Cover Page for Supporting Information

Unusual Electronic Structures of Square planar Iron-Nitrosyl Complexes

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General Experimental Details

Unless otherwise noted, all manipulations were carried out under an atmosphere of nitrogen or argon by using standard Schlenk techniques or glovebox techniques. Solvents were dried by standard methods: *n*-Hexane, Et_2O and THF were dried by distilling from Na/benzoquinone under N_2 atmosphere; PhF was distilled from CaH_2 under N_2 atmosphere. All the solvents were stored in activated 4 Å molecular sieves in the glovebox. Commercially available reagents were purchased from Tokyo Chemical Industry and used as received.

For the single crystal X-ray structural analyses, the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. Data collections were performed on Rigaku diffractometer at a low temperature. Crystal data collection and refinement parameters are summarized in the Supporting Information. Structures were solved by SHELXTL[1] or Olex[2] program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Organometallic samples for NMR spectroscopic measurements were prepared in glovebox by the use of J. Young value NMR tubes (Wilmad 528-JY). 1H, 13C and ^{31}P NMR spectra were recorded on Bruker ARX400 spectrometer at room temperature. All chemical shifts were reported in units of ppm with references to the residual protons of the deuterated solvents for proton chemical shifts.

Infrared spectra of samples were recorded on Bruker AlphaII using a KBr cell. UV-vis spectra were recorded with an Olis 8453 equipped with a cryostat from Unisoku Scientific Instruments, Osaka, Japan.

Structural optimization and relative energy calculations were performed with the ORCA program system[3,4], with the B3LYP, BP86, and TPSSh functionals, for each of the possible broken symmetry pairs of the respective complex. In all calculations, the def2-TZVP basis set was applied for Fe, N, and O, and the def2-SVP basis set was used for all other elements. The RIJCOSX approximation was used in order to accelerate the calculations and D3BJ was employed to account for van-der-Waals dispersion interactions. The calculations converged to one specific broken symmetry state for each complex.

Synthesis

Synthesis of [FeBr(NO)(PCP)] (2): The precursor [Fe^{II}Br(PCP)] (**1**) were synthesized by following the published procedures. [5] Under an atmosphere of nitrogen, **1** (0.97 mmol, 513 mg) were dissolved in Hexane (40 mL), followed by 23.5 mL of NO gas injection at room temperature, rapidly yielding a dark green solution. Stirring was continued for 1 h, filter the mixture and collect the resulting filtrate. The solvent was removed and dried *in vacuo*, affording the green powder of **2** (509 mg, 94%). Single crystals of **2** suitable for X-ray crystallography were obtained by recrystallization from Hexane at room temperature. IR (KBr, cm^{-1}) : 1683 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{24}H_{43}BrFeNOP_2$ (%) : C, 51.54; H, 7.75; N, 2.50. Found: C, 52.30; H, 7.86; N, 2.19.

Synthesis of [Fe(NO)(PCP)][BAr^F_4] (3): **2** (0.19 mmol, 107 mg) and $NaBAr^F_4$(0.21 mmol, 187 mg) were dissolved in PhF (10 mL), yielding an orange solution. Stirring was continued for 30 min, filter the mixture and collect the resulting filtrate. The solvent was removed and dried *in vacuo* to leave **3** (235 mg, 93%) as an orange powder. Single crystals of **3** suitable for X-ray crystallography were obtained by recrystallization from Et_2O at room temperature. IR (KBr, cm^{-1}) : 1785 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{56}H_{55}BF_{24}FeNOP_2$ (%) : C, 50.10; H, 4.13; N, 1.04; Found: C, 49.98; H, 4.35; N, 1.13.

Synthesis of [Fe(NO)(PCP)] (4): **3** (0.27 mmol, 370.3 mg) were dissolved in THF (10 mL) yielding an orange solution, the suspension of KC_8 (0.22 mmol, 32 mg) in THF (2 mL) was added into the solution. Stirring was continued for at -80 ℃, Filter the mixture and collect the resulting filtrate. he solvent was removed and dried in vacuo. The resulting solid was washed with *n*-Hexane (5 mL) and dried under vacuum to leave **4** as a green powder (108.9 mg, 84%). Single crystals of **4** suitable for X-ray crystallography were obtained by recrystallization from *n*-Hexane at room temperature. ^{1}H NMR of **4** in benzene-d_6 at room temperature. ^{1}H NMR (400 MHz, Benzene-d_6) : δ 6.90 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.4 Hz, 2H), 3.94 (m, J = 3.9 Hz, 4H), 1.56 – 1.48 (m, 36H). ^{31}P NMR (162 MHz, Benzene-d_6) : δ 100.98. IR (KBr, cm^{-1}) : 1660 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{24}H_{43}FeNOP_2$ (%) : C, 60.13; H, 9.04; N, 2.92; Found: C, 60.04; H, 9.37; N, 2.45.

EPR Spectroscopy

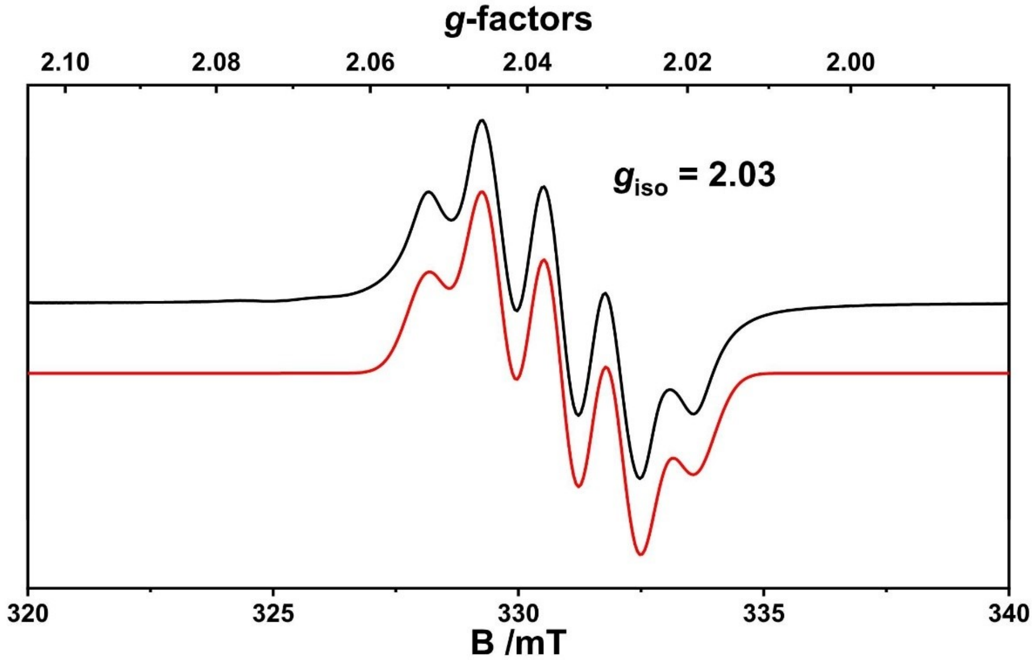

Figure S1. X-band EPR spectra were recorded for a 1 mM 2-MeTHF solution of complex **2** at room temperature. Black and red lines represent the experimental and simulated spectra, respectively. Acquisition conditions: temperature = 304 K, microwave power = 10 mW and modulation amplitude = 1 G. Simulation parameters: g_{iso} = 2.03, $A_{iso}(^{14}N)$ = 36.6 MHz and $A_{iso}(^{31}P)$ = 29.1 MHz.

Figure S2. X-band EPR spectra were recorded for a 1 mM 2-MeTHF solution of complex **2** at 92 K. Black and red lines represent the experimental and simulated spectra, respectively. Acquisition conditions: temperature = 92 K, microwave power = 1 mW and modulation amplitude = 3 G. Simulation parameters: $g_{x,y,z}$ = 2.05, 2.04, 2.01, $A_{x,y,z}(^{14}N)$ = 36.3, 34.5, 43.2 MHz, and $A_{x,y,z}(^{31}P)$ = 28.5, 21.6, 35.7 MHz.

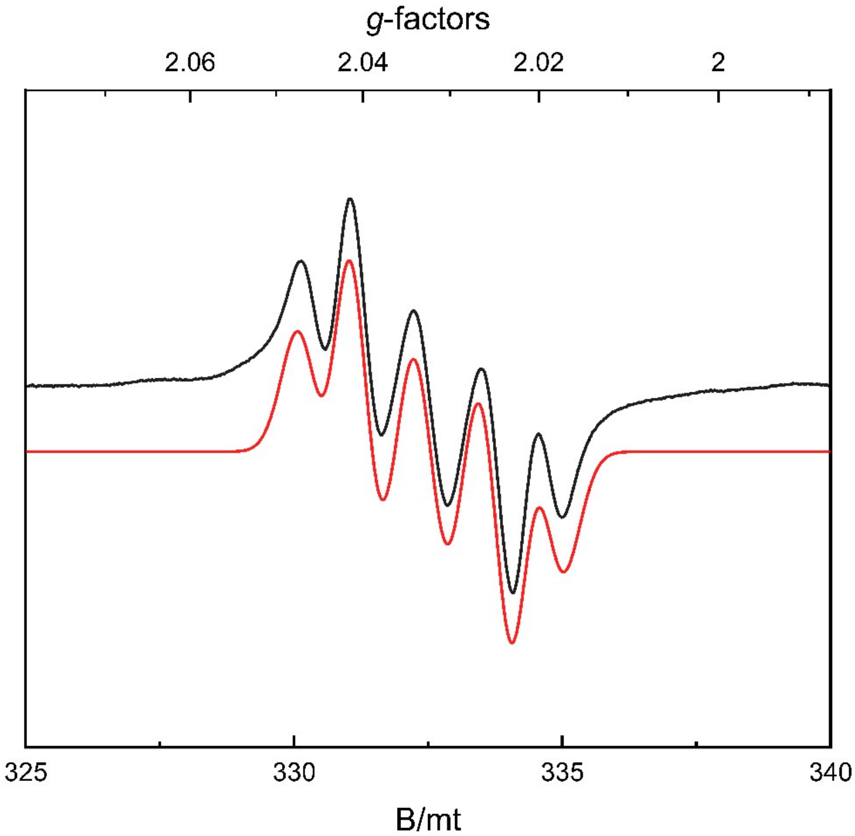

Figure S3. X-band EPR spectra of **3** recorded in a 5:1 mixture of toluene and dichloromethane at room temperature. Acquisition conditions: temperature = 300 K, microwave power = 10 mW and modulation amplitude = 5 G. Simulation parameters: g_{iso} = 2.03, $A_{iso}(^{14}N)$ = 36.6 MHz and $A_{iso}(^{31}P)$ = 29.1 MHz.

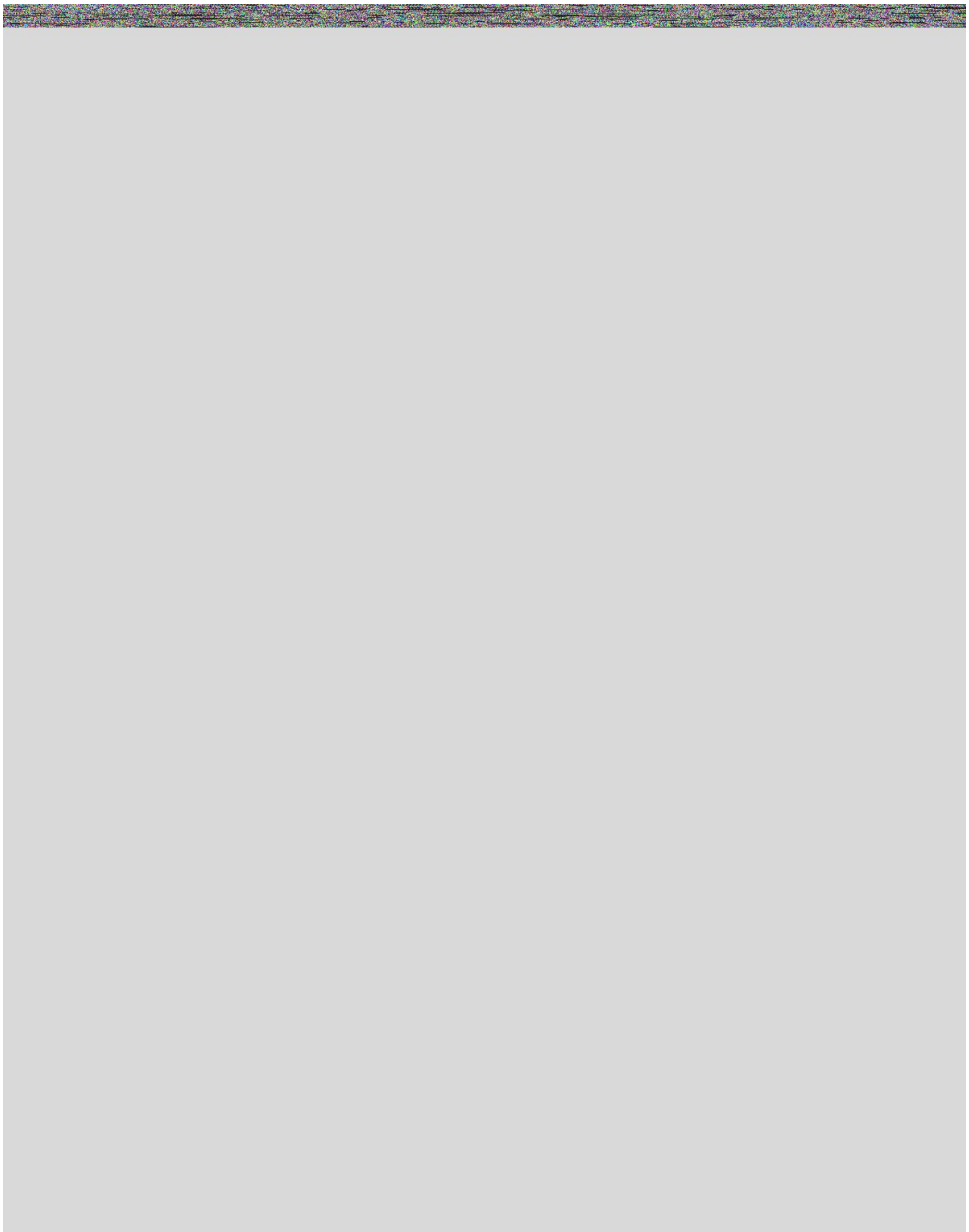

Figure S4. The X-band spectra of **3** in a 5:1 mixture of toluene and dichloromethane measured at 113 K. The experimental spectra are overlaid with their corresponding simulations (green line for **2**; blue line for **3**) Acquisition conditions: temperature = 113 K, microwave power = 1mW and modulation amplitude = 3 G. Simulation parameters: for **2** (9%, green line), $g_{x,y,z}$ = 2.05, 2.04, 2.01, $A_{x,y,z}(^{14}N)$ = 36.3, 34.5, 43.2 MHz and $A_{x,y,z}$ (^{31}P) = 28.5, 21.6, 35.7 MHz; for **3** (92 %, blue green), $g_{x,y,z}$ = 1.93, 1.96, 2.95. Excellent simulations indicate that the observed signal originates predominantly from **3**, with a minor contribution (~9%) from residual complex **2**.

