Supporting Information
for

Introducing a New Azoaromatic Pincer Ligand. Isolation and Characterization of Redox Events in its Ferrous Complexes

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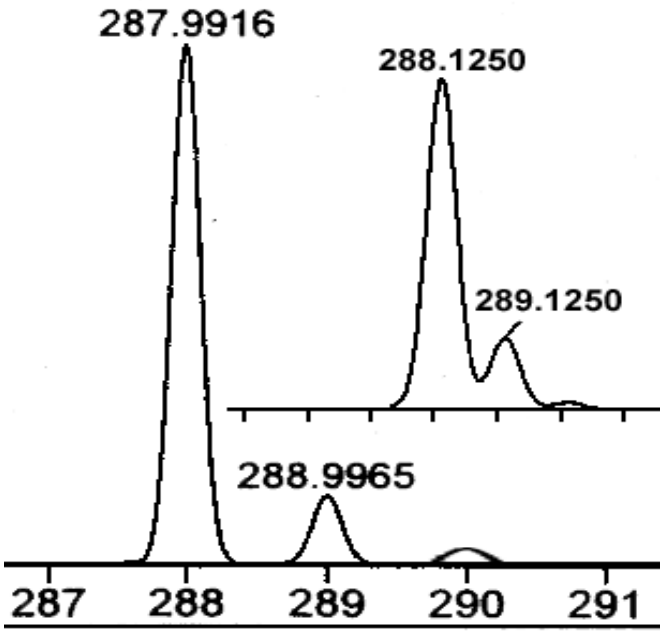

Figure S1: ESI mass spectrum of the ligand, **L**. Inset: simulated isotopic pattern.

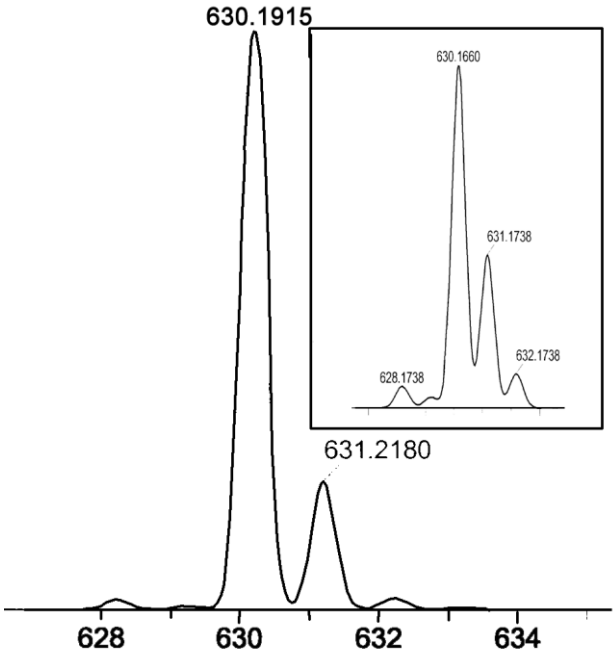

Figure S2: ESI mass spectrum of the compound, $[\mathbf{2}]^{+}$. Inset: simulated isotopic pattern.

