Nitric oxide (NO) reactivity studies on mononuclear Iron(II) complexes supported by a tetradentate Schiff base Ligand

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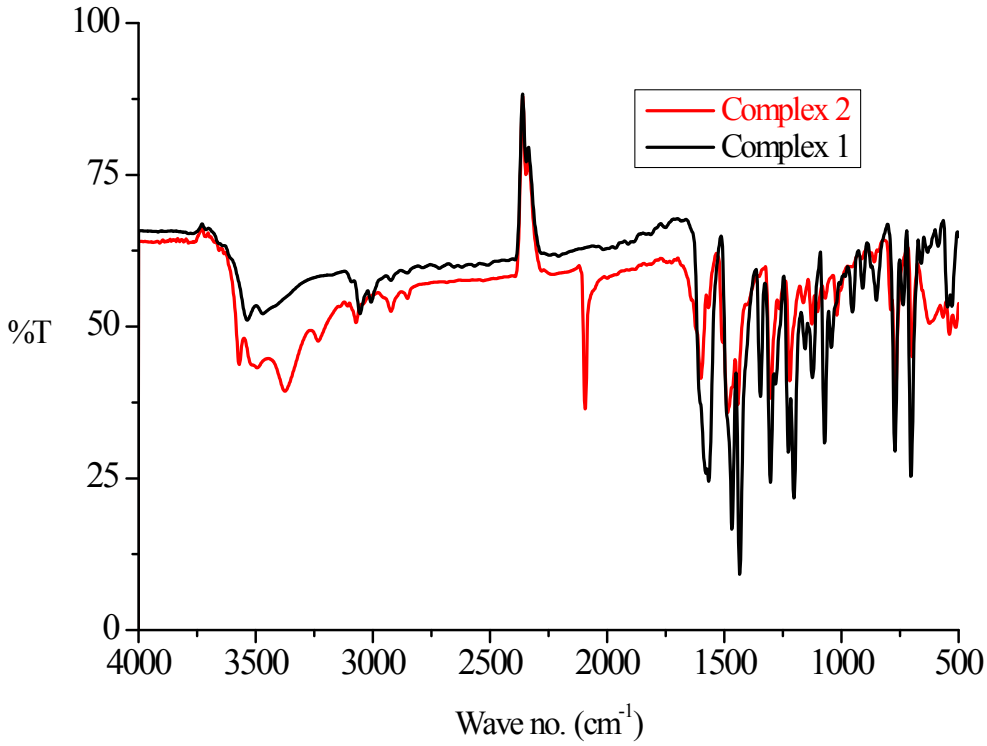
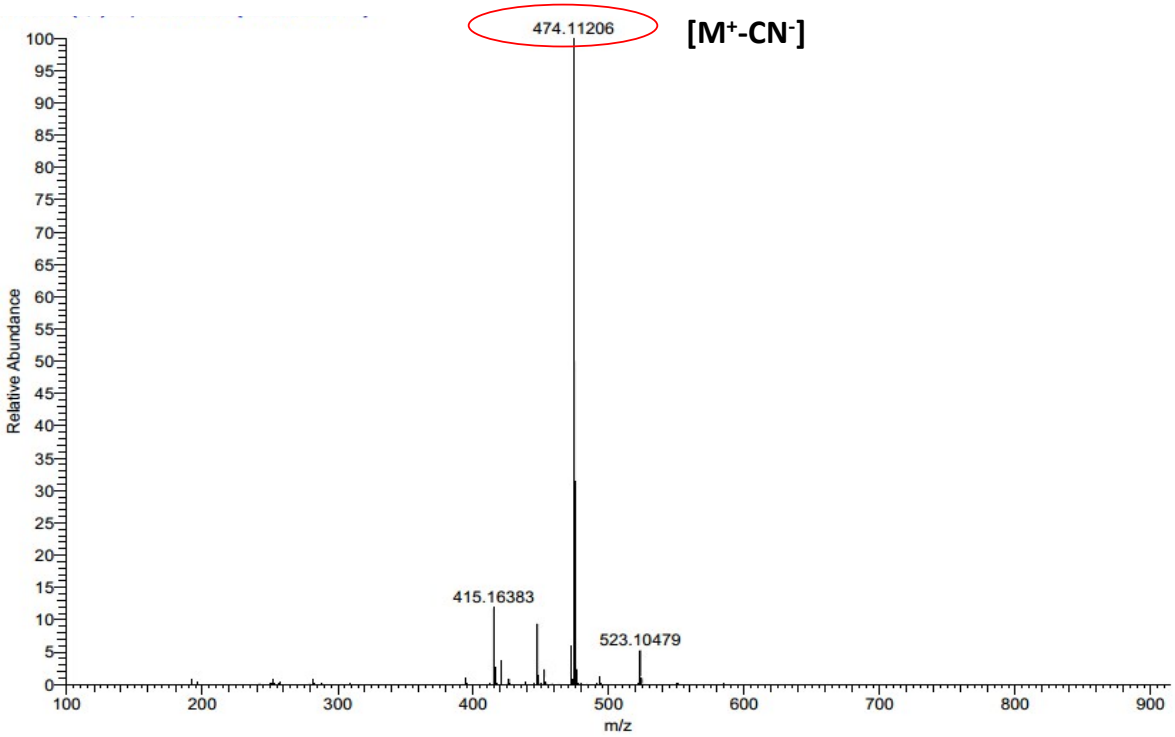
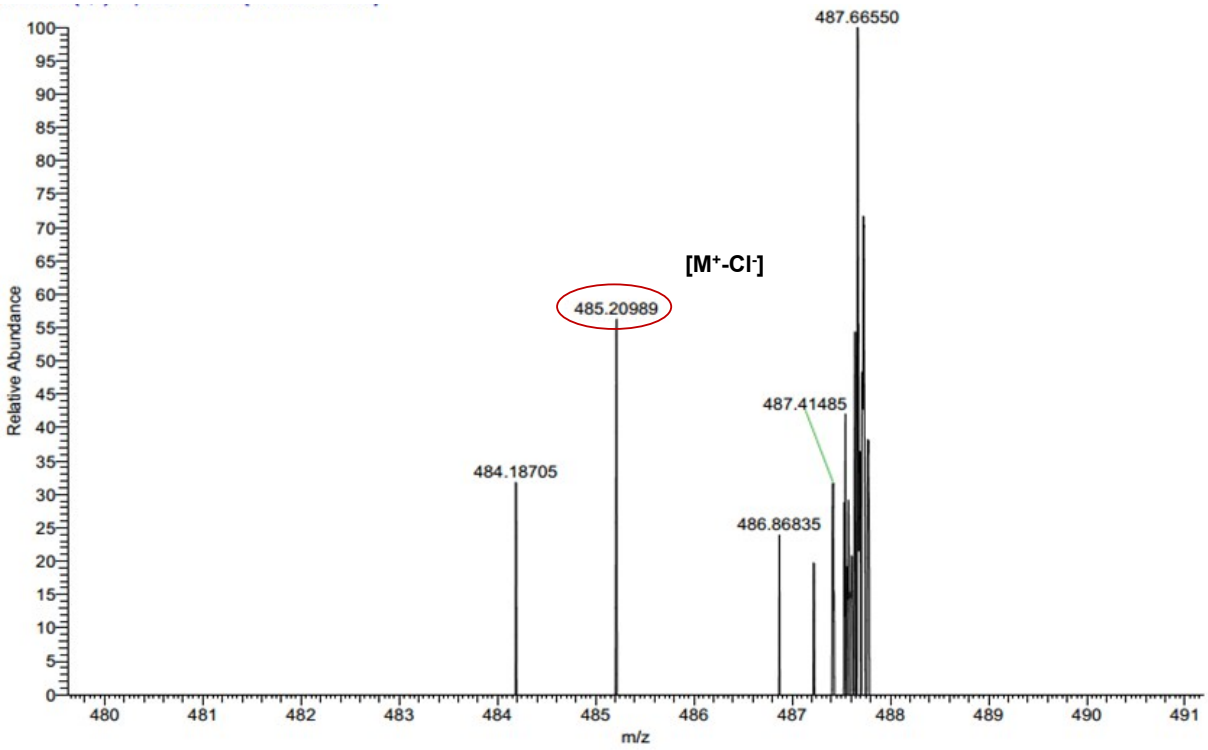