Copies of NMR Spectroscopy

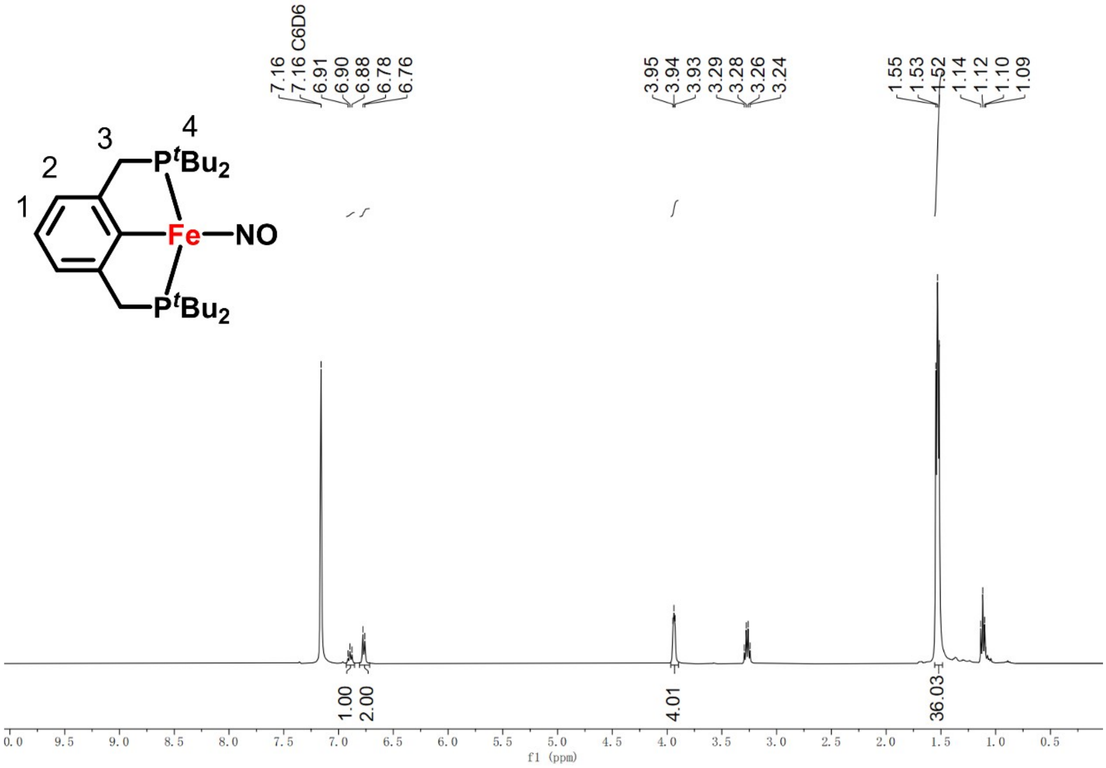

Figure S5 ^{1}H NMR spectrum of **4** recorded in benzene-d_6 at room temperature. ^{1}H NMR (400 MHz, benzene-d_6) : δ 6.90 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.4 Hz, 2H), 3.94 (m, J = 3.9 Hz, 4H), 1.56 – 1.48 (m, 36H).

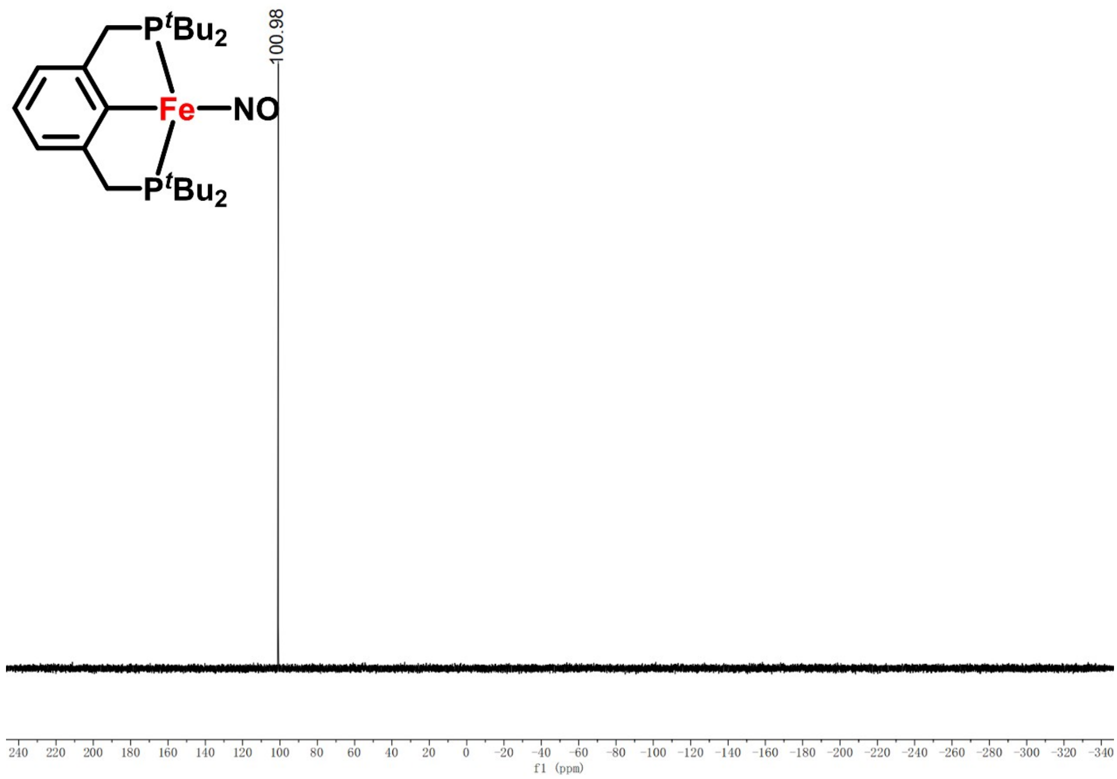

Figure S6 ^{31}P NMR of **4** recorded in benzene-d_6 at room temperature. ^{31}P NMR (162 MHz, Benzene-d_6): δ 100.98 ppm.

Copies of IR Spectroscopy

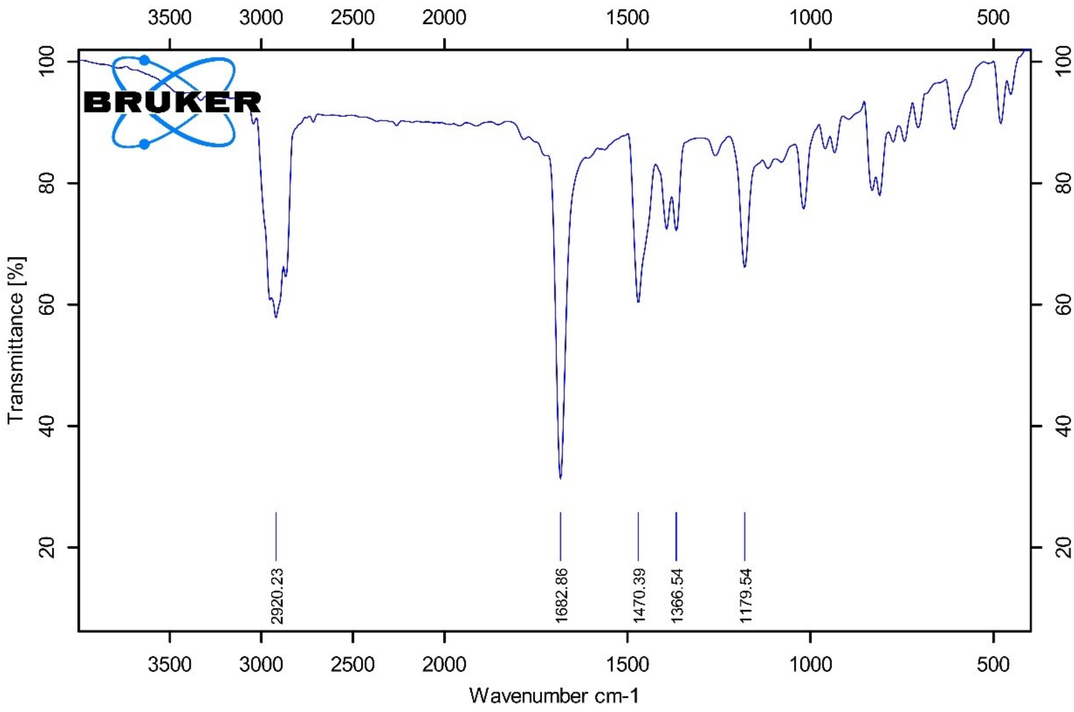

Figure S7. IR spectrum of **2** at room temperature.

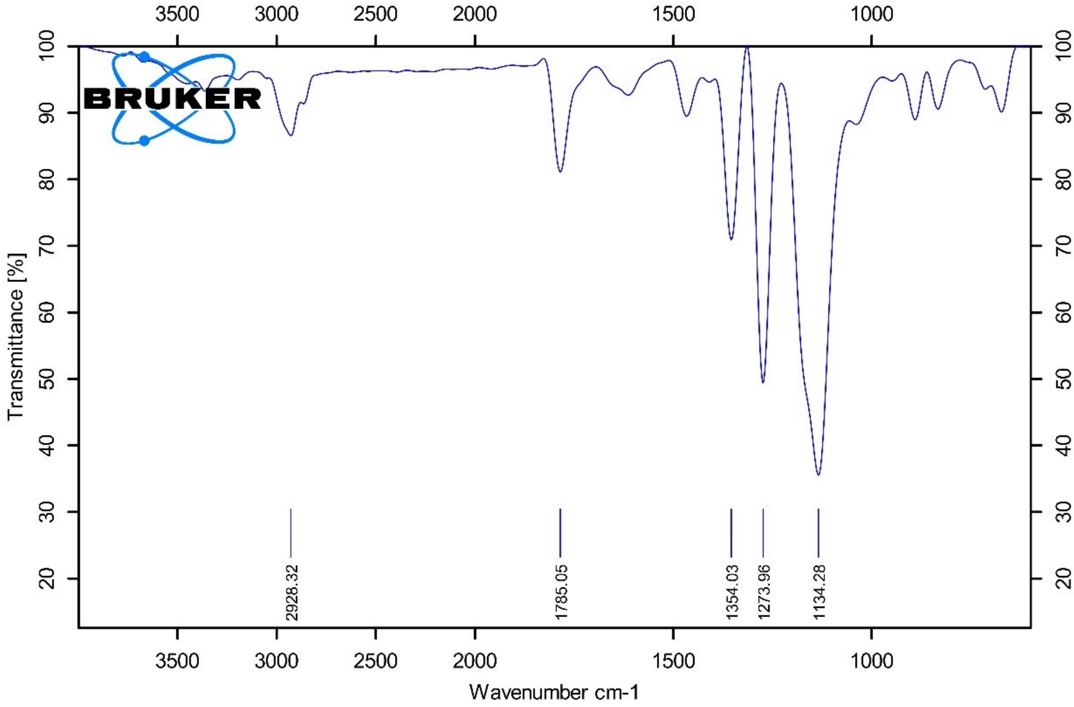

Figure S8. IR spectrum of **3** at room temperature.

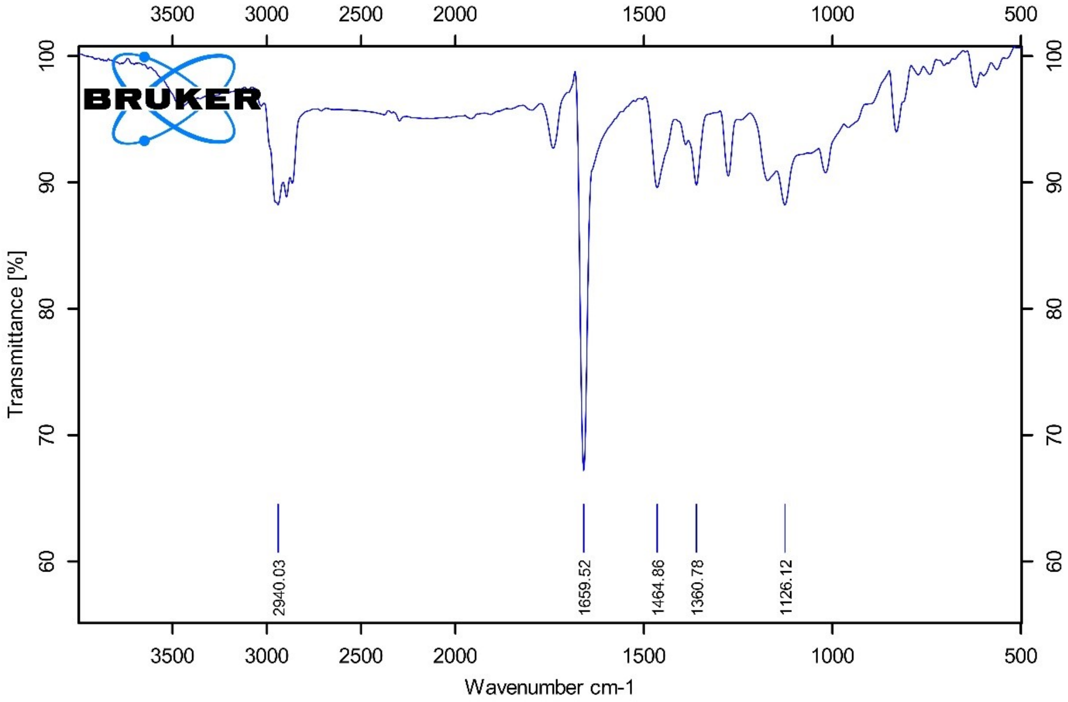

Figure S9. IR spectrum of **4** at room temperature.

