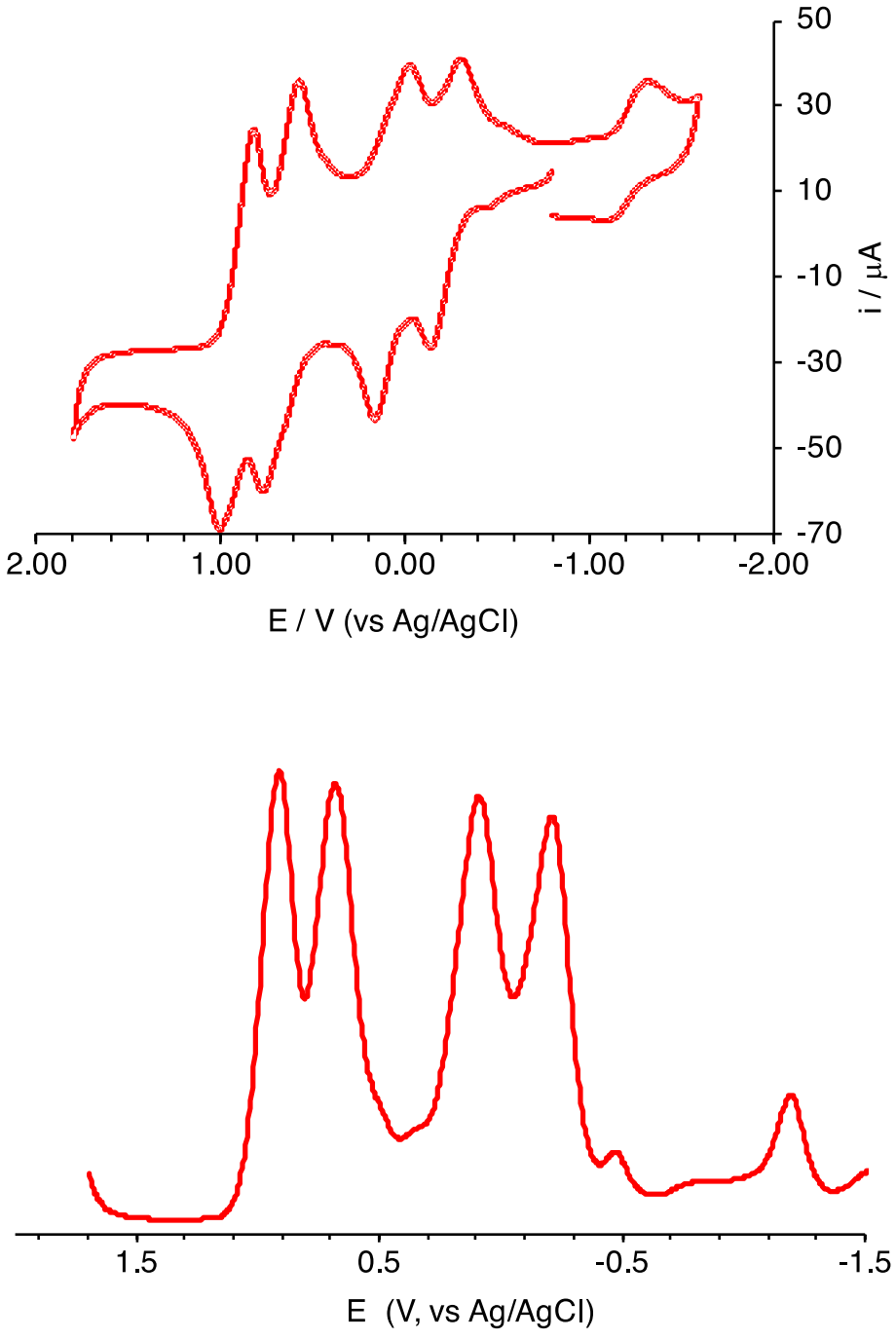


Figure S18. EPR spectrum of **2** (powder) at 100K.