Fig. S1. IR Spectra of the complexes **1** and **2**



(A)



(B)

Fig.S2.ESI-MS spectra of complexes (A) **1** and (B)**2.**

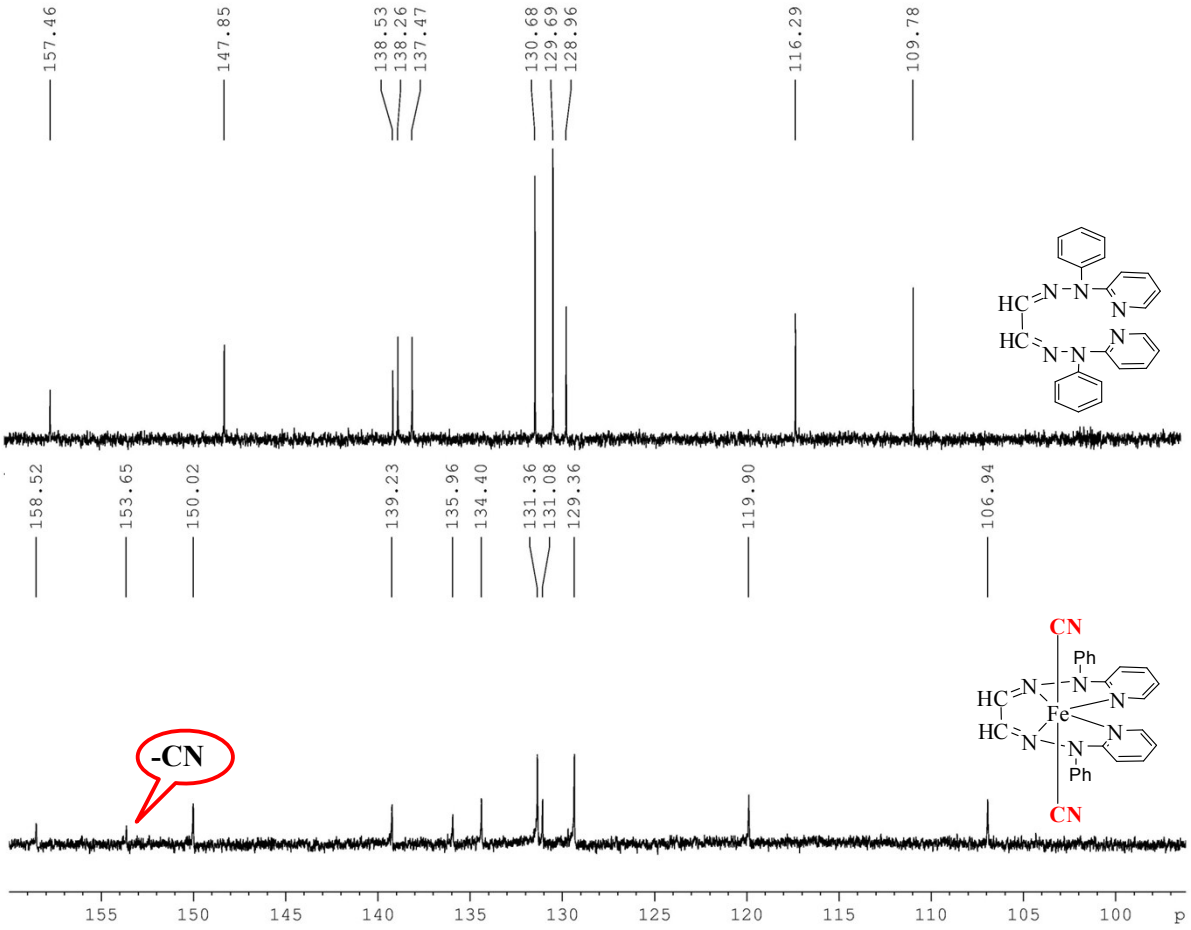
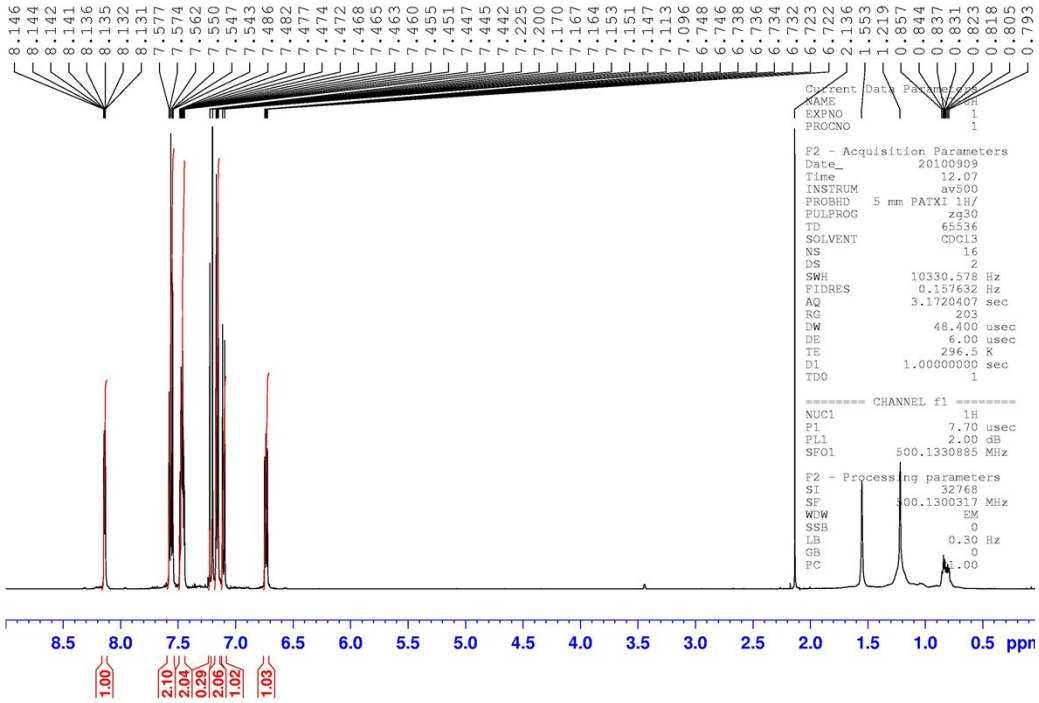
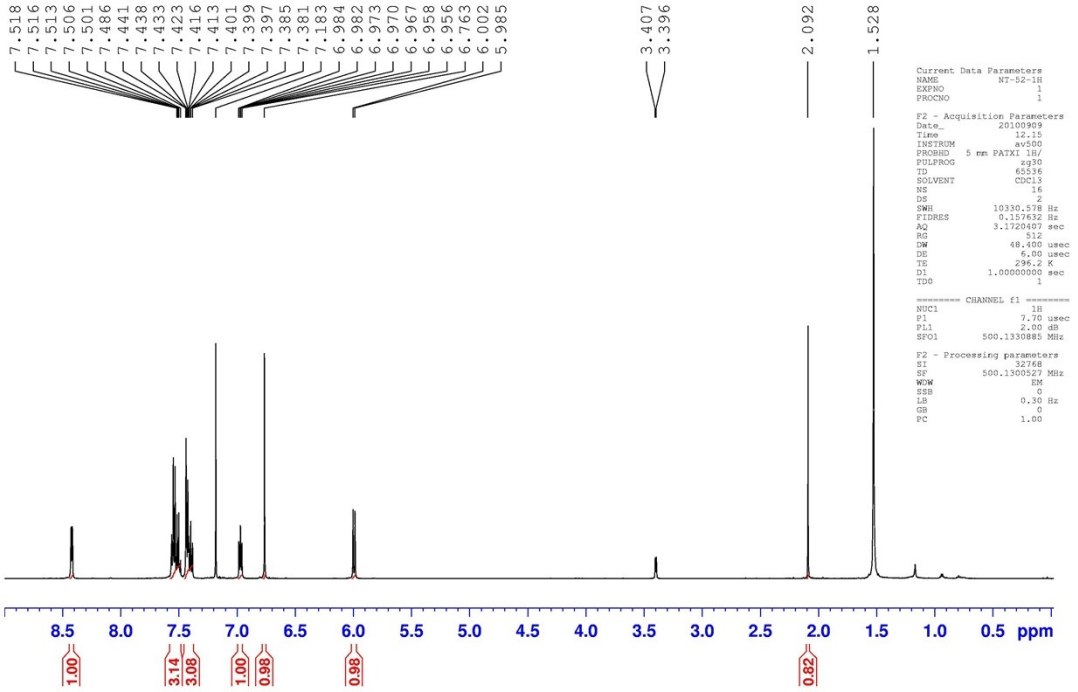