Copies of UV-vis Spectra

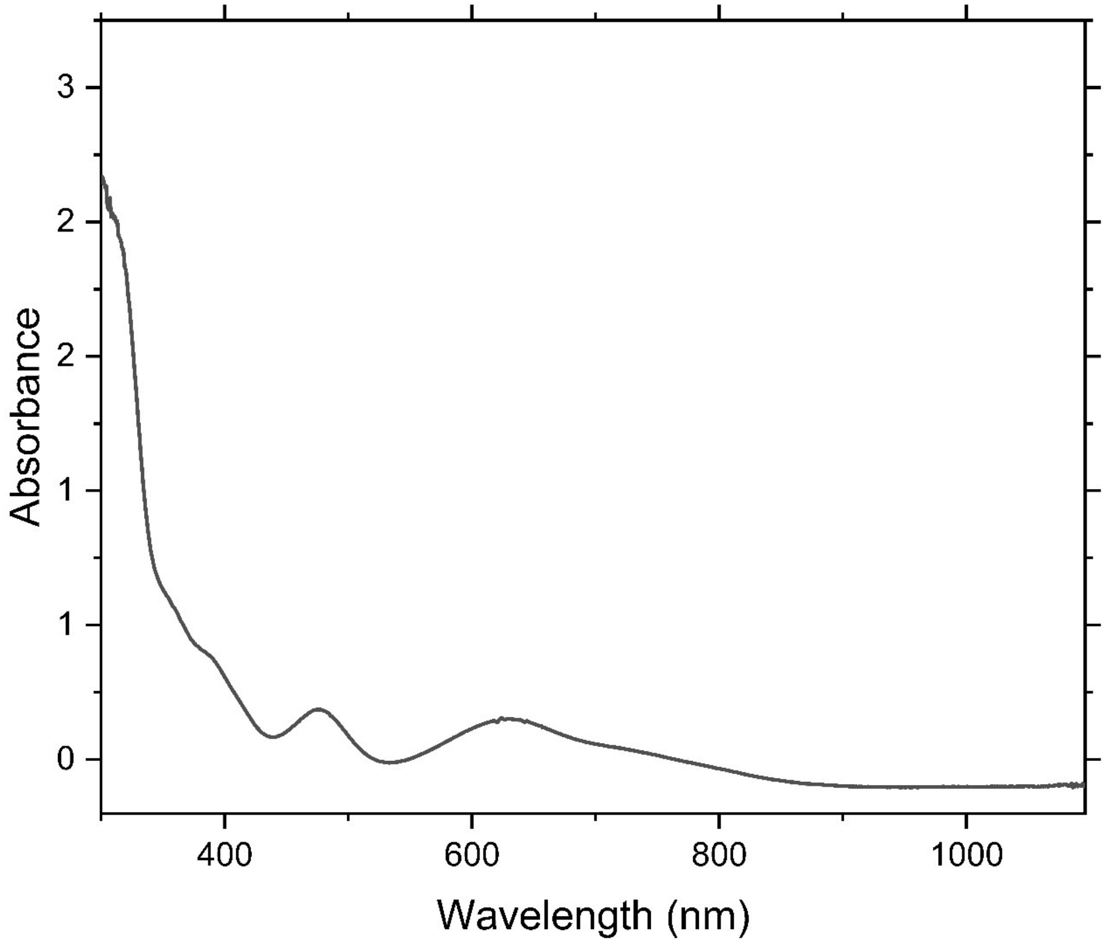

Figure S10. UV-vis spectrum of **2** in Me-THF at room temperature

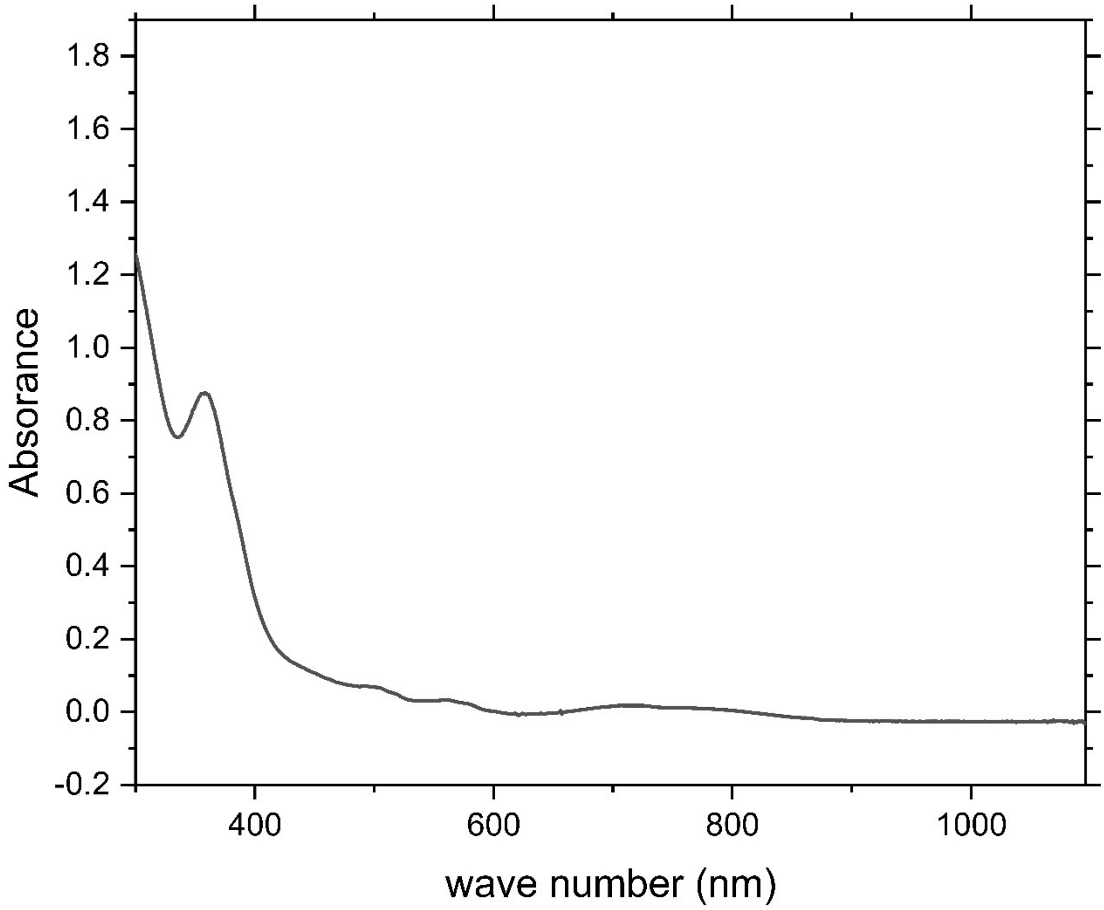

Figure S11. UV-vis spectrum of **3** in dichloromethane at room temperature.

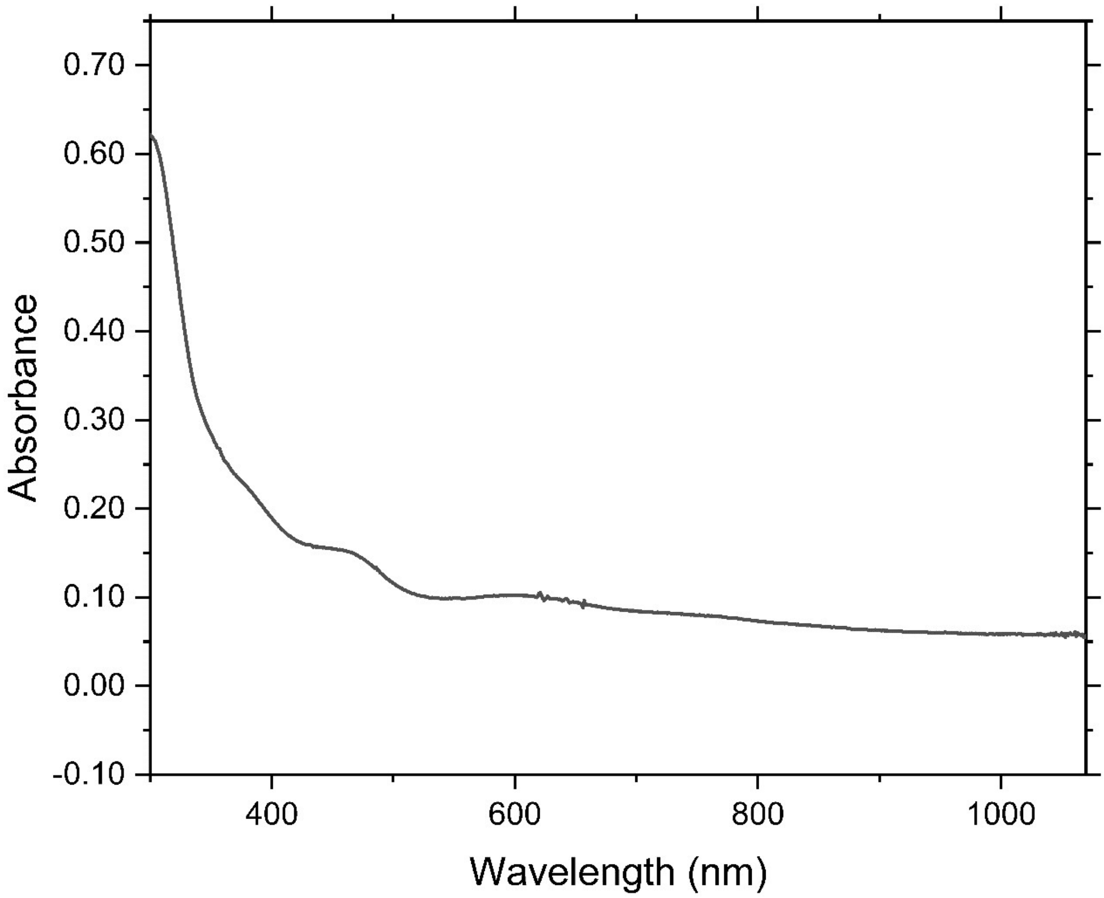

Figure S12. UV-vis spectrum of **4** in dichloromethane at room temperature.

Cyclic Voltammetry

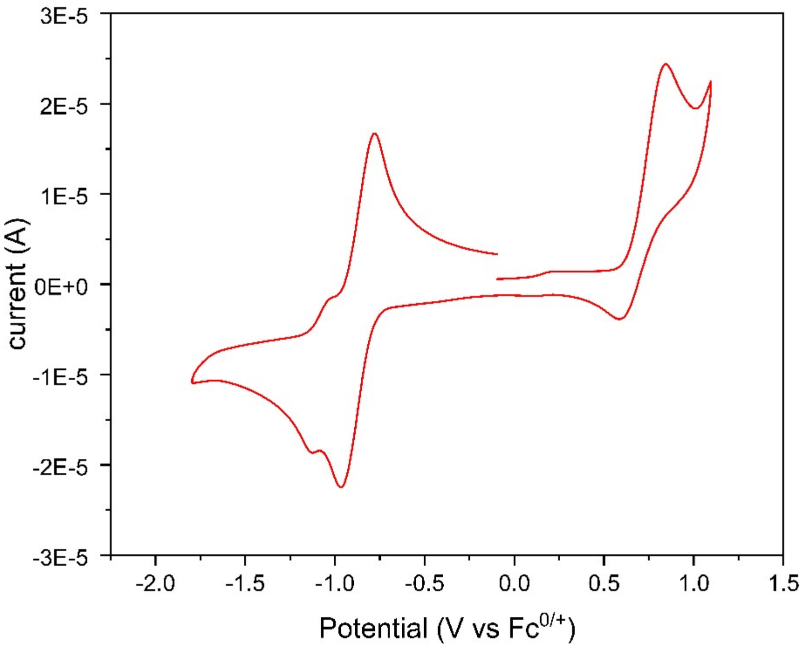

Figure S13. Cyclic Voltammetry of complex **3** (2 mM) in THF
Conditions: $^{n}Bu_4NPF_6$ (0.3 M) as the supporting electrolyte; scan rate, 100 mV/s; potentials vs $Fc^{0/+}$; under N_2 (1 atm).