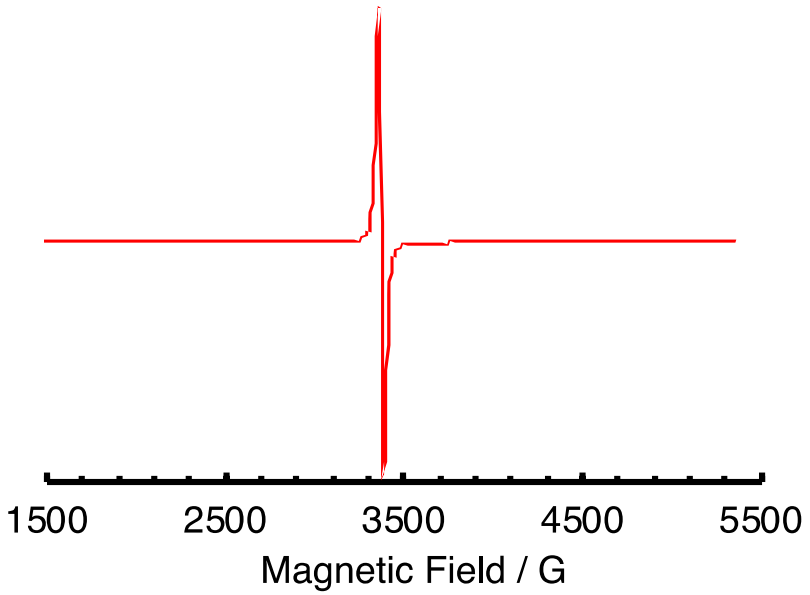


Figure S19. Variable temperature magnetic susceptibility data for **2** (external field 2000 Oe).

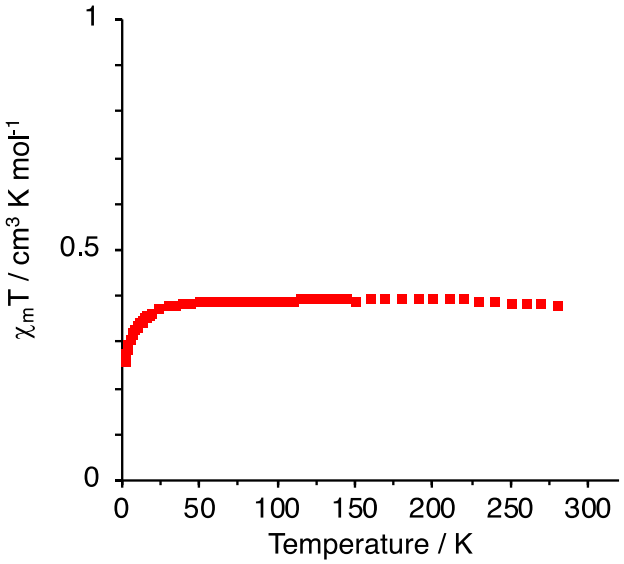


Table S13. Atomic coordinates for **1** (unrestricted singlet state).

Fe	6.999000	14.564000	5.181000
O	8.772000	14.041000	5.603000
O	7.609000	15.646000	3.766000
N	6.984000	15.995000	6.393000
N	5.854000	16.697000	6.533000
N	5.200000	15.197000	4.864000
N	6.857000	13.043000	4.048000
N	6.050000	12.027000	4.503000
N	6.299000	13.280000	6.460000
C	9.544000	14.533000	6.482000
C	10.804000	13.858000	6.678000
H	10.991000	13.075000	6.176000
C	11.713000	14.306000	7.546000
H	12.530000	13.832000	7.642000
C	11.492000	15.479000	8.335000
C	12.446000	15.967000	9.217000
H	13.269000	15.501000	9.309000
C	12.235000	17.111000	9.965000
H	12.910000	17.429000	10.553000
C	11.045000	17.783000	9.853000
H	10.903000	18.571000	10.365000
C	10.030000	17.321000	8.988000
C	8.801000	17.981000	8.893000
H	8.653000	18.764000	9.410000
C	7.808000	17.524000	8.078000
H	6.970000	17.973000	8.066000
C	8.006000	16.387000	7.243000
C	9.242000	15.696000	7.294000
C	10.245000	16.159000	8.202000
C	4.901000	16.264000	5.637000
C	3.681000	16.925000	5.531000
H	3.485000	17.675000	6.082000
C	2.763000	16.466000	4.610000
H	1.930000	16.912000	4.507000
C	3.054000	15.358000	3.836000
H	2.421000	15.019000	3.213000
C	4.280000	14.757000	3.989000
H	4.487000	13.999000	3.454000
C	8.246000	15.226000	2.710000
C	8.934000	16.212000	1.952000