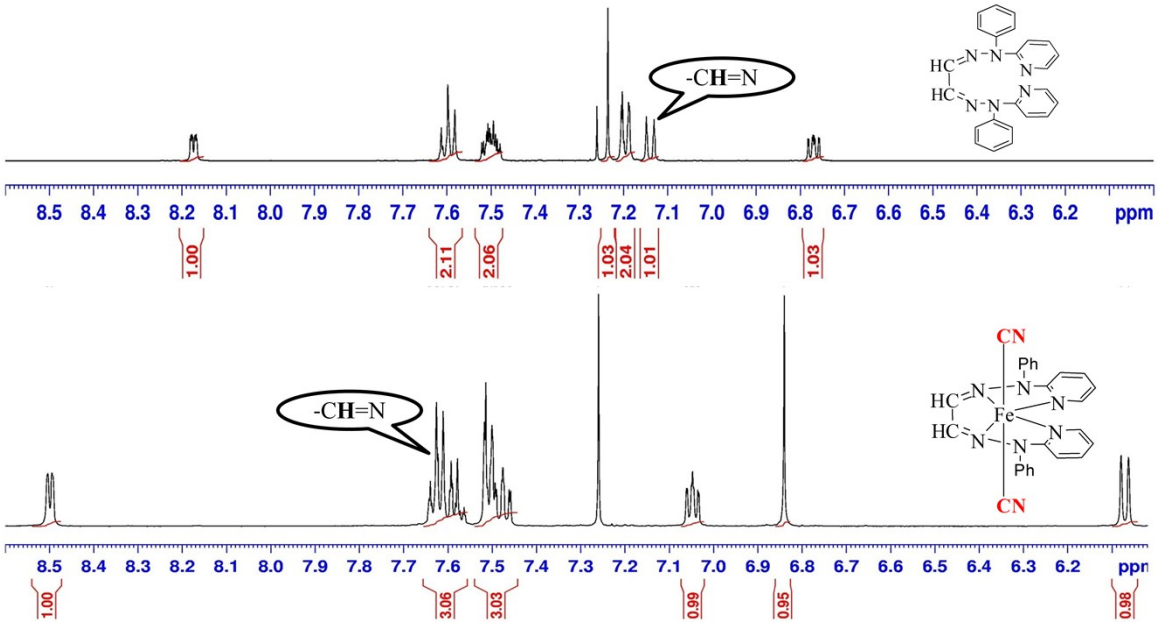
Fig. 3. ^{13}C NMR spectra of **Gimpy** and complex **2.**



(a)



(b)



(c)

Fig.S4. ^{1}H NMR spectra of (a) ligand (**Gimpy**), (b) complex **2** and (c) expanded ^{1}H NMR spectra of ligand and complex **2**.