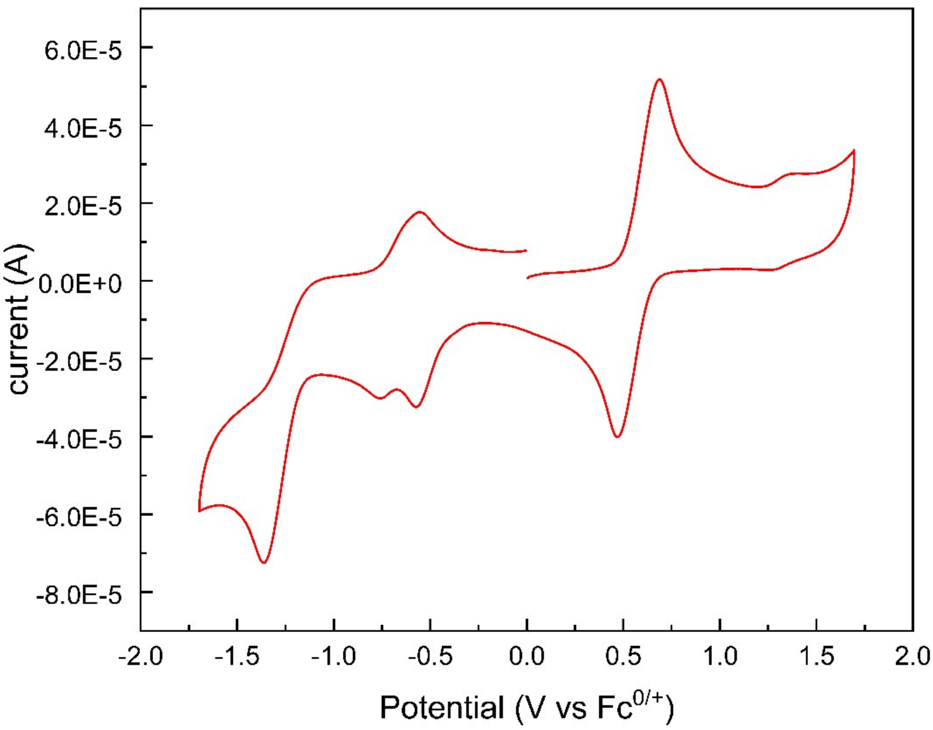

Figure S14. Cyclic Voltammetry of complex 3 (1 mM) in CH_2Cl_2
Conditions: $^{n}Bu_4NPF_6$ (0.3 M) as the supporting electrolyte; scan rate, 100 mV/s; potentials vs $Fc^{0/+}$; under N_2 (1 atm).

Computational Results

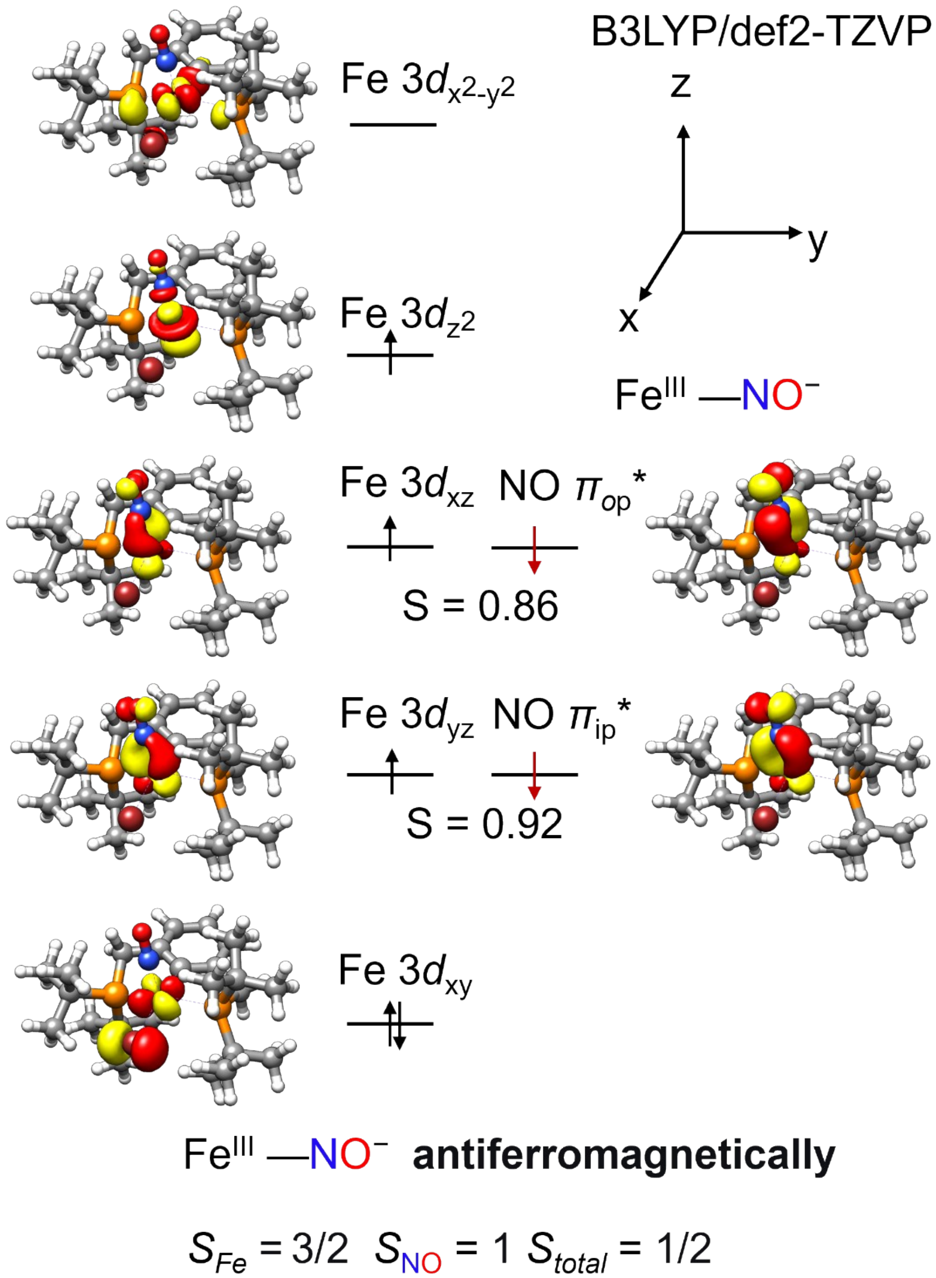

Figure S15. MO diagram obtained from the DFT calculations of **2**.

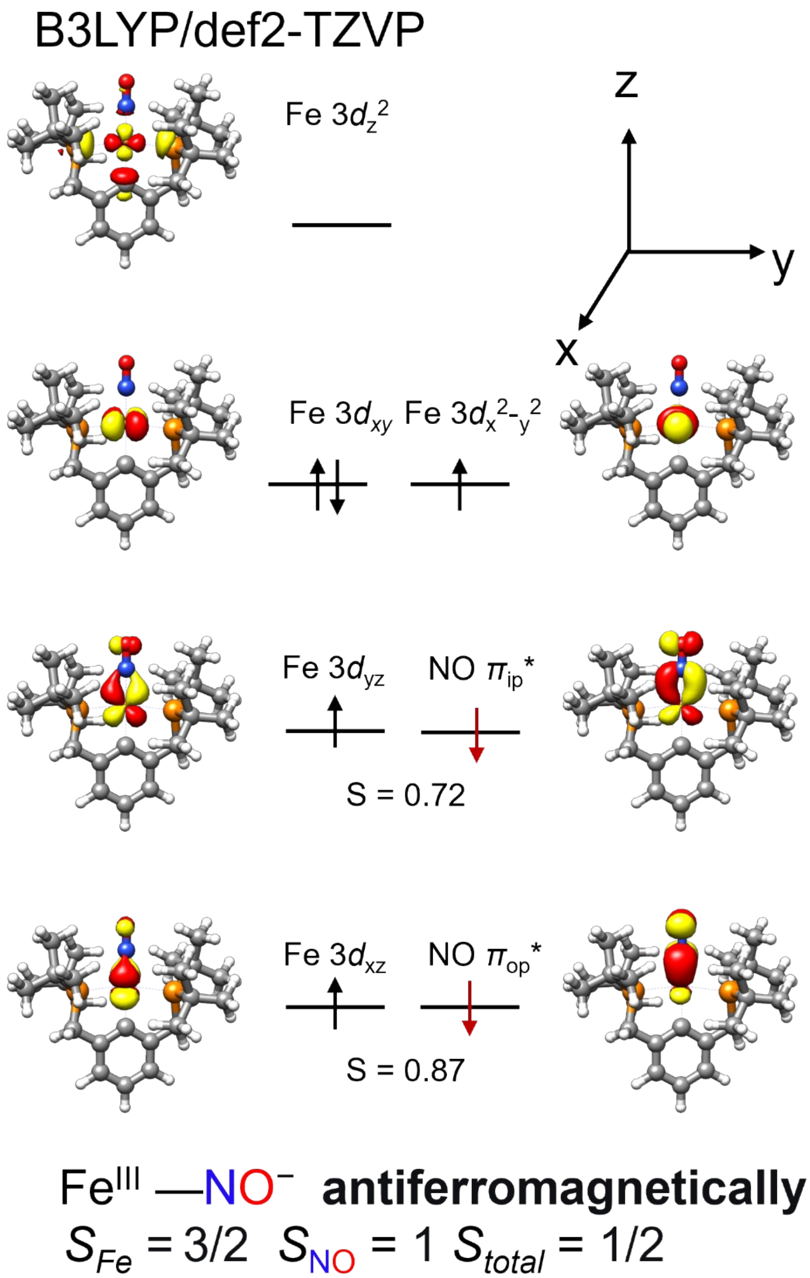

Figure S16. MO diagram obtained from the DFT calculations of **3**.

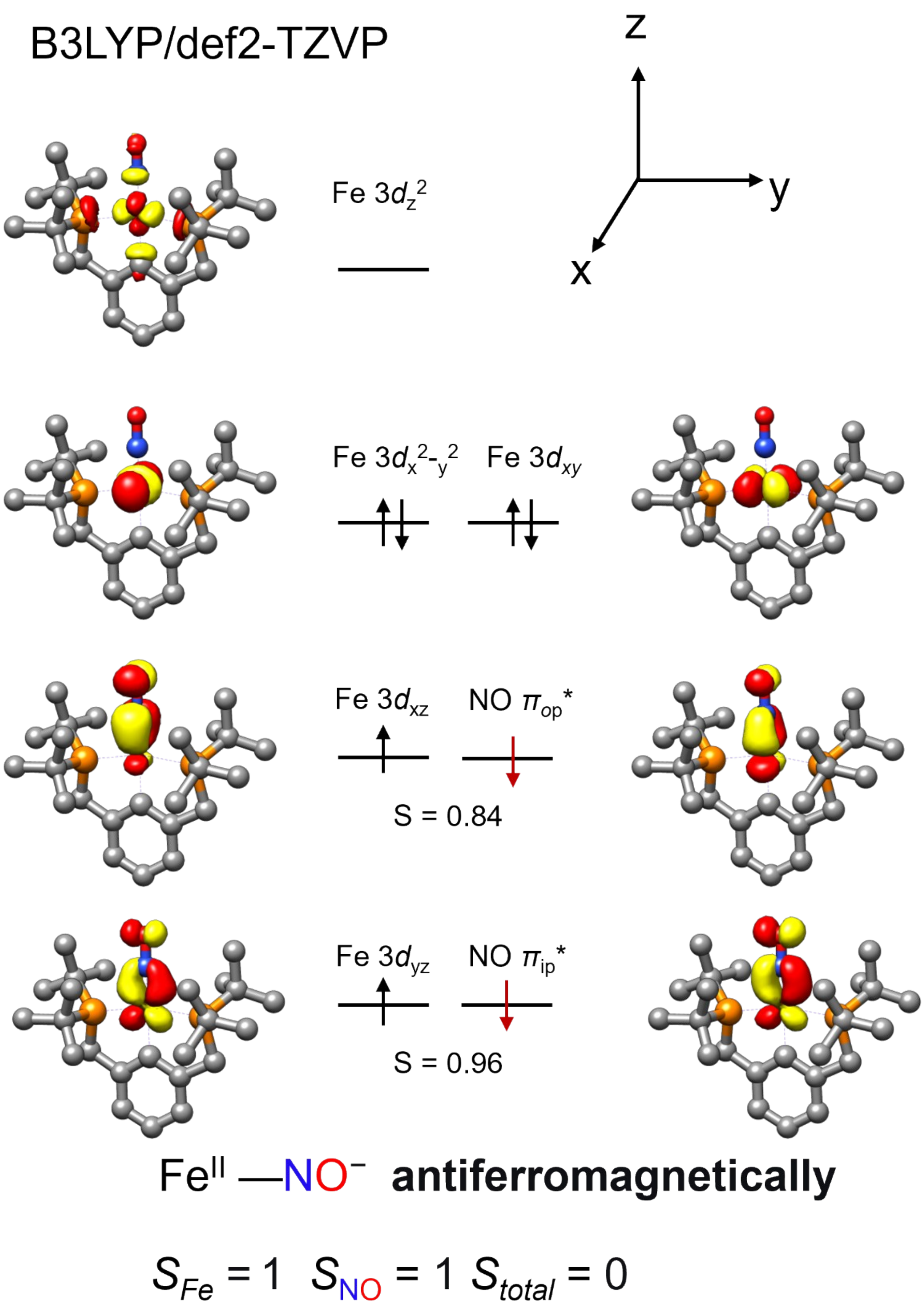

Figure S17. MO diagram obtained from the DFT calculations of **4**.