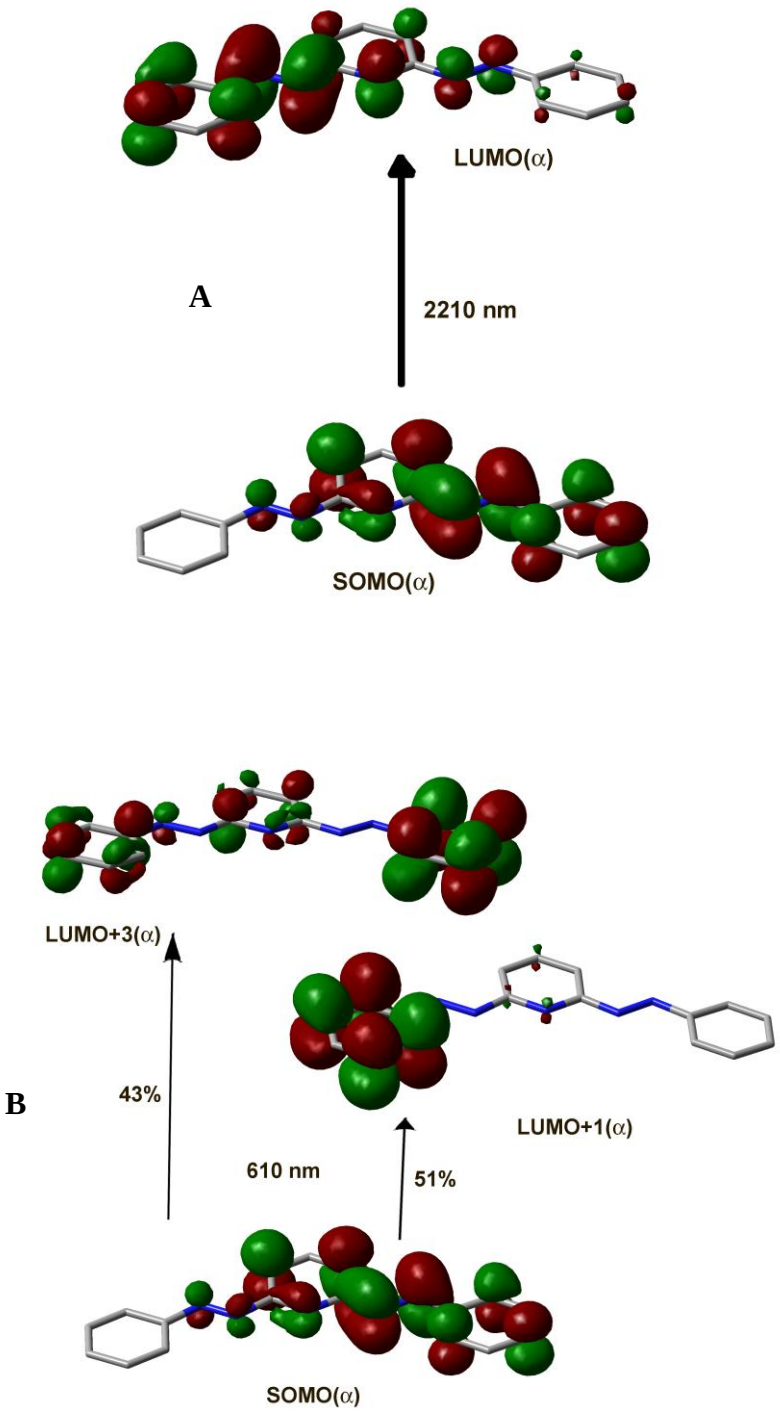

Figure S3: Orbitals involved in electronic transition of $[L^{\bullet}]^{-}$.

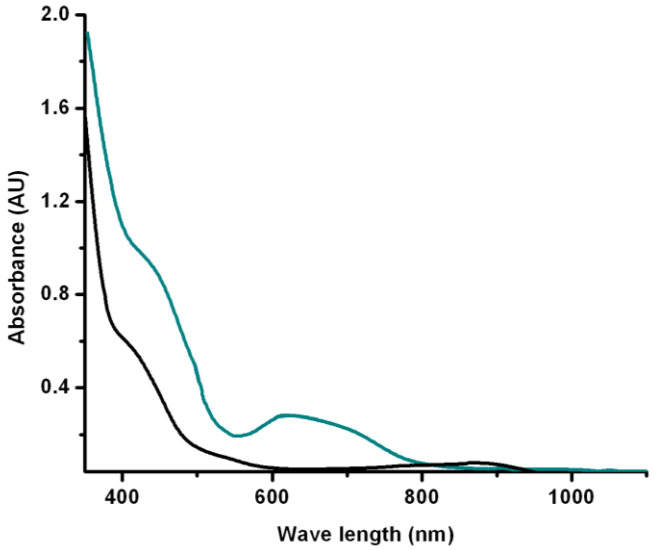

Figure S4: Electronic spectra of **1** and $\mathbf{1}^-$ in acetonitrile/TEAP (0.1 M) solution.