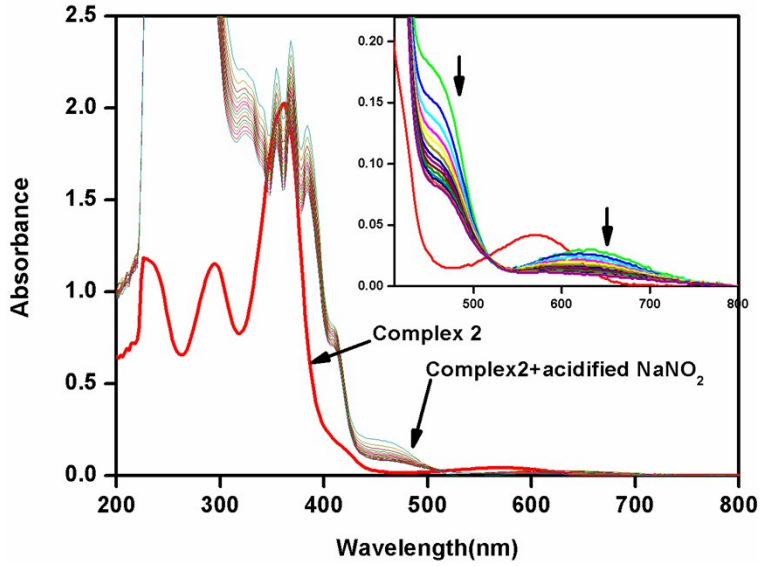


Fig. S5. *In-situ* UV-Visible spectral changes of complex **2** in presence of acidified $NaNO_2$

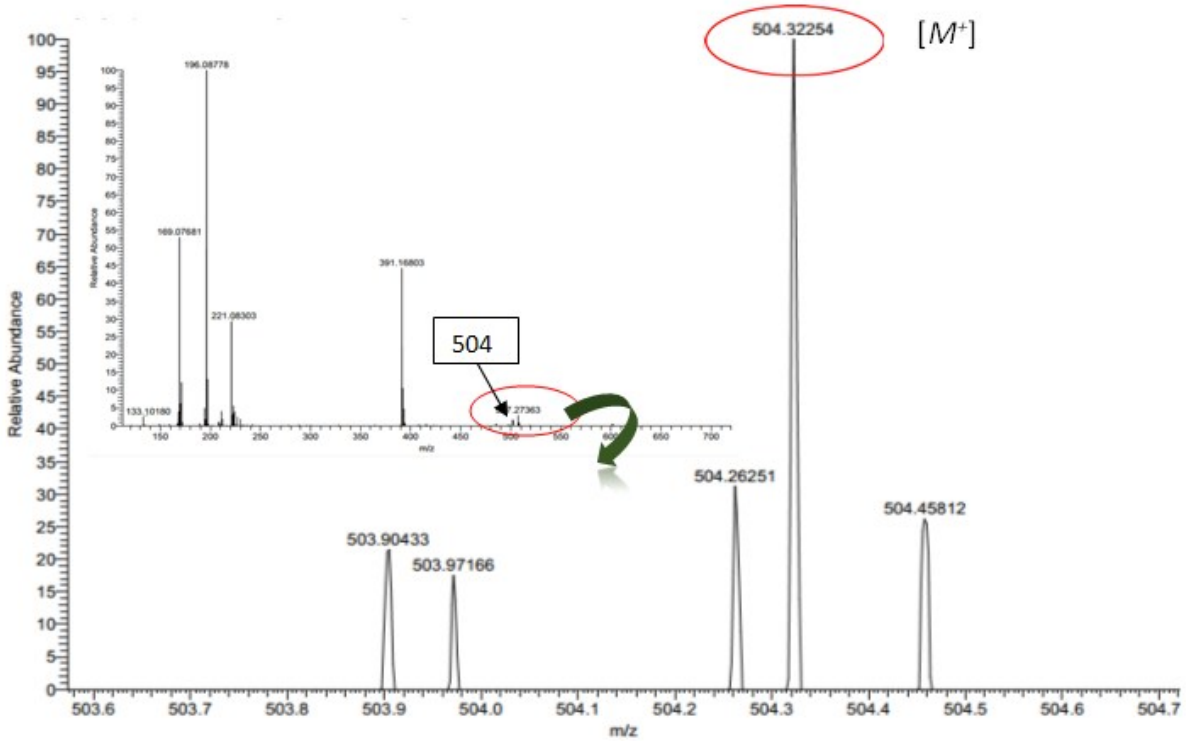
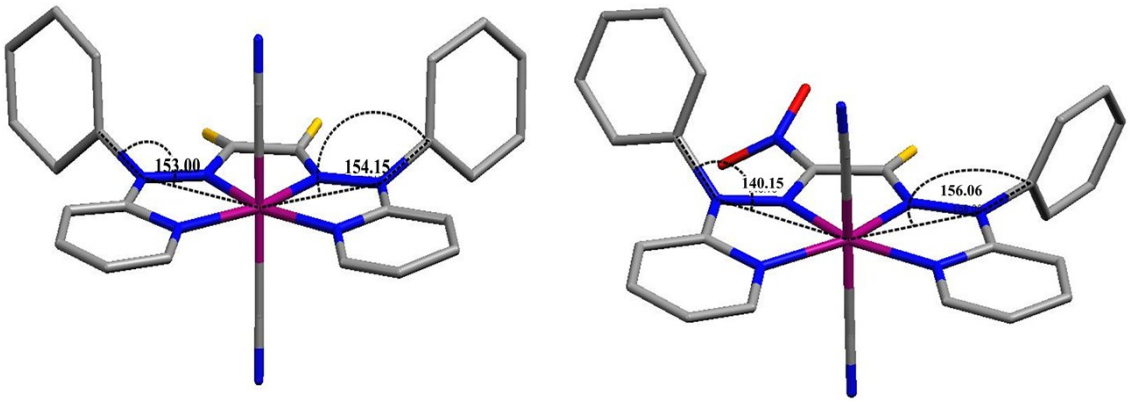