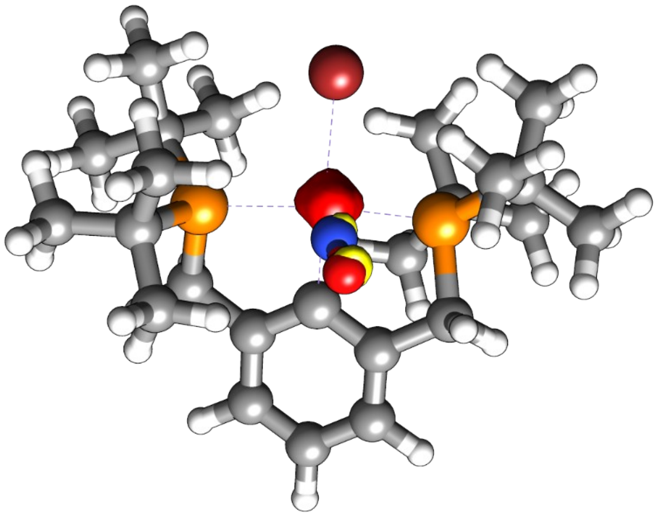

Figure S18. The calculated spin densities of **2**. (isovalue = 0.06)

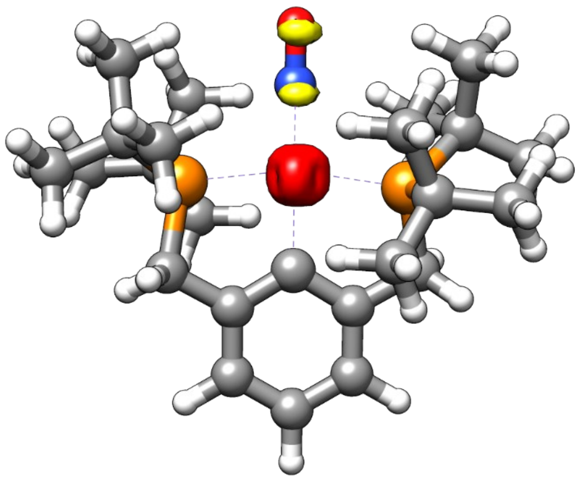

Figure S19. The calculated spin densities of **3**. (isovalue = 0.06)

Table S1. Configurations (≥ 5 %) of the ground state for **2** obtained by CASSCF(9,8). ‘2’ stands for doubly occupied orbitals, ‘1’ stands for singly occupied orbital and ‘0’ stands for unoccupied orbitals.

configuration	weight(%)
22221000	66
22201200	6
22021020	5
22111110	5

orbital ordering: (nb-Fe $3d_{xy}$) (σ_{eq}) (π_y) (π_x) (nb-Fe $3d_{z2}$) (π^*_x) (π^*_y) (σ^*_{eq})

Table S2. NEVPT2 corrected states energies of complex **2** averaging 5 states.

	energy (cm^{-1}).
1	0
2	7700
3	16000
4	16800
5	17000

Table S3. Configurations (≥ 5 %) of the ground state for **3** obtained by CASSCF(9,8). ‘2’ stands for doubly occupied orbitals, ‘1’ stands for singly occupied orbital and ‘0’ stands for unoccupied orbitals.

configuration	weight(%)
22221000	64
22201200	7
22111110	5
22021020	5

orbital ordering: (nb-Fe $3d_{xy}$) (σ_{ip}) (π_y) (π_x) (nb-Fe $3d_{x^2-y^2}$) (π^*_x) (π^*_y) (σ^*_{ip})

Table S4. NEVPT2 corrected states energies of **3** averaging 5 states.

	energy (cm^{-1}).
1	0
2	1900
3	12300
4	16300
5	19600

Table S5. The calculated *g* factors of complex **2** and **3** obtained from CASSCF/NEVPT2 with different roots.

CASSCF/NEVPT2	**2**			**3**		
Number of states	g_x	g_y	g_z	g_x	g_y	g_z
2	2.00	2.00	2.05	1.88	1.88	3.23
3	2.00	2.02	2.05	1.88	1.90	3.25
4	2.00	2.02	2.05	1.91	1.92	3.20
5	2.02	2.04	2.05	1.91	1.91	3.12

Table S6. The computed *g*-factors of complex **2** and **3** by DFT calculations.

	2			**3**		
DFT	g_x	g_y	g_z	g_x	g_y	g_z
Experiment	2.05	2.04	2.01	1.93	1.96	2.95
B3LYP	2.03	2.06	2.06	2.04	2.04	2.28
BP86	2.01	2.04	2.05	2.01	2.04	2.19
TPSSh	2.02	2.04	2.05	2.02	2.04	2.15

Table S7. The computed Mössbauer spectrum parameter of complex **2**, **3** and **4** by DFT calculations.

	2		**3**		**4**	
Experiment	0.19	1.89	-0.02	0.73	0.08	1.15
Calculated	δ	$\|\Delta E_Q\|$	δ	$\|\Delta E_Q\|$	δ	$\|\Delta E_Q\|$
B3LYP	0.19	1.54	0.05	1.97	0.07	1.72
BP86	0.15	1.64	0.01	1.42	0.02	1.70
TPSSh	0.12	1.51	-0.02	1.69	0.00	1.85

Table S8. The selected structural data of complex **2** obtained by DFT calculations.

	Fe1-N1	**N1-O1**	**∠(Fe-N-O)**	**ν(N-O)**
experiment	1.673(4)	1.133(5)	169°	1682 cm^{-1}
B3LYP	1.723	1.176	155°	1818 cm^{-1}
TPSSH	1.652	1.174	159°	1824 cm^{-1}
BP	1.648	1.186	160°	1767 cm^{-1}

Table S9. The selected structural data of complex **3** obtained by DFT calculations.

	Fe1-N1	**N1-O1**	**∠(Fe-N-O)**	**ν(N-O)**
experiment	1.658(3)	1.174(4)	178°	1783 cm^{-1}
B3LYP	1.697	1.167	179°	1904 cm^{-1}
TPSSH	1.667	1.166	179°	1912 cm^{-1}
BP	1.648	1.174	177°	1868 cm^{-1}

Table S10. The selected structural data of complex **4** obtained by DFT calculations.

	Fe1-N1	**N1-O1**	**∠(Fe-N-O)**	**ν(N-O)**
experiment	1.615(15)- 1.652(12)	1.171(17)- 1.206(16)	173.3°(13)- 179.7°(14)	1659 cm^{-1}
B3LYP	1.649	1.189	177°	1781 cm^{-1}
TPSSH	1.617	1.190	174°	1778 cm^{-1}
BP	1.614	1.198	169°	1757 cm^{-1}

Table S11. The Mulliken spin populations of complex **2** predicted by DFT.

	B3LYP	TPSSH	BP
Fe	1.88	1.51	1.12
N	-0.39	-0.19	-0.03
O	-0.35	-0.18	-0.07

Table S12. The Mulliken spin population of complex **3** predicted by DFT.

	B3LYP	TPSSH	BP
Fe	2.30	2.04	1.59
N	-0.57	-0.45	-0.23
O	-0.49	-0.34	-0.15

Table S13. The Mulliken spin populations of complex **2** predicted by CASSCF/def2-TZVP.

	2
Fe	1.37
N	-0.19
O	-0.09

Table S14. The Mulliken spin populations of complex **3** predicted by CASSCF/def2-TZVP.

	3
Fe	1.43
N	-0.24
O	-0.12

X-ray Crystallographic Data

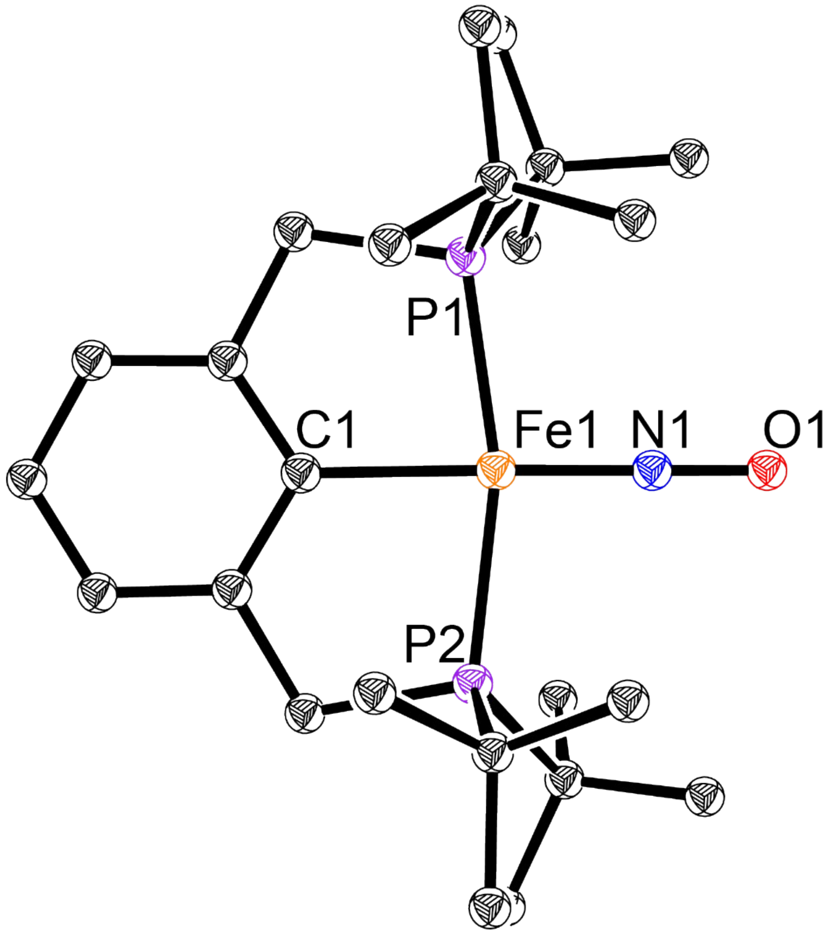

Figure S20. Crystal structures of complex **4** with thermal ellipsoids at 30 % probability. H atoms are omitted for clarity.

Table S15. Selected distances of complex **2-4.**

	Fe1-N1	**Fe1-C1**	**Fe1-P1**	**Fe1-P2**	**N1-O1**	**∠(Fe-N-O)**
2	1.673(4)	2.001(4)	2.3318(11)	2.2965(11)	1.133(5)	168.5(4)°
3	1.658(3)	2.030(3)	2.2812(8)	2.2804(8)	1.174(4)	177.9(4)°
4	1.615(15)-1.652(12)	2.021(12)-2.029(13)	2.220(5)-2.228(5)	2.221(5)-2.231(5)	1.171(17)-1.206(16)	173.3(13)-179.7(13)°

Table S16. X-ray crystallographic data for **2**

	2
CCDC number	2515198
Empirical formula	$C_{24}H_{43}BrFeNOP_2$
Formula weight	559.29
Temperature/K	250
Crystal system	orthorhombic
Space group	Pna21
a/Å	12.0905(12)
b/Å	15.6218(16)
c/Å	14.3413(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2708.7(5)
Z	4
ρ_{calc}g/cm^3	1.371
μ/mm^{-1}	2.166
F(000)	1172
Crystal size/mm^3	0.04 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.21 to 54.97
Index ranges	-15 ≤ h ≤ 15, -20 ≤ k ≤ 20, -18 ≤ l ≤ 18
Reflections collected	83036
Independent reflections	6223 [R_{int} = 0.0587, R_{sigma} = 0.0348]
Data/restraints/parameters	6223/1/283
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0617
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.0670
Largest diff. peak/hole / e Å^{-3}	0.36/-0.37

Table S17. X-ray crystallographic data for **3**

	3
CCDC number	2515199
Empirical formula	$C_{56}H_{55}BF_{24}FeNOP_2$
Formula weight	1342.61
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	12.5784(2)
b/Å	12.3693(2)
c/Å	38.8756(6)
α/°	90
β/°	95.8670(10)
γ/°	90
Volume/Å^3	6016.82(17)
Z	4
ρ_{calc}g/cm^3	1.482
μ/mm^{-1}	3.543
F(000)	2732
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.57 to 155.476
Index ranges	-14 ≤ h ≤ 15, -12 ≤ k ≤ 15, -49 ≤ l ≤ 47
Reflections collected	34660
Independent reflections	11667 [R_{int}= 0.0526, R_{sigma}= 0.0515]
Data/restraints/parameters	11667/90/815
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0563, wR_2 = 0.1544
Final R indexes [all data]	R_1 = 0.0725, wR_2 = 0.1651
Largest diff. peak/hole / e Å^{-3}	0.68/-0.56

Table S18. X-ray crystallographic data for **4**

	4
CCDC number	2515200
Empirical formula	$C_{96}H_{172}Fe_4N_4O_4P_8$
Formula weight	1917.53
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	45.7112(6)
b/Å	14.9762(3)
c/Å	15.2800(3)
α/°	90
β/°	91.2267(13)
γ/°	90
Volume/$Å^3$	10458.0(3)
Z	4
$\rho_{calc}g/cm^3$	1.218
μ/mm^{-1}	5.878
F(000)	4128
Crystal size/mm^3	0.195 × 0.149 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	3.866 to 169.492
Index ranges	-56 ≤ h ≤ 55, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	33047
Independent reflections	33047 [R_{int} = 0.20, R_{sigma} = 0.0310]
Data/restraints/parameters	33047/594/1094
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.1480, wR_2 = 0.3663
Final R indexes [all data]	R_1 = 0.1648, wR_2 = 0.3769
Largest diff. peak/hole / e $Å^{-3}$	1.43/-1.48

Table S19. *g*-factors of {M-NO}[7] complexes.