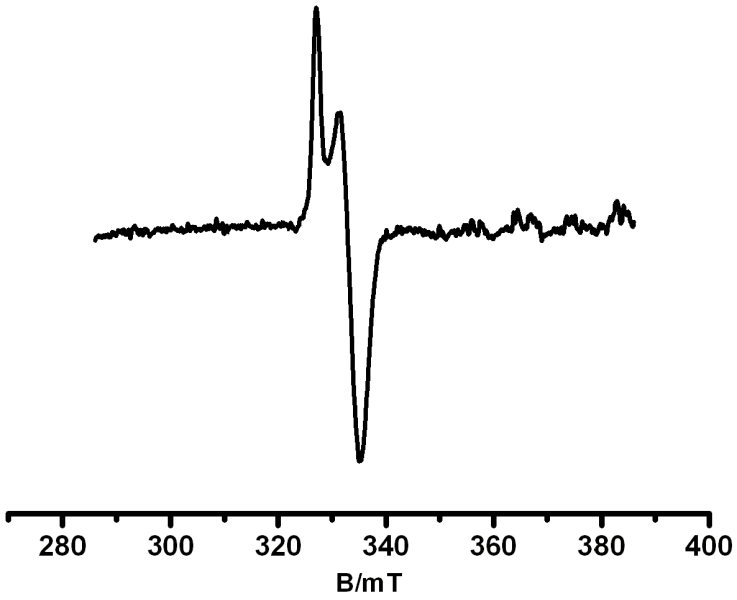

Figure S5: X-band EPR spectra of $\mathbf{1}^-$ in CH_3CN solution at 120 K. (conditions: microwave frequency 9.124 GHz; power 0.998 mW; modulation amplitude 0.1 mT).

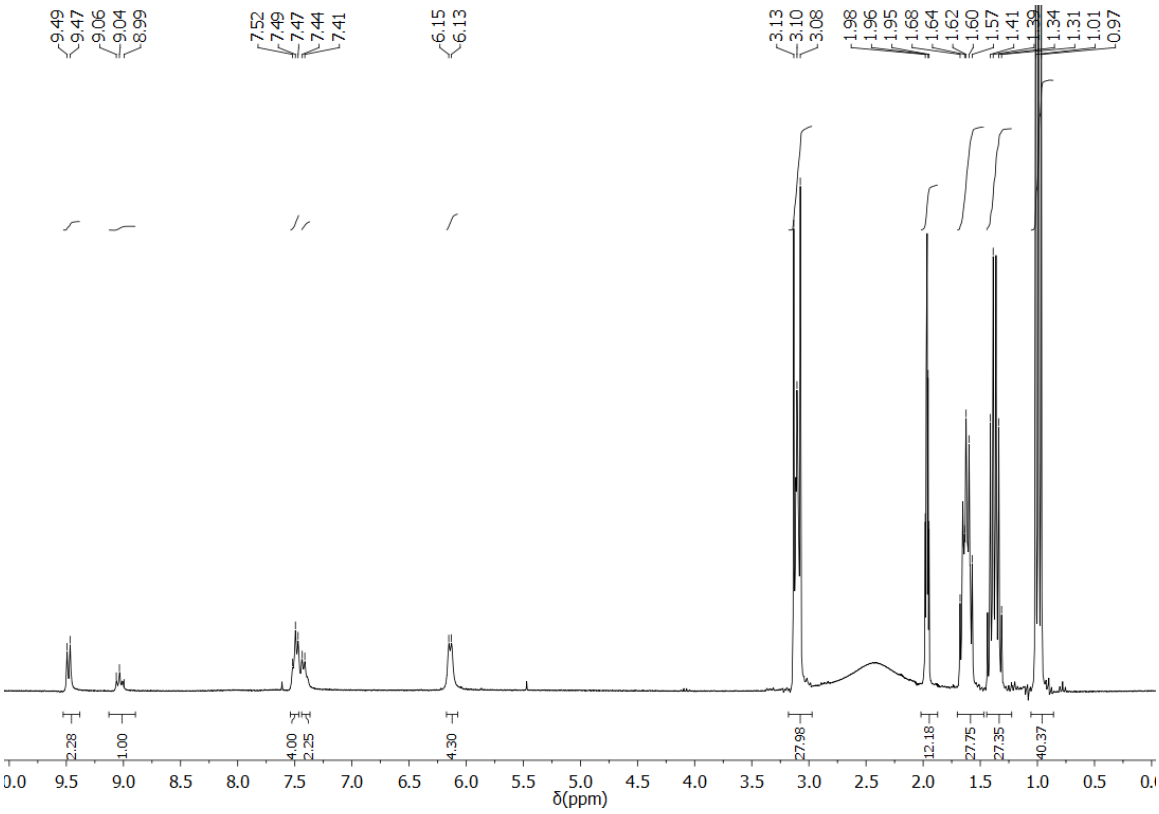

Figure S6: ^{1}H NMR spectrum in CD_3CN of the electrogenerated oxidized compound, $[\mathbf{2}]^{2+}$.