Fig. S6. *In-situ* ESI-MS spectra of iron-nitrosyl complex $[Fe(\mathbf{Gimpy})(NO)(CN)]^{2+}$, **4**. 504



(a) **(b)**

Fig. S7. Comparison of orientation of phenyl rings in **(a)**[Fe(**Gimpy**)$(CN)_2$]·$3H_2O$ and **(b)**[Fe(**Gimpy**-NO_2)$(CN)_2$]·CH_2Cl_2

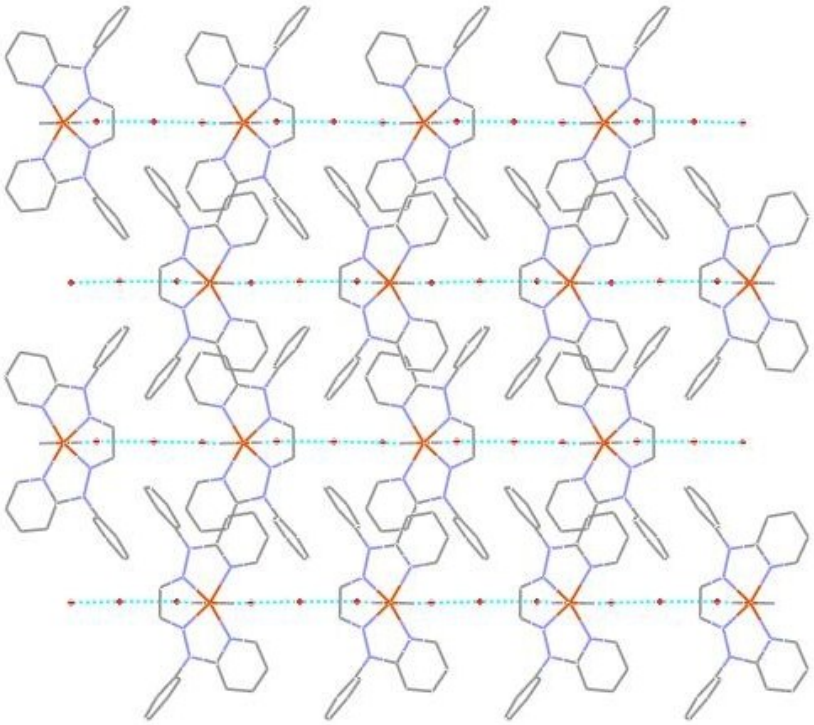
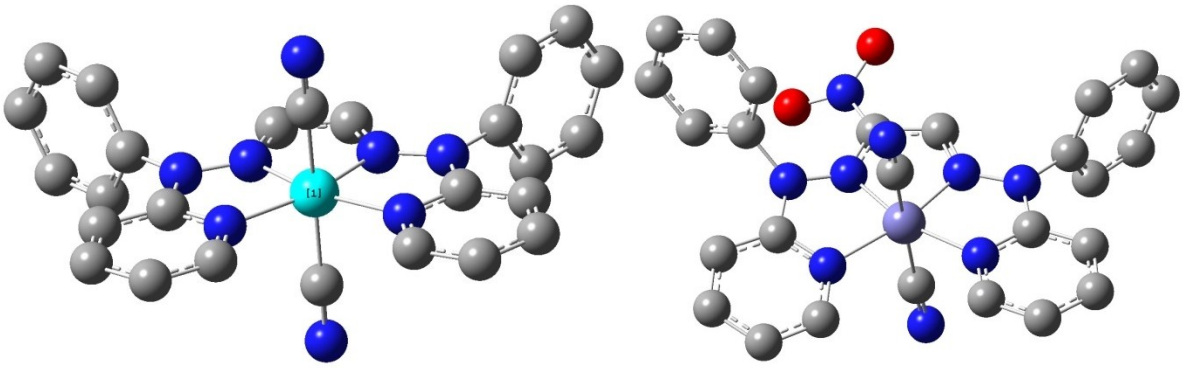
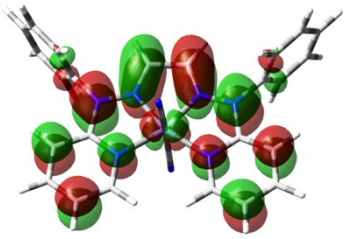


Fig. S8. Packing diagram ofcomplex**2**along c axis

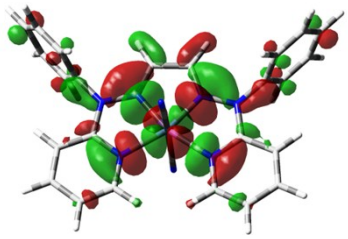


Complex 2 **Complex 3**

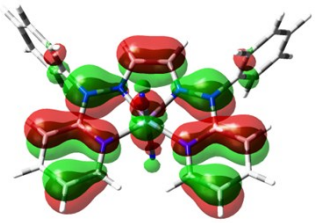
Fig. S9. Geometry optimized structure for complexes **2** and **3**