Fe(LN_4^{PhCl})NO	*g* = 2.07, 2.03, 2.03	*J. Inorg. Biochem.* 2013, 118, 115-127.
Fe(TPP)(NO)(4-NMe_2Py	*g* = 2.07, 2.00, 1.97	Inorg. Chem. **2003**, 42, 5722-5734
Fe(TPP)(NO)(1-MeIm)	*g* = 2.08, 2.00, 1.97	Inorg. Chem. **2003**, 42, 5722-5734
Fe(TPP)(NO)(4-MePip)	*g* = 2.09, 2.00, 1.98	Inorg. Chem. **2003**, 42, 5722-5734
Fe(TPP)(NO)	*g* = 2.10, 2.03, 2.00	Inorg. Chem. **2003**, 42, 5722-5734
$[(NC)_5Fe(NO)]^{3-}$	*g* = 1.99, 1.99, 1.92	*J. Chem. Phys.* **1966**, *45*, 3914.
[($PaPy_3$)Fe(NO)](ClO4)	*g* = 2.03, 2.00, 1.94	*Inorg. Chem.* **2003**, 42, 6812−6823
[Ph_4P][Fe(bpy)$(CN)_3$(NO)]	*g* = 2.04, 2.03, 1.97	*Eur. J. Inorg. Chem.* **2015**, 1033–1040
[Fe(TpivPP)(NO_2)(NO)]	*g* = 2.09, 2.03, 2.01	*J. Am. Chem. Soc.* **1997**, *119*, 6274–6283.
$[Fe(TIM)(MeCN)(NO)]^{2+}$	*g* = 2.01, 2.00, 1.97	*Inorg. Chim. Acta* **1997**, *260*, 163–172.
$[Fe(N_3PyS)(NO)]^{+}$	*g* = 2.05, 2.01, 1.96	*J. Am. Chem. Soc.* **2013**, *135*, 14024–14027.
$[Fe(N_4Py)(NO)]^{2+}$	*g* = 2.03, 2.00, 1.95	*J. Am. Chem. Soc.* **2013**, *135*, 14024–14027.
$[Fe(S_2C_2(pTol)_2)_2(NO)]^{2-}$	*g* = 2.05, 2.03, 2.01	*Inorg. Chem.* **2007**, *46*, 522–532
$[Fe(S_2C_2(CN)_2)_2(NO)]^{2-}$	*g* = 2.06, 2.03, 2.01	*Inorg. Chem.* **2007**, *46*, 522–532
[Fe(í-S,S-C_6H_4)(ON)$]_3$	*g* = 2.01, 2.00, 1.99	*J. Am. Chem. Soc.* **2007**, *129*, 1151–1159.
[Fe(To-F_2PP-C_3IM)(NO)]	*g* = 2.09, 2.00, 1.98	*J. Am. Chem. Soc.* **2009**, *131*, 17116–17126
[Fe(To-F_2PP-C_4IM)(NO)]	*g* = 2.07, 1.99, 1.97	*J. Am. Chem. Soc.* **2009**, *131*, 17116–17126
[Fe(To-F_2PP-BzIM)(NO)]	*g* = 2.08, 2.01, 1.98	*J. Am. Chem. Soc.* **2009**, *131*, 17116–17126
[Fe(TMP-mPy)(NO)]	*g* = 2.10, 2.04, 2.01	*J. Am. Chem. Soc.* **2009**, *131*, 17116–17126
Im-Heme-NO	*g* = 2.08, 2.00, 1.98	*J. Biol. Chem.***1980,** *255*, 7876
FeFur–NO	*g* = 2.04, 2.03, 2.02	*Proc. Natl. Acad. Sci. U.S.A.* **2002**, *26*, 16619-16624

$[(PaPy3)Fe(NO)](ClO_4)$	*g* = 2.00	Angewandte Chemie International Edition. **2003**, *42*,4517-4521.
$[Fe(NO)(pyN_44HBr)](Br)_2$	*g* = 2.05, 2.01, 1.97	*Chem. Eur. J.* **2002,** *8*, 5709-5722
$[Fe(NO)(S2C2(p\text{-}tolyl)_2)_2]^{2-}$	*g* = 2.05, 2.03, 2.00	*Chem. Eur. J.* **2002,** *8*, 5709-5722
$[Fe(NO)(S2C2(4,4\text{-}diphenyl)_2)_2]^{2-}$	*g* = 2.05, 2.03, 2.01	*Chem. Eur. J.* **2002,** *8*, 5709-5722
$[Fe(bztpen)(NO)](PF_6)_2$	*g* = 2.05	*Chem. Eur. J.* **2016**, *22*, 12741-12751
$[Fe(cyclam)(NO)Cl]Cl_2$	*g* = 2.00	*Polyhedron* **2007**, *26*, 4653-4658.
$(Et_4N)_2[Fe(PhPepS)(NO)]$	*g* = 2.03	*Inorg. Chem.* **2005**, *44*, 6918-6920.
Trans-K$\{[FeCl(NO^0)(cyclam)]\cdot[FeCl(NO^+)(cyclam)]_2\}(PF_6)_6$	*g* = 2.03	*Dalton Trans.* **2002,** *9*, 1903-1906.
$[Fe((CH_2Py_2)_2Me[9]aneN_3)(NO)](BF_4)_2$	*g* = 2.04, 2.01, 1.96	*Dalton Trans.* **2017**, *46*, 16058-16064
$[Ph_4P][Fe(bpy)(CN)_3(NO)]$	*g* = 2.04, 2.03, 1.97	*Dalton Trans.* **2017**, *46*, 16058-16064
[(tpp)Fe(NO)]	*g* = 2.10, 2.06 ,2.01	*Eur. J. Inorg. Chem.* ***2015***, 6, 1033-1040.
[(tpp)Fe(NO)]	*g* = 2.10, 2.06, 2.01	*J. Am. Chem. Soc.* **1974**, *96*, 6037
[(tpp)Fe(NO)(pip)]	*g* = 2.08, 2.04, 2.00	*J. Am. Chem. Soc.* **1974**, *96*, 6037
$[(Me_2dtc)_2Fe(NO)]$	*g* = 2.04, 2.04, 2.03	*Zeitschrift für Naturforschung B* **1997** *52, 919-926.*
$[(das)_2Fe(NO)Br]^+$	*g* = 2.02, 1.99	*Inorg. Chim. Acta* **1980**, *40,* 37.
$[(TpivPP)Fe(NO)(NO)_2]^-$	*g* = 2.09, 2.03, 2.01	*J. Chem. Soc.A* **1969**, *2987.*
HbNO	*g* = 2.08, 2.03, 1.99	*J. Chem. Phys.* **1969**, *51,* 4220.
MbNO	*g* = 2.07, 2.00, 1.99	*J. Am. Chem. Soc.* ***1971***, *93,* 5036.
trans-[(cyclam)-[(cyclam)Fe(NO)Cl](ClO_4)	*g* = 2.05, 2.02, 1.97	*J. Am. Chem. Soc.* **2000**, *122,* 4352-4365
*ba*3-NO	g = 2.10, 2.01, 1.97	*J. Am. Chem. Soc.* **2007** *129,* 14952-14958
sGC-NO	g = 2.10,	*Biochemistry* **2008,** *47*, ,

	2.03, 2.01	3892-3899
(bme*-daco)Fe(NO)	g = 2.04	*Inorg. Chem.* **2005**, *44,* 9007-9016
(bme-dach)Fe(NO)	g = 2.05	*Inorg. Chem.* **2005**, *44,* 9007-9016
[(NO)Fe(SC9H6N)$_2$]	g =2.03	*Journal of the Chinese Chemical Society* **2010**, *57*, 909-915
$[(NC)_5Ru(NO)]^{3-}$	*g* = 2.00, 2.00, 1.87	*Inorg. Chem.* **2001,** *40,* 5704-5707
$[(bpy)_2(CH_3CN)Ru(NO)]^{2+}$	*g* = 1.99, 1.88, 1.97	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.
$[(bpy)_2ClRu(NO)]^{+}$	*g* = 1.99, 1.88, 1.97	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.
$[(bpy)_2ClRu(NO)]^{1+}$	*g* = 2.03, 1.99, 1.88	*Eur. J. Inorg. Chem.* **2004**, 2902-2907
$[(bpydip)ClRu(NO)]^{1+}$	*g* = 2.03, 1.99, 1.89	*Dalton Trans.* **2003**, 458.
$[(cyclam)ClRu(NO)]^{1+}$	*g* = 2.04, 2.00, 1.88	*Inorg. Chem.* **2000**, *39*, 3577.
$[(depe)_2ClRu(NO)]^{1+}$	*g* = 2.01, 1.98, 1.89	*Inorg. Chem.* **2000**, *39*, 3577.
$[(Me_3P)_2(C_5Me_5)Ru(NO)]^{1+}$	*g* = 2.01, 2.00, 1.92	*Organomet. Chem.* **2003**, *675*, 21.
$[(NC)(py)_4Ru(\mu\text{-}CN)(py)_4Ru(NO)]^{2+}$	*g* = 1.99, 1.87, 1.96	*Inorg. Chem.* **2002,** *41*, 1930
$[(Ph_3P)_2(C_5Me_5)Ru(NO)]^{1+}$	*g* = 2.01, 1.98, 1.90	*Organomet. Chem.* **2003**, *675*, 21.
$[(PhMe_2P)_2(C_5Me_5)Ru(NO)]^{1+}$	*g* = 2.00, 2.00, 1.92	*Organomet. Chem.* **2003**, *675*, 21.
$[(py)_4(NH_3)Ru(NO)]^{2+}$	*g* = 2.02, 1.99, 1.88	*Eur. J. Inorg. Chem.* **2004**, 2902-2907
$[(py)_4(OH)Ru(NO)]^{+}$	*g* = 1.99, 1.89, 1.97	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.
$[(py)_4(SCN)Ru(NO)]^{+}$	*g* =1.99, 1.88, 1.96	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.
$[(py)_4ClRu(NO)]^{+}$	*g* = 1.99, 1.89, 1.97	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.
$[(terpy)(bpy)Ru(NO)]^{2+}$	*g* = 2.00,1.88, 1.97	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.
$[(terpy)(bpz)Ru(NO)]^{2+}$	*g* = 2.00,1.89, 1.97	*Eur. J. Inorg. Chem.* **2004**.*14*, 2902-2907.

$[DCl(OC)(P\mathit{i}Pr_3)_2Ru(NO)]$	*g* =2.00, 1.99, 1.91	*Inorg. Chem.* **2004**, *43*, 351.
$[HCl(OC)(P\mathit{i}Pr_3)_2Ru(NO)]$	*g* = 2.01, 1.99, 1.91	*Inorg. Chem.* **2004**, *43*, 351.
$[Ru((CH_2py)_2Me[9]aneN_3)(NO)]^{2+}$	*g* = 2.01, 2.00, 1.88	*Eur. J. Inorg. Chem.* **2021**, 4842 –4855
$[Ru(Me3[9]aneN3)(bpy)(NO)]^{2+}$	*g* = 2.03, 1.99, 1.88	*Inorg. Chem.* **2016**, 55, 7808-7810
$[Ru(trpy)(bik)(NO)](ClO_4)_2$	*g* = 2.02, 2.00, 1.88	*Eur. J. Inorg. Chem.* **2009**, 2702-2710.
$[Ru^{II}(trpy)(tmp)(NO)](ClO_4)_2$	*g* = 2.02, 2.00, 1 .88	*Inorg. Chim. Acta* *2010,363,*2945-2954
$[Ru^{II}(tpm)(pap)(NO^+)]^{2+}$	*g* = 1.99.	*Inorg. Chim. Acta* **2011**, *372,* 250-258
trans-$[RuCl(Hind)_4(NO)]Cl_2 \cdot H_2O$	*g* = 2.03, 1.96, 1.87	*Inorg. Chem.* **2018,** *57,* 10702-10717
trans-$[RuOH(Hind)_4(NO)]Cl_2 \cdot H_2O$	*g* = 2.03, 1.99, 1.88	*Inorg. Chem.* **2018,** *57,* 10702-10717
$[RuCl(ind)_2(Hind)_4(NO)]$	*g* = 2.02, 1.98, 1.88	*Inorg. Chem.* **2018,** *57,* 10702-10717
$[RuOH(ind)_2(Hind)_2(NO)]$	*g* = 2.01, 1.98, 1.88	*Inorg. Chem.* **2018,** *57,* 10702-10717
[(TPP)Ru(NO)(4-cyanopyridine)]	*g* = 2.10, 1.99, 1.88	*Inorg. Chem.* **2008,** *47,* 7106-7113
[(OEP)Ru(NO)(4-cyanopyridine)]	*g* = 2.10, 1.99, 1.89	*Inorg. Chem.* **2008,** *47,* 7106-7113
[(TPP)Ru(NO)(pyridine)]	*g* = 2.03, 1.98, 1.88	*Inorg. Chem.* **2008,** *47,* 7106-7113
[(OEP)Ru(NO)(4-N,N-dimethylaminopyridine)]	*g* = 2.02, 1.99, 1.87	*Inorg. Chem.* **2008,** *47,* 7106-7113
[(TPP)Ru(NO)(4-N,N-dimethylaminopyridine)]	*g* = 2.04, 1.99, 1.88	*Inorg. Chem.* **2008,** *47,* 7106-7113
[Ru(bpy)(tpm)NO]2+	*g* = 2.03, 1.99, 1.87	*Inorg. Chem.* **2006,** *45, 8608*-8617
Ru2(dpf)4(NO)2	*g* = 1.98, 1.95	*Inorg. Chem.* **2004,** *43*, 7741-7751
Ru(salophen)(NO)Cl	*g* = 2.30, 2.12, 1.84	*Dalton Trans.* **2022**, *51,*11404–11415
Ru(naphophen)(NO)Cl	*g* = 2.29, 2.08, 1.88	*Dalton Trans.* **2022**, *51,*11404–11415
$[Cl_5Os(NO)]^{3-}$	*g* = 2.00, 1.95, 1.70	*Inorg. Chem.* **2006**, 45, 4602-4609
$[(NC)_5Os(NO)]^{3-}$	*g* = 1.96,	*Inorg. Chem.* **2001,** *40,*

	1.93, 1.63	5704-5707
$[Cl_5Ir(NO)]^{2-}$	*g* = 1.98, 1.89,1.67	*Dalton Trans.* **2004**, 1797–1800