H	8.853000	17.122000	2.204000
C	9.696000	15.894000	0.883000
H	10.177000	16.578000	0.429000
C	9.786000	14.549000	0.429000
C	10.584000	14.189000	-0.674000
H	11.120000	14.849000	-1.098000
C	10.600000	12.901000	-1.147000
H	11.148000	12.672000	-1.889000
C	9.829000	11.950000	-0.548000
H	9.836000	11.067000	-0.894000
C	9.030000	12.235000	0.563000
C	8.206000	11.259000	1.172000
H	8.173000	10.385000	0.800000
C	7.461000	11.535000	2.275000
H	6.903000	10.858000	2.644000
C	7.506000	12.832000	2.888000
C	8.272000	13.874000	2.271000
C	9.031000	13.555000	1.091000
C	5.835000	12.166000	5.825000
C	5.201000	11.152000	6.572000
H	4.806000	10.410000	6.128000
C	5.154000	11.235000	7.932000
H	4.750000	10.542000	8.441000
C	5.707000	12.348000	8.574000
H	5.696000	12.419000	9.522000
C	6.263000	13.333000	7.807000
H	6.642000	14.088000	8.241000

Table S14. Atomic coordinates for **2** ($S = ½$).

Co	6.72400	14.36700	5.18100
O	8.49500	13.84700	5.55500
O	7.34300	15.52200	3.82300
N	6.72300	15.82000	6.40000
N	5.61200	16.55900	6.45700
N	4.95400	14.98000	4.84900
N	6.58100	12.88100	4.03600
N	5.82600	11.82600	4.53700
N	6.07400	13.11900	6.47100
C	9.25300	14.32200	6.46800
C	10.50800	13.64600	6.64500
H	10.69800	12.88100	6.11300
C	11.42400	14.06000	7.53800
H	12.23900	13.57900	7.62800
C	11.19700	15.20900	8.35500
C	12.15100	15.66400	9.26300
H	12.97300	15.19300	9.34800
C	11.93000	16.78500	10.04400
H	12.59500	17.07600	10.65500
C	10.74600	17.47300	9.93300
H	10.60200	18.24900	10.46200
C	9.74500	17.03900	9.04200
C	8.51500	17.72600	8.95100
H	8.36800	18.49300	9.49200
C	7.53900	17.31300	8.10600
H	6.71400	17.78200	8.08300
C	7.72800	16.18600	7.25000
C	8.95300	15.46300	7.30100
C	9.96000	15.89700	8.22900
C	4.66700	16.09200	5.58400
C	3.43300	16.74200	5.45200
H	3.24000	17.51600	5.97000
C	2.50700	16.24600	4.56800
H	1.66900	16.68100	4.46100
C	2.80300	15.10900	3.82900
H	2.17000	14.75200	3.21700
C	4.03000	14.50200	3.99800
H	4.22900	13.72100	3.49600
C	7.94500	15.11400	2.72900
C	8.61800	16.11800	1.99000

H	8.54700	17.02300	2.27300
C	9.36300	15.83000	0.89000
H	9.82800	16.52600	0.44000
C	9.45300	14.49400	0.40600
C	10.24400	14.16100	-0.70800
H	10.76200	14.83600	-1.13000
C	10.28100	12.88100	-1.19700
H	10.82800	12.67000	-1.94400
C	9.51600	11.90000	-0.59700
H	9.52800	11.01800	-0.95500
C	8.72800	12.16700	0.51800
C	7.93000	11.16500	1.13700
H	7.91300	10.29500	0.75700
C	7.19300	11.40700	2.24700
H	6.66000	10.71300	2.61700
C	7.20600	12.70600	2.87900
C	7.95300	13.77900	2.25500
C	8.71200	13.48700	1.06300
C	5.64300	11.97200	5.84700
C	5.06000	10.93400	6.62800
H	4.68700	10.16900	6.20600
C	5.04300	11.04500	7.98100
H	4.67500	10.34600	8.50800
C	5.56700	12.19000	8.61000
H	5.57400	12.26500	9.55800
C	6.06500	13.19100	7.82600
H	6.42000	13.96600	8.24400

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