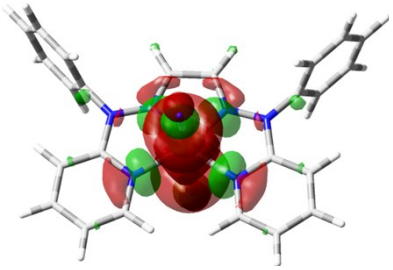
HOMO



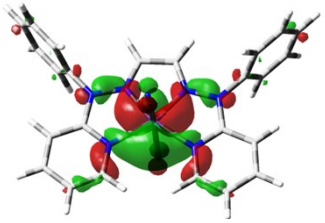
LUMO



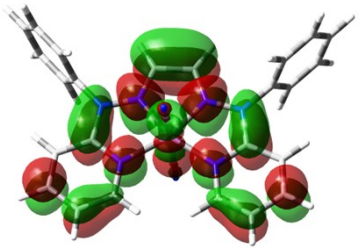
HOMO-1



LUMO+1

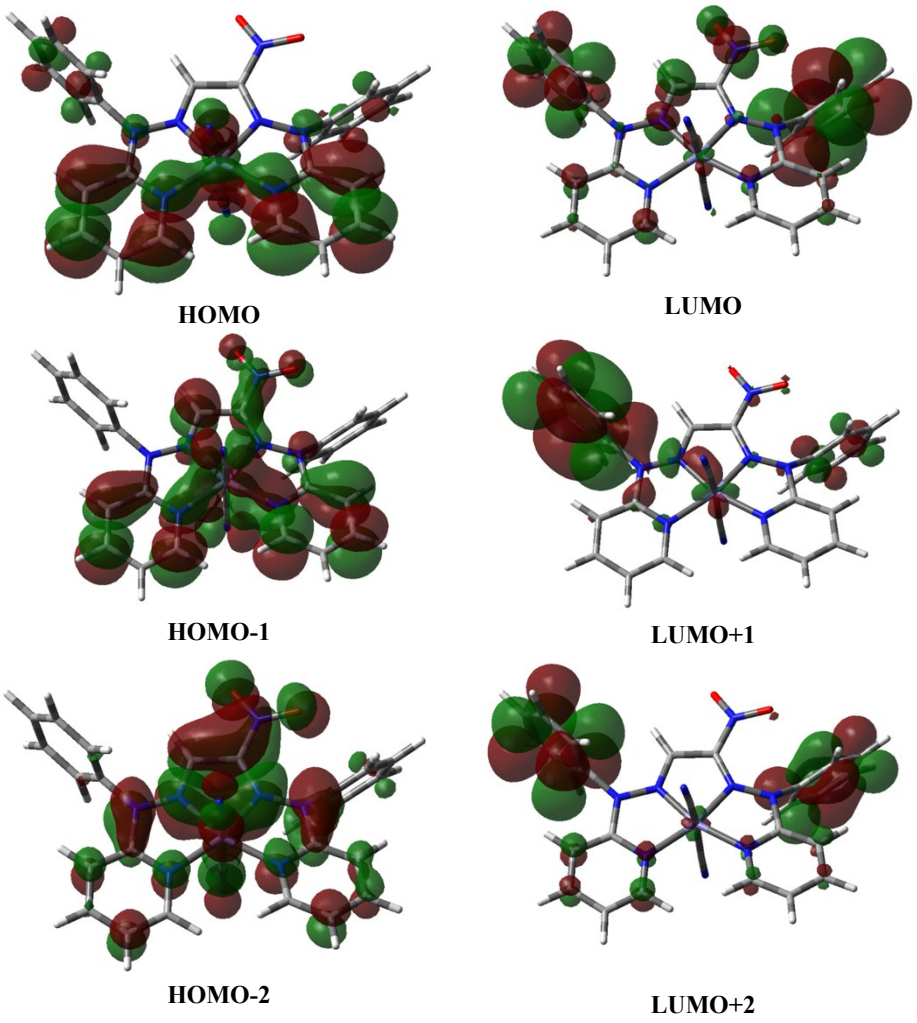


HOMO-2



LUMO+2

(a)



(b)

Fig. S10. Frontier orbitals diagram for the HOMO, HOMO-1, HOMO-2, and LUMO, LUMO+1, LUMO+2, of **(a)** complex **2(b)** complex **3**.

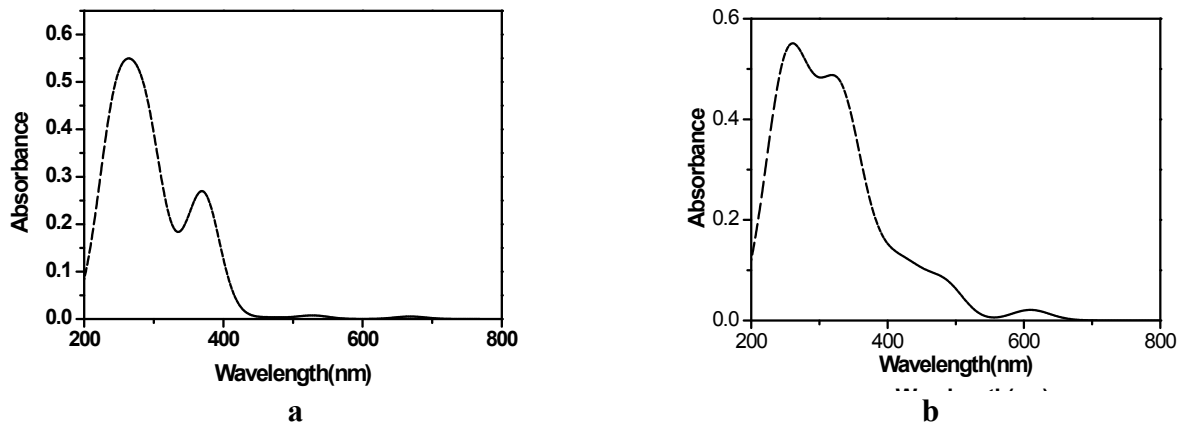


Fig. S11. UV-vis spectra of complexes a)**2** and b) **3** obtained from TD-DFT calculation

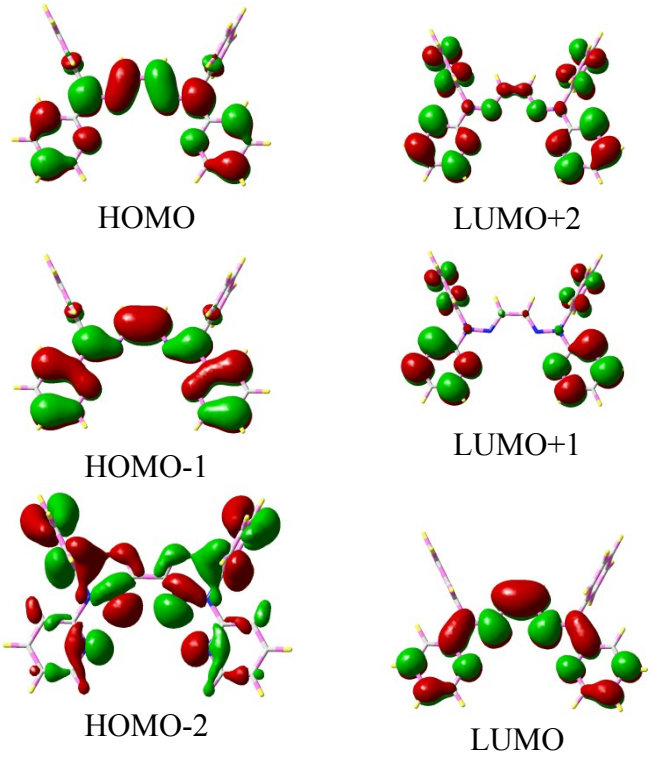


Fig. S12. Frontier orbitals diagram for ligand, **Gimpy**.