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XYZ Coordinates

Table S20.XYZ coordinate of **2** computed by DFT/B3LYP

Br	7.491421	9.533186	9.060427
Fe	8.294628	7.547893	7.794556
P	6.132737	6.813736	7.238972
P	10.29928	8.586905	7.275858
C	8.360009	4.612351	4.619866
H	7.6312	4.012653	4.066009
C	9.724087	4.435002	4.388267
H	10.06632	3.688826	3.666459
C	6.435488	5.843953	5.685522
H	5.81748	4.934106	5.635764
H	6.114459	6.474897	4.84142
C	4.136999	8.727961	7.916789
H	3.490704	8.022485	8.458562
H	3.496334	9.554844	7.566001
H	4.878683	9.142602	8.612616
C	7.912795	5.567571	5.54604
N	8.906159	6.444184	8.967846
O	9.545058	5.535053	9.352692
C	10.65014	5.230969	5.067903
H	11.71967	5.115707	4.867895
C	5.512258	6.175013	9.885971
H	6.527652	6.517057	10.12732
H	5.209155	5.421775	10.63271
H	4.842559	7.039544	9.98614
C	9.627006	8.979768	4.584562
H	10.24916	8.133256	4.263656
H	9.530864	9.673754	3.732582
H	8.629413	8.58681	4.820876
C	4.014312	5.097897	8.167798
H	3.282965	5.909025	8.282667
H	3.731209	4.298501	8.873563
H	3.922634	4.684009	7.151675
C	5.447368	5.550601	8.481114
C	5.581545	9.14578	5.908123
H	6.295852	9.669653	6.556491
H	4.869746	9.886449	5.506539
H	6.128379	8.718568	5.051824

C	10.21465	6.179291	6.001033
C	3.727999	7.464821	5.786761
H	4.142913	7.033249	4.864478
H	3.036579	8.269284	5.483471
H	3.132231	6.692689	6.288186
C	10.23228	9.754017	5.77094
C	11.61851	10.27113	5.358716
H	12.0612	10.93382	6.1143
H	11.51764	10.85729	4.429459
H	12.32611	9.452938	5.153259
C	11.06406	10.77657	8.937621
H	11.38096	11.43933	8.120239
H	11.6103	11.09212	9.842485
H	9.989705	10.91748	9.121651
C	8.835333	6.348149	6.27805
C	6.364771	4.313188	8.427548
H	6.294851	3.787573	7.464257
H	6.046372	3.607481	9.212914
H	7.418226	4.553854	8.605059
C	4.808894	8.072294	6.699654
C	9.296978	10.93617	6.082778
H	8.306735	10.59155	6.407482
H	9.174887	11.54048	5.167959
H	9.686092	11.59316	6.868842
C	11.20832	7.07111	6.710664
H	12.09251	7.29208	6.092634
H	11.5745	6.579324	7.62834
C	12.89298	9.152849	8.332478
H	13.19249	8.099684	8.231894
H	13.47769	9.578304	9.165738
H	13.1884	9.683726	7.418657
C	11.39564	9.301803	8.658718
C	11.08437	8.489768	9.929679
H	10.03522	8.609701	10.23169
H	11.7277	8.856318	10.74719
H	11.29125	7.417168	9.804497

Table S21. XYZ coordinate of **2** computed by DFT/BP86

Br	7.521931	9.537822	8.981779
Fe	8.302698	7.542436	7.775309
P	6.182857	6.841822	7.231437

P	10.25891	8.553984	7.287216
C	8.365746	4.628847	4.584834
H	7.630372	4.041968	4.010552
C	9.737563	4.433752	4.368109
H	10.08202	3.684718	3.638716
C	6.444451	5.884347	5.655861
H	5.79538	4.986629	5.5903
H	6.134536	6.549913	4.821988
C	4.182344	8.746583	7.954303
H	3.55558	8.025743	8.515028
H	3.516536	9.571285	7.620912
H	4.942617	9.172455	8.637377
C	7.915966	5.582408	5.520643
N	8.886787	6.474085	8.885888
O	9.501052	5.569095	9.344533
C	10.66875	5.214898	5.071981
H	11.74742	5.089428	4.88402
C	5.596893	6.169151	9.882327
H	6.623238	6.513708	10.10922
H	5.305446	5.405124	10.63412
H	4.924089	7.039087	10.00147
C	9.572219	8.925149	4.590249
H	10.17962	8.054811	4.277367
H	9.478048	9.611477	3.721758
H	8.564421	8.548717	4.848571
C	4.062594	5.12188	8.169802
H	3.334081	5.943382	8.305908
H	3.779257	4.310465	8.87417
H	3.951619	4.717483	7.143338
C	5.506387	5.558267	8.470436
C	5.596882	9.181252	5.917062
H	6.32998	9.702343	6.561331
H	4.874833	9.930531	5.528191
H	6.133583	8.755077	5.043845
C	10.23053	6.162272	6.014685
C	3.747128	7.487818	5.816851
H	4.156547	7.057535	4.882005
H	3.043126	8.294602	5.520012
H	3.156087	6.706115	6.326522
C	10.1966	9.711316	5.761494
C	11.59612	10.19823	5.34721

H	12.05293	10.86608	6.102294
H	11.50854	10.78153	4.405482
H	12.29479	9.360396	5.148565
C	11.00509	10.78432	8.930075
H	11.33734	11.4372	8.099816
H	11.54344	11.11717	9.843108
H	9.920244	10.93005	9.098123
C	8.841334	6.349982	6.280716
C	6.41748	4.315892	8.376332
H	6.32585	3.804034	7.39844
H	6.108985	3.592194	9.160421
H	7.483672	4.547601	8.537073
C	4.836838	8.103049	6.718206
C	9.280178	10.913	6.063277
H	8.287916	10.58525	6.425293
H	9.140319	11.49731	5.128936
H	9.6987	11.59215	6.826151
C	11.21338	7.050664	6.742531
H	12.11586	7.28169	6.140279
H	11.56621	6.563104	7.678343
C	12.84011	9.142772	8.374812
H	13.14315	8.080556	8.299087
H	13.41974	9.587745	9.211854
H	13.14876	9.659534	7.447575
C	11.337	9.301604	8.681719
C	10.9996	8.504609	9.957916
H	9.935794	8.629701	10.23751
H	11.62993	8.882321	10.79091
H	11.20908	7.422581	9.848827

Table S22. XYZ coordinate of **2** computed by DFT/TPSSh

Br	7.512014	9.535358	8.990233
Fe	8.300353	7.5534	7.775408
P	6.163746	6.832551	7.236472
P	10.27237	8.565783	7.279384
C	8.359713	4.636251	4.599911
H	7.629652	4.046673	4.037452
C	9.724573	4.449371	4.374703
H	10.06522	3.706118	3.649812
C	6.439704	5.87197	5.674046
H	5.812046	4.967981	5.620142

H	6.120667	6.52012	4.84047
C	4.166619	8.739794	7.935171
H	3.541567	8.028396	8.495005
H	3.509001	9.554102	7.586384
H	4.918692	9.168508	8.612265
C	7.913664	5.586819	5.532233
N	8.8856	6.473675	8.880455
O	9.498391	5.57092	9.312499
C	10.6525	5.233145	5.067212
H	11.72239	5.111492	4.874494
C	5.581579	6.185922	9.882964
H	6.602563	6.528503	10.10076
H	5.292882	5.430427	10.6331
H	4.91254	7.050445	9.993316
C	9.620053	8.947177	4.585478
H	10.24459	8.098495	4.272746
H	9.528702	9.641091	3.732599
H	8.621533	8.556693	4.825465
C	4.048863	5.120162	8.186881
H	3.323712	5.935109	8.318578
H	3.778297	4.318683	8.895219
H	3.940233	4.711706	7.16994
C	5.489487	5.566307	8.477026
C	5.585919	9.150695	5.904463
H	6.32139	9.66313	6.540021
H	4.869129	9.89755	5.523481
H	6.107285	8.71706	5.035215
C	10.21669	6.177305	6.005536
C	3.737767	7.463519	5.814554
H	4.149573	7.019816	4.896155
H	3.048781	8.268237	5.506447
H	3.143471	6.699338	6.33085
C	10.21972	9.726196	5.771807
C	11.6126	10.23524	5.369616
H	12.04732	10.904	6.125558
H	11.51992	10.81249	4.433973
H	12.31849	9.41156	5.179709
C	11.02067	10.77051	8.937894
H	11.34718	11.42663	8.118062
H	11.56131	11.0856	9.846342
H	9.944064	10.91198	9.110825

C	8.835474	6.359911	6.277854
C	6.39967	4.324622	8.395065
H	6.285788	3.797177	7.436406
H	6.109624	3.625707	9.197375
H	7.460927	4.564132	8.525291
C	4.826413	8.080713	6.712689
C	9.285524	10.91305	6.068528
H	8.298612	10.5684	6.4051
H	9.159047	11.49857	5.142065
H	9.681509	11.5833	6.840752
C	11.20559	7.061201	6.729325
H	12.09625	7.287913	6.121784
H	11.56106	6.570234	7.653102
C	12.8516	9.138057	8.362331
H	13.14552	8.082759	8.264707
H	13.42341	9.561121	9.205667
H	13.15966	9.67007	7.452759
C	11.34991	9.293098	8.667898
C	11.01777	8.484778	9.93588
H	9.95887	8.599287	10.20911
H	11.63973	8.860388	10.76585
H	11.23834	7.413594	9.814545

Table S23. XYZ coordinate of **3** computed by DFT/B3LYP

Fe	7.545488	3.441836	14.80367
P	6.885085	2.361356	16.72364
P	8.500293	4.029848	12.79663
O	6.010104	5.82984	15.18381
N	6.629249	4.853541	15.02489
C	8.666534	1.774525	14.55761
C	8.844414	0.839047	15.61399
C	9.312196	1.48893	13.32304
C	6.904596	3.404486	18.29999
C	5.27091	1.427647	16.41681
C	9.621851	-0.312	15.43901
H	9.742286	-1.01651	16.26623
C	10.09505	0.339182	13.16412
H	10.58279	0.142793	12.20563
C	8.210008	1.103307	16.95732
H	8.952006	1.535326	17.64803
H	7.83162	0.18952	17.44112

C	9.121786	2.420078	12.15118
H	8.352794	2.020256	11.47095
H	10.03389	2.544138	11.54723
C	5.650487	4.286887	18.40238
H	5.494257	4.905355	17.50813
H	5.765731	4.971063	19.25845
H	4.742491	3.694503	18.58069
C	5.563511	0.362677	15.3428
H	5.960374	0.806051	14.41748
H	4.621341	-0.15223	15.09577
H	6.279864	-0.39817	15.68314
C	7.029545	2.529794	19.56023
H	6.171126	1.859973	19.69464
H	7.074614	3.188778	20.44264
H	7.946283	1.923027	19.5634
C	10.24975	-0.56138	14.21842
H	10.85922	-1.45867	14.08833
C	7.283261	4.653516	11.49043
C	10.007	5.135776	13.06732
C	4.740864	0.744876	17.68551
H	5.484616	0.07031	18.13641
H	3.861291	0.134506	17.42361
H	4.421225	1.470599	18.44563
C	8.152602	4.303041	18.18048
H	9.07777	3.722416	18.03778
H	8.271922	4.882427	19.11003
H	8.065101	5.02207	17.35246
C	6.926044	6.130941	11.71616
H	6.565995	6.329414	12.73492
H	6.117127	6.410209	11.02197
H	7.774862	6.797203	11.50918
C	4.22924	2.413582	15.85624
H	3.986034	3.222956	16.55645
H	3.296678	1.868135	15.64002
H	4.572534	2.867057	14.91355
C	9.593973	6.343713	13.92774
H	8.831142	6.969491	13.4473
H	10.47867	6.975521	14.10649
H	9.209839	6.028389	14.91014
C	11.03855	4.302174	13.85233
H	10.62947	3.918777	14.79913

H	11.90028	4.945695	14.09165
H	11.41392	3.44319	13.27868
C	7.827441	4.462234	10.06335
H	8.737038	5.046944	9.877322
H	7.063311	4.803876	9.346234
H	8.03972	3.408858	9.831229
C	6.018118	3.789986	11.67105
H	6.226925	2.712099	11.58121
H	5.287817	4.047285	10.8872
H	5.534953	3.967961	12.64352
C	10.6256	5.606123	11.74299
H	10.88157	4.7655	11.08026
H	11.55947	6.150779	11.95736
H	9.964769	6.292674	11.19645

Table S24. XYZ coordinate of **3** computed by DFT/BP86

Fe	7.558259	3.464339	14.81658
P	6.914802	2.394706	16.70666
P	8.474781	4.011224	12.82031
O	6.215338	5.902756	15.27434
N	6.745462	4.875833	15.06942
C	8.668251	1.798284	14.5727
C	8.89006	0.882763	15.65057
C	9.277495	1.479141	13.31719
C	6.850968	3.441713	18.28788
C	5.329838	1.407502	16.35672
C	9.679561	-0.26892	15.48037
H	9.834484	-0.95559	16.32702
C	10.07078	0.328482	13.16119
H	10.53055	0.109079	12.18504
C	8.268977	1.172702	16.99497
H	9.005617	1.656582	17.67134
H	7.911818	0.261926	17.51824
C	9.034586	2.388764	12.13842
H	8.206742	1.997454	11.50946
H	9.914928	2.491062	11.47122
C	5.558919	4.276564	18.34774
H	5.405427	4.891694	17.4413
H	5.6191	4.97206	19.21042
H	4.662956	3.644765	18.50015
C	5.687691	0.333377	15.30864