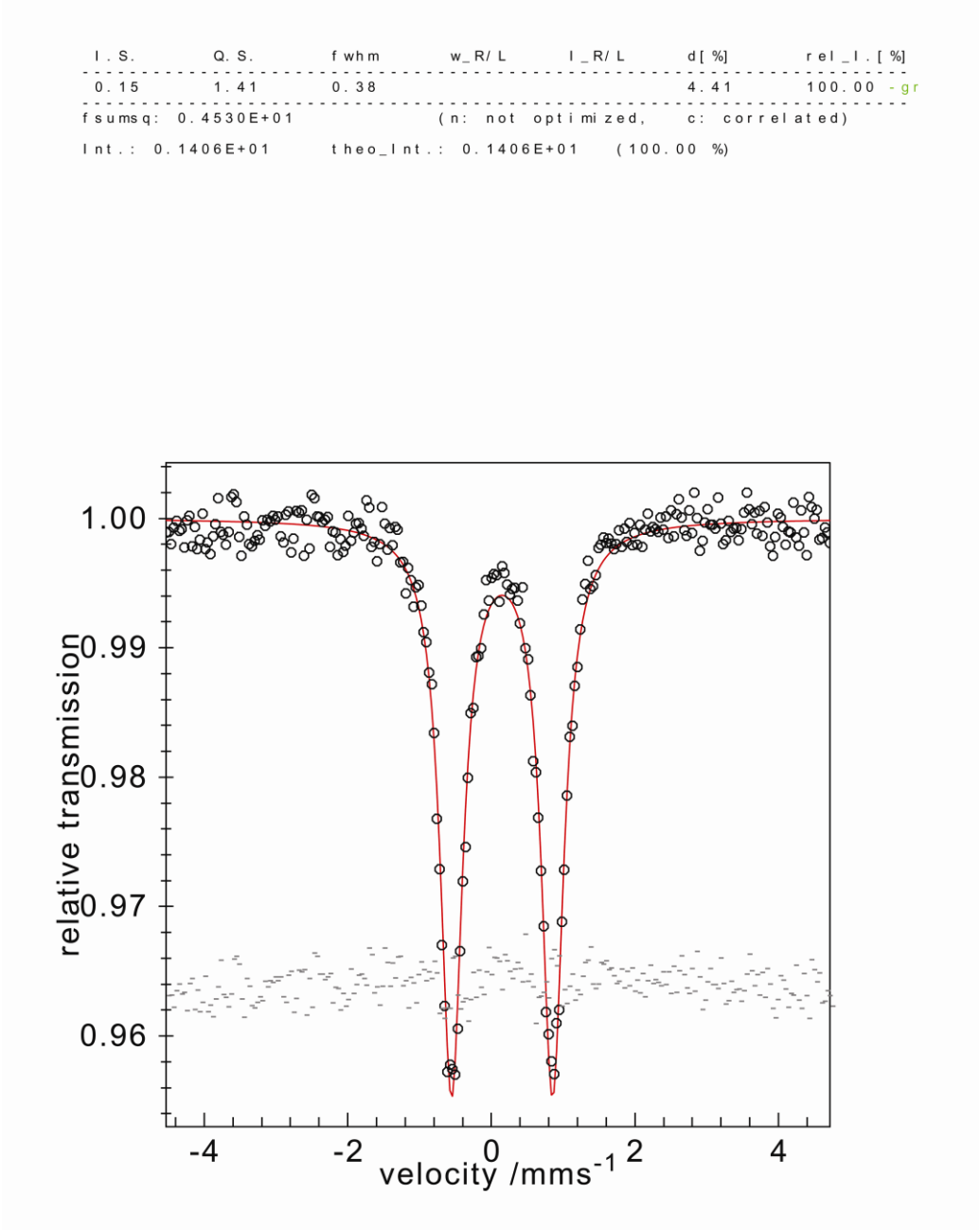

Figure S7: Mössbauer spectrum (solid material, 80 K) of the electrogenerated oxidized compound, $[\mathbf{2}]^{2+}$.