Table S1. Crystallographic parameters of complex **2** and **3**

Complex	**Complex 2**	**Complex 3**
Colour	purple	green
Formula weight [g mol^{-1}]	554.40	661.31
Temperature [K]	293(2)	293(2)
λ [Å] (Mo-Kα)	0.71073	0.71073
Crystal system	orthorhombic	Triclinic
Space group	*Pn21a*	*P -1*
a [Å]	16.979(5)	9.885(4)
b [Å]	15.130(5)	12.712(5)
c [Å]	10.163(5)	13.207(5)
α [º]	90.000(5)	94.82(2)
β [º]	90.000(5)	111.057(19)
γ [º]	90.000(5)	101.56(2)
V [Å^3]	2610.8(17)	1495.1(11)
Crystal size[mm]	0.28 x 0.19 x 0.10	0.29 x 0.19 x 0.11
Z	4	2
ρcalc [gcm^{-3}]	1.373	1.469
F(000)	1152.0	678
θ range for data Collection	2.34-28.33	1.66-22.88
Index ranges	-22<h<22, -19<k<19, -13<l<13	-10<h<10, -13<k<13, -14<l<14
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data/restraints/parameters	6180/1/375	3809/0/384
GOF on F^2	0.813	1.085
R_1[b][I>2σ(I)]	0.0367	0.0842
R_1[all data]	0.0582	0.1754
wR_2[c][I> 2σ(I)]	0.0964	0.2154
wR_2 [all data]	0.1160	0.2650

[a]GOF = $[\Sigma[w(F_o^2-F_c^2)^2] /M-N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, [c] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$

Table S2. Electrochemical data for Fe(III)/Fe(II) redox couple at 298 K[a]vsAg/AgCl

Complex	Fe(III)/Fe(II)		
	E_{pa}/V	E_{pc}/V	$E_{1/2}$[b], V (ΔE_p[c], mV)
1	-0.082	-0.435	-
2	0.860	0.703	0.782 (157)
3	1.210	1.120	1.165 (90)

[a]measured in dichloromethane for **1**, **2** and **3** with 0.1 M tetrabutylammonium perchlorate (TBAP).[b]Data from cyclic voltammetric measurements; $E_{1/2}$ is calculated as average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials $E_{1/2} = 1/2(E_{pa}+E_{pc})$; and [c]$\Delta E_p = E_{pa}-E_{pc}$ at scan rate 0.1 V/s.

Table S3: Cartesian coordinates for complex [Fe(Gimpy)$(CN)_2$]

Atom types=4

Charge=26.0 Atoms=1

Fe 0.000099000 0.732841000 0.000149000

Charge=7.0 Atoms=8

N 1.728058000 1.817882000 0.009819000

N 2.575749000 -0.372278000 0.005649000

N 1.229650000 -0.688409000 0.004019000

N -1.229400000 -0.688460000 -0.003171000

N -2.575501000 -0.372380000 -0.005201000

N -1.727912000 1.817820000 -0.010061000

N 0.015529000 0.974061000 -3.143391000

N -0.019011000 0.977331000 3.143389000

Charge=6.0 Atoms=26

C 0.010789000 0.879341000 -1.954611000

C -0.011101000 0.880631000 1.954789000

C 1.909508000 3.158572000 0.016469000

C 3.176358000 3.755702000 0.021079000

C 4.308628000 2.917163000 0.018999000

C 4.140749000 1.527033000 0.013429000

C 2.828919000 1.007752000 0.009389000

C -1.909432000 3.158490000 -0.017131000

C -3.176312000 3.755569000 -0.022141000

C -4.308542000 2.916979000 -0.019991000

C -4.140591000 1.526849000 -0.013931000

C -2.828741000 1.007630000 -0.009511000

C -0.721850000 -1.913159000 -0.000801000

C 0.722160000 -1.913139000 0.002089000

C 5.075341000 -2.892997000 1.209839000

C 4.088370000 -1.890017000 1.220919000

C 3.600850000 -1.386938000 -0.001261000

C 4.080340000 -1.880477000 -1.230561000

C 5.067271000 -2.883507000 -1.233721000

C -4.087580000 -1.890401000 -1.220761000

C -3.600560000 -1.387081000 0.001519000

C -4.080510000 -1.880411000 1.230719000

C -5.067399000 -2.883481000 1.233689000

C -5.564499000 -3.388782000 0.015369000

C -5.074529000 -2.893401000 -1.209871000

C 5.564861000 -3.388577000 -0.015511000

Charge=1.0 Atoms=20

H 1.011128000 3.761691000 0.018849000

H 3.267887000 4.836192000 0.026219000

H	**5.309448000**	**3.339903000**	**0.022159000**
H	**4.992549000**	**0.857533000**	**0.012469000**
H	**-1.011092000**	**3.761670000**	**-0.019501000**
H	**-3.267893000**	**4.836049000**	**-0.027611000**
H	**-5.309382000**	**3.339648000**	**-0.023441000**
H	**-4.992361000**	**0.857309000**	**-0.012861000**
H	**5.458511000**	**-3.283857000**	**2.148719000**
H	**3.696170000**	**-1.496707000**	**2.155369000**
H	**3.681960000**	**-1.479857000**	**-2.159271000**
H	**5.444231000**	**-3.267027000**	**-2.178121000**
H	**-3.695020000**	**-1.497251000**	**-2.155121000**
H	**-3.682500000**	**-1.479601000**	**2.159519000**
H	**-5.444709000**	**-3.266852000**	**2.178009000**
H	**-6.327329000**	**-4.163382000**	**0.020729000**
H	**-5.457319000**	**-3.284452000**	**-2.148831000**
H	**6.327721000**	**-4.163146000**	**-0.021021000**
H	**-1.316989000**	**-2.818400000**	**-0.000631000**
H	**1.317331000**	**-2.818349000**	**0.002119000**

Table S4: Cartesian coordinates for complex [Fe(Gimpy-NO_2)$(CN)_2$]