H	6.106287	0.776924	14.3837
H	4.761816	-0.21531	15.03781
H	6.418475	-0.40903	15.68363
C	6.969374	2.561078	19.54846
H	6.132001	1.847513	19.65028
H	6.95408	3.218786	20.4426
H	7.918805	1.992445	19.58212
C	10.2732	-0.5445	14.24012
H	10.89326	-1.4445	14.11293
C	7.237923	4.683298	11.54736
C	10.02771	5.073453	13.05671
C	4.768618	0.733888	17.6198
H	5.5108	0.068509	18.10458
H	3.899052	0.103953	17.33795
H	4.412789	1.468522	18.36684
C	8.075747	4.380055	18.20634
H	9.027987	3.824875	18.07973
H	8.157681	4.955342	19.1519
H	7.990119	5.112924	17.3809
C	6.942996	6.174192	11.7913
H	6.612269	6.379543	12.82681
H	6.123274	6.49408	11.11507
H	7.817458	6.814894	11.56816
C	4.295942	2.372222	15.74022
H	3.986706	3.176436	16.43323
H	3.38596	1.802581	15.45961
H	4.689231	2.846654	14.81748
C	9.66659	6.274205	13.95453
H	8.887549	6.923734	13.51521
H	10.5722	6.896034	14.11046
H	9.317745	5.940924	14.9529
C	11.06022	4.196129	13.79542
H	10.66437	3.801421	14.75239
H	11.9516	4.81658	14.02353
H	11.40014	3.332345	13.19229
C	7.735852	4.470889	10.10421
H	8.670828	5.020254	9.890367
H	6.963039	4.847264	9.40174
H	7.897576	3.402108	9.864195
C	5.951124	3.858361	11.77495
H	6.118389	2.767588	11.65933

H	5.18724	4.153121	11.02575
H	5.518051	4.037166	12.77953
C	10.60989	5.548419	11.71452
H	10.83309	4.705295	11.03037
H	11.5663	6.079063	11.90384
H	9.939563	6.257117	11.19213

Table S25.XYZ coordinate of **3** computed by DFT/TPSSh

Fe	7.537473	3.463324	14.80853
P	6.902302	2.386157	16.71386
P	8.476831	4.02276	12.80909
O	6.044288	5.837638	15.20312
N	6.649459	4.855781	15.03444
C	8.652786	1.804323	14.56483
C	8.87433	0.890705	15.63546
C	9.260336	1.488935	13.31528
C	6.856774	3.434869	18.28331
C	5.327475	1.394706	16.39073
C	9.655986	-0.25868	15.46293
H	9.809149	-0.94216	16.30172
C	10.04495	0.339921	13.15565
H	10.49996	0.123241	12.186
C	8.266432	1.1805	16.98448
H	9.003968	1.669305	17.64322
H	7.925841	0.273131	17.50781
C	9.025433	2.399256	12.13694
H	8.201364	2.013538	11.51354
H	9.903587	2.492263	11.4787
C	5.564895	4.263832	18.36669
H	5.396534	4.869703	17.46568
H	5.641542	4.955476	19.22095
H	4.6822	3.630763	18.53454
C	5.676889	0.318835	15.3441
H	6.084667	0.76092	14.42249
H	4.754219	-0.22548	15.08608
H	6.406458	-0.41415	15.71767
C	7.007093	2.569971	19.54866
H	6.179845	1.859881	19.67376
H	7.010014	3.235239	20.42739
H	7.953194	2.009794	19.56085
C	10.24356	-0.53339	14.22669

H	10.85445	-1.42921	14.09729
C	7.267857	4.699876	11.52617
C	10.02338	5.071381	13.06477
C	4.782447	0.720674	17.65859
H	5.532281	0.071538	18.13601
H	3.924328	0.086611	17.38264
H	4.427935	1.45238	18.39777
C	8.070434	4.381525	18.1734
H	9.01678	3.832292	18.04237
H	8.156556	4.967351	19.10261
H	7.963443	5.091852	17.34012
C	6.977123	6.190917	11.76025
H	6.642218	6.396811	12.78638
H	6.170371	6.505837	11.07912
H	7.852865	6.818894	11.54398
C	4.276874	2.342458	15.78106
H	3.98123	3.149529	16.46457
H	3.372512	1.764294	15.53272
H	4.648169	2.798054	14.84906
C	9.662044	6.267829	13.96516
H	8.910901	6.929179	13.51367
H	10.56956	6.865336	14.14723
H	9.283427	5.929845	14.94284
C	11.04444	4.18864	13.80936
H	10.63682	3.794237	14.75274
H	11.92776	4.803156	14.04657
H	11.38181	3.334109	13.20531
C	7.776863	4.483375	10.08913
H	8.709641	5.025372	9.886586
H	7.014557	4.859683	9.387692
H	7.934753	3.419739	9.859137
C	5.972414	3.886742	11.7326
H	6.138787	2.802258	11.62922
H	5.234235	4.180607	10.96922
H	5.525537	4.076332	12.72042
C	10.62895	5.552904	11.73766
H	10.85542	4.716456	11.05889
H	11.57724	6.073287	11.94861
H	9.97206	6.262046	11.21508

Table S26. XYZ coordinate of **4** computed by DFT/B3LYP

Fe	31.79534	-1.27305	9.579078
P	33.23654	0.116652	8.581079
P	30.09493	-2.12508	10.7547
O	32.33681	-3.56568	7.998504
C	31.64169	0.257277	10.93356
N	32.08765	-2.59504	8.638443
C	27.23391	-2.50158	10.54814
C	32.40842	1.448076	10.80529
C	32.16383	2.573278	11.60421
C	30.28113	-3.88	11.4511
C	30.42969	1.368309	12.77233
C	29.93976	-1.0508	12.25619
C	29.35194	-4.1723	12.64099
C	33.38381	1.934704	6.338018
C	28.24475	-0.37154	9.699697
C	30.0587	-4.92925	10.34963
C	31.74657	-3.96314	11.92384
C	30.67402	0.241506	11.97477
C	28.44658	-1.8935	9.832839
C	28.57998	-2.48118	8.416645
C	34.96453	-0.54799	8.161551
C	31.16333	2.5403	12.57808
C	32.43418	1.003248	7.101585
C	36.02356	0.555852	8.003889
C	33.54921	1.464496	9.812319
C	34.92372	-1.41164	6.890187
C	31.84218	-0.0532	6.152241
C	31.27096	1.833065	7.678282
C	35.34651	-1.44425	9.356663
H	37.00254	0.08831	7.801103
H	35.80315	1.23436	7.170528
H	36.13426	1.159061	8.916857
H	36.3694	-1.83146	9.209875
H	35.33082	-0.89356	10.31034
H	34.66104	-2.29698	9.45302
H	35.89397	-1.92361	6.772293
H	34.14424	-2.18431	6.939491
H	34.76352	-0.80621	5.986307
H	32.44412	-3.84383	11.08364
H	31.98711	-3.18939	12.66966
H	31.92429	-4.94689	12.39115

H	29.51508	-3.47784	13.47811
H	28.29015	-4.13305	12.36695
H	29.55897	-5.1892	13.01641
H	30.33879	-5.92323	10.73824
H	29.00492	-4.98633	10.04083
H	30.6755	-4.73376	9.461598
H	30.43807	-1.57668	13.08702
H	28.89402	-0.90211	12.56984
H	34.48775	1.214711	10.33428
H	33.70829	2.448779	9.343387
H	32.76071	3.480651	11.46793
H	30.96492	3.422118	13.19344
H	29.66393	1.329046	13.55354
H	28.73836	-3.56735	8.421844
H	27.65589	-2.27846	7.848706
H	29.42425	-2.02367	7.88154
H	29.11277	0.107264	9.225634
H	27.35987	-0.17969	9.069826
H	28.08197	0.121733	10.66841
H	27.13721	-2.13968	11.58358
H	26.31264	-2.2143	10.01244
H	27.27125	-3.59988	10.56729
H	32.61198	-0.68762	5.693958
H	31.14211	-0.71089	6.687192
H	31.2932	0.451422	5.338792
H	34.16928	1.381954	5.80351
H	32.81159	2.501818	5.583519
H	33.86601	2.668418	7.002262
H	31.61318	2.648179	8.331359
H	30.70358	2.282249	6.845686
H	30.5835	1.207083	8.263545

Table S27. XYZ coordinate of **4** computed by DFT/BP86

Fe	31.79039	-1.25659	9.585789
P	33.21776	0.10123	8.593902
P	30.11055	-2.10527	10.7376
O	32.65462	-3.63418	8.38552
C	31.65799	0.244622	10.9381
N	32.20686	-2.60371	8.800669
C	27.23321	-2.46977	10.52569
C	32.42068	1.449661	10.80406

C	32.16673	2.582136	11.6017
C	30.28751	-3.87848	11.41292
C	30.43179	1.366728	12.78208
C	29.94973	-1.06032	12.26465
C	29.34487	-4.16713	12.59685
C	33.33573	1.926724	6.336163
C	28.26834	-0.32914	9.707938
C	30.05459	-4.91242	10.29589
C	31.75182	-3.97511	11.89536
C	30.68261	0.231654	11.98684
C	28.45058	-1.85712	9.818031
C	28.59935	-2.43067	8.395309
C	34.95117	-0.56358	8.160432
C	31.16164	2.548083	12.58049
C	32.40088	0.981786	7.104988
C	35.99234	0.557108	7.973727
C	33.55448	1.468167	9.805235
C	34.897	-1.44199	6.896935
C	31.81874	-0.09395	6.167513
C	31.2292	1.788846	7.701689
C	35.35756	-1.43672	9.368155
H	36.98143	0.099308	7.755999
H	35.74541	1.230483	7.13309
H	36.11247	1.173696	8.886067
H	36.40098	-1.79313	9.226895
H	35.32058	-0.87357	10.32302
H	34.69972	-2.31892	9.472028
H	35.87485	-1.9539	6.767804
H	34.1186	-2.22507	6.967276
H	34.71818	-0.84268	5.982451
H	32.4625	-3.88947	11.05299
H	32.00394	-3.18355	12.63023
H	31.91063	-4.95806	12.38963
H	29.51987	-3.483	13.45037
H	28.27739	-4.10247	12.31792
H	29.53149	-5.19977	12.96303
H	30.32155	-5.92271	10.67416
H	28.99352	-4.95128	9.98005
H	30.6829	-4.71436	9.406964
H	30.45861	-1.60696	13.0876
H	28.89735	-0.91741	12.58883

H	34.50754	1.218164	10.31964
H	33.70864	2.456414	9.32284
H	32.76203	3.498891	11.45859
H	30.95615	3.438452	13.19508
H	29.66068	1.325715	13.56883
H	28.70442	-3.5316	8.390729
H	27.70206	-2.1722	7.79268
H	29.49547	-2.00493	7.900662
H	29.14429	0.142198	9.220349
H	27.36976	-0.11141	9.091934
H	28.13346	0.160406	10.69188
H	27.12751	-2.10823	11.5689
H	26.30734	-2.18102	9.982122
H	27.27123	-3.57634	10.5422
H	32.60362	-0.70029	5.678467
H	31.16259	-0.78526	6.7339
H	31.21795	0.392838	5.369253
H	34.13496	1.381929	5.796497
H	32.75049	2.487242	5.574887
H	33.81048	2.676406	7.00123
H	31.56353	2.601044	8.375803
H	30.64284	2.246752	6.876535
H	30.55478	1.131784	8.28517

Table S28. XYZ coordinate of **4** computed by DFT/TPSSh

Fe	31.79177	-1.2624	9.57046
P	33.21753	0.106946	8.57176
P	30.11963	-2.11223	10.7478
O	32.50771	-3.60983	8.216172
C	31.65247	0.245851	10.92025
N	32.15635	-2.59714	8.732947
C	27.24119	-2.43402	10.57973
C	32.36741	1.468012	10.76115
C	32.10615	2.58982	11.56209
C	30.26726	-3.89919	11.36245
C	30.46671	1.325014	12.80346
C	30.04442	-1.11076	12.30131
C	29.35913	-4.20235	12.56681
C	33.33739	1.891928	6.296369
C	28.27156	-0.26664	9.866959
C	29.97741	-4.89484	10.227

C	31.73985	-4.05187	11.79613
C	30.72432	0.20413	12.00199
C	28.45324	-1.79642	9.888994
C	28.5698	-2.28905	8.435367
C	34.96942	-0.52507	8.221923
C	31.14385	2.525386	12.57255
C	32.42534	0.913634	7.045857
C	36.00135	0.598335	8.023718
C	33.47897	1.519546	9.739768
C	34.979	-1.45511	6.997732
C	31.91895	-0.18957	6.099691
C	31.19696	1.666002	7.595128
C	35.34129	-1.34074	9.47703
H	37.00001	0.145932	7.897336
H	35.79568	1.203097	7.130664
H	36.05435	1.271578	8.891915
H	36.3705	-1.72491	9.371297
H	35.30113	-0.72684	10.391
H	34.65806	-2.19043	9.613031
H	35.96451	-1.94632	6.927863
H	34.21612	-2.24218	7.072577
H	34.8234	-0.89731	6.062232
H	32.42171	-3.92969	10.94423
H	32.02029	-3.31441	12.56492
H	31.8879	-5.05837	12.22399
H	29.56434	-3.53548	13.41741
H	28.2925	-4.12668	12.31901
H	29.55058	-5.23511	12.9054
H	30.22225	-5.91381	10.57235
H	28.91549	-4.89149	9.939614
H	30.58651	-4.68887	9.335924
H	30.62821	-1.66179	13.05876
H	29.02411	-0.99995	12.704
H	34.44526	1.354527	10.24614
H	33.55763	2.491198	9.22463
H	32.66121	3.518578	11.39837
H	30.93303	3.403386	13.18852
H	29.73365	1.260686	13.61329
H	28.68599	-3.37965	8.370811
H	27.6602	-2.00948	7.87649
H	29.44293	-1.82957	7.947766

H	29.14231	0.234041	9.419384
H	27.38054	-0.0207	9.264549
H	28.12771	0.153233	10.87309
H	27.16061	-2.12959	11.63508
H	26.31991	-2.10396	10.0692
H	27.26718	-3.5323	10.5341
H	32.73823	-0.75186	5.632319
H	31.28549	-0.90319	6.64767
H	31.31981	0.268186	5.293998
H	34.16422	1.376234	5.785968
H	32.75144	2.419571	5.523933
H	33.7633	2.654984	6.966791
H	31.47212	2.503855	8.252536
H	30.60904	2.067763	6.752606
H	30.55662	0.984461	8.175434