Atom types=5

Charge=26.0 Atoms=1

Fe	**-0.109501000**	**0.910856000**	**-0.119861000**

Charge=8.0 Atoms=2

O	**2.345968000**	**-2.852464000**	**-1.510872000**

O 0.641445000 -4.012520000 -0.560680000

Charge=7.0 Atoms=9

N 1.130481000 -0.456366000 -0.419574000

N 2.467333000 -0.112732000 -0.407177000

N -1.335973000 -0.513058000 -0.044317000

N -2.662003000 -0.207827000 0.175303000

N -1.785594000 1.960471000 0.377823000

N 1.243588000 -2.911311000 -0.854975000

N 0.593110000 0.857848000 2.948424000

N -0.938494000 1.522902000 -3.091251000

N 1.520544000 2.050879000 -0.403349000

Charge=6.0 Atoms=26

C 1.618133000 3.394937000 -0.538458000

C 2.848793000 4.046938000 -0.674143000

C 4.022866000 3.267704000 -0.677479000

C 3.929896000 1.873781000 -0.576536000

C 2.652099000 1.295228000 -0.455728000

C 0.584361000 -1.682567000 -0.488510000

C -0.846869000 -1.713290000 -0.278622000

C -2.889227000 1.157100000 0.412807000

C -4.174721000 1.665397000 0.690232000

C -4.306786000 3.034059000 0.954566000

C -3.164894000 3.860349000 0.947633000

C -1.926248000 3.277713000 0.655314000

C 3.491568000 -0.955812000 0.204303000

C 3.390769000 -1.224477000 1.583590000

C 4.396721000 -1.991905000 2.199272000

C 5.489614000 -2.465583000 1.447664000

C 5.577360000 -2.180018000 0.070244000

C 4.571888000 -1.427231000 -0.559259000

C -3.702976000 -1.203113000 0.062739000

C -4.087638000 -1.940015000 1.199004000

C -5.085961000 -2.924005000 1.075171000

C -5.687081000 -3.165807000 -0.176289000

C -5.290929000 -2.426019000 -1.308867000

C -4.293252000 -1.440957000 -1.194311000

C 0.301810000 0.890932000 1.793343000

C -0.596908000 1.272476000 -1.977739000

Charge=1.0 Atoms=19

H 0.685095000 3.943325000 -0.551951000

H 2.882859000 5.126030000 -0.775431000

H 4.997374000 3.737693000 -0.772670000

H 4.813639000 1.249126000 -0.592802000

H -1.417678000 -2.629968000 -0.331012000

H -5.032423000 1.003747000 0.700953000

H -5.286790000 3.449207000 1.171836000

H -3.228784000 4.920610000 1.165081000

H -1.017274000 3.865277000 0.656963000

H 2.559776000 -0.825906000 2.161541000

H 4.329868000 -2.205116000 3.262657000

H	**6.264840000**	**-3.056028000**	**1.929654000**
H	**6.411829000**	**-2.558068000**	**-0.514087000**
H	**4.595918000**	**-1.241716000**	**-1.628357000**
H	**-3.609853000**	**-1.742378000**	**2.155131000**
H	**-5.389042000**	**-3.498264000**	**1.946394000**
H	**-6.455992000**	**-3.928511000**	**-0.269331000**
H	**-5.751651000**	**-2.616994000**	**-2.274200000**
H	**-3.969270000**	**-0.864992000**	**-2.057568000**

Table S5. Selected bond distances (Å) for complexes **2** and **3** with optimized DFT bond parameters in gas phase.

Bond distances (Å)			
Complex 2		**Complex 3**	
Fe1-N6	2.04042	Fe1-N1	2.00924
Fe1-N4	1.87929	Fe1-N3	1.86994
Fe1-N3	1.87930	Fe1-N4	1.88082
Fe1-N1	2.04041	Fe1-N6	2.03928

Table S6. Calculated TD-DFT oscillator strengths (*f*) and nature of transitions in the complexes **2** and **3**

	λ_{max}(nm)	**f**	**Transition**	**Significant contribution**	**Energy for transition**
Complex 2	370	0.2274	HOMO-1 → LUMO+1	19.6%	3.3466eV
Complex 3	609	0.0210	HOMO-1 → LUMO	70%	2.0350 eV
			HOMO-2 → LUMO	2.2%	
	484	0.0691	HOMO → LUMO	11%	2.5615 eV
			HOMO-3 → LUMO	42%	
	430	0.0721	HOMO → LUMO+1	63%	2.8806 eV
			HOMO-1 → LUMO	3.2%	
	326	0.1120	HOMO → LUMO+1	2.14%	3.7927 eV

Table S7. Percentage orbitals contribution of complex [Fe(Gimpy)$(CN)_2$]

Orbitals	Fe	CN-1	CN-2	Py-1	Py-2	Ph-1	Ph-2	Nimi-1	Nimi-2	Main bond type
LUMO+3	2	0	0	34	33	13	14	2	2	d(Fe)+ **π*(L)**
LUMO+2	0	0	0	0	0	48	46	2	2	**π*(L)**
LUMO+1	1	0	0	37	38	11	11	1	1	d(Fe)+ **π*(L)**
LUMO	9	3	3	14	14	0	0	28	28	d(Fe)+ **π*(L)**
HOMO	51	3	3	6	6	0	0	15	15	d(Fe)+ **π(L)**
HOMO-1	65	10	10	1	1	0	0	6	6	d(Fe)+ **π(L)**
HOMO-2	84	2	2	3	3	1	1	2	2	d(Fe)+ **π(L)**
HOMO-3	18	13	13	11	11	1	1	15	15	d(Fe)+ **π(L)**

Table S8. Percentage orbitals contribution of complex [Fe(Gimpy-NO_2)$(CN)_2$]

Orbitals	Fe	CN-1	CN-2	Py-1	Py-2	Ph-1	Ph-2	NO2	Nimi-1	Nimi-2	Main bond type
LUMO+3	2	0	0	61	21	8	0	1	2	5	d(Fe)+ π*(L)
LUMO+2	2	0	0	23	70	2	1	0	1	1	d(Fe)+ π*(L)
LUMO+1	3	1	1	17	6	0	1	31	7	32	d(Fe)+ π*(L)
LUMO	12	2	2	2	6	0	1	45	27	3	d(Fe)+ π*(L)
HOMO	42	3	2	9	4	1	1	4	13	20	d(Fe)+ π(L)
HOMO-1	65	11	10	1	3	0	1	1	8	5	d(Fe)+ π(L)
HOMO-2	51	15	10	7	5	1	1	0	6	6	d(Fe)+ π(L)
HOMO-3	52	6	5	10	6	1	5	0	6	9	d(Fe)+ π(L)

Table S9. Percentage contribution of ligand, **Gimpy**

Orbitals	Nimine1	Nimine2	Phenyl1	Phenyl2	Pyridine1	Pyridine2
LUMO+2	4	4	13	13	33	33
LUMO+1	1	1	7	7	43	43
LUMO	32	32	0	0	17	17
HOMO	34	34	1	1	15	15
HOMO-1	26	26	1	1	23	23
HOMO-2	17	17	25	25	8	8

“End”