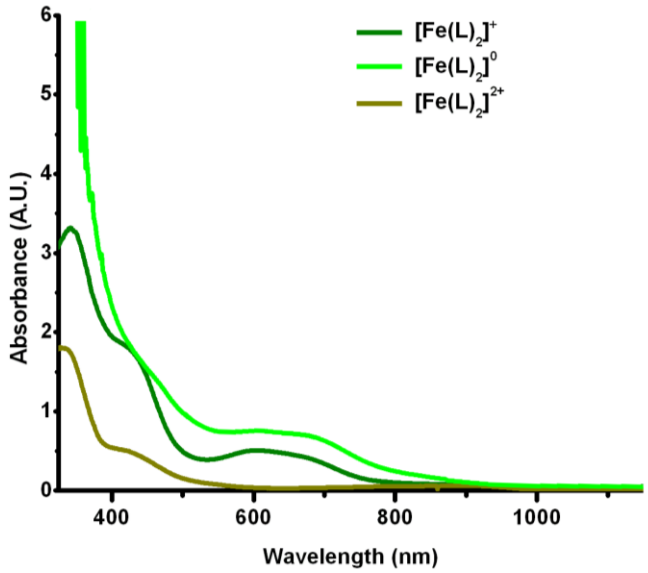

Figure S8: Electronic spectra of [**2**]$^{+}$, [**2**]$^{2+}$ and [**2**]^{0} in dichloromethane/TBAP (0.1 M) solution.

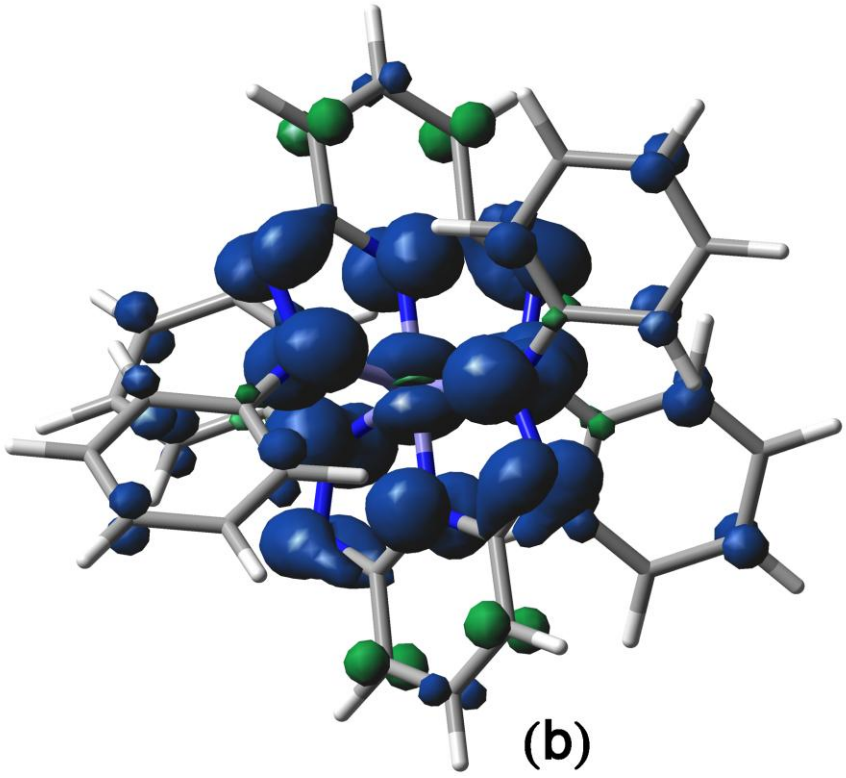

Figure S9: Spin density plot of the one electron reduced compound, $[\mathbf{2}]^{0}$.

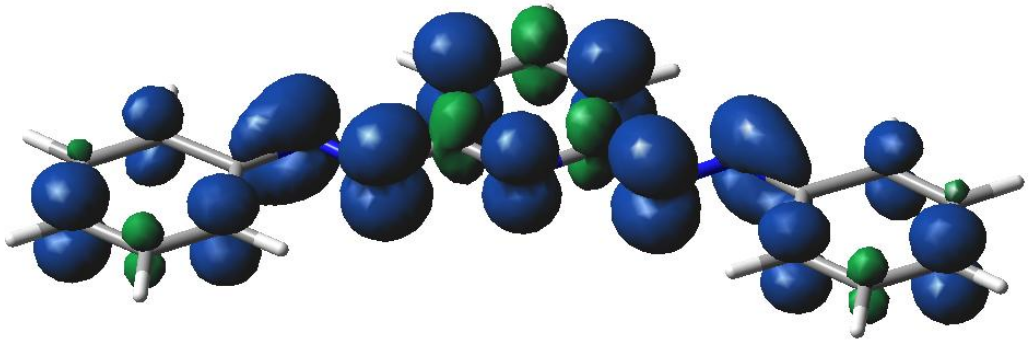

Figure S10: Spin density plot of the two electron reduced ligand, $(L^{\bullet\bullet})^{2-}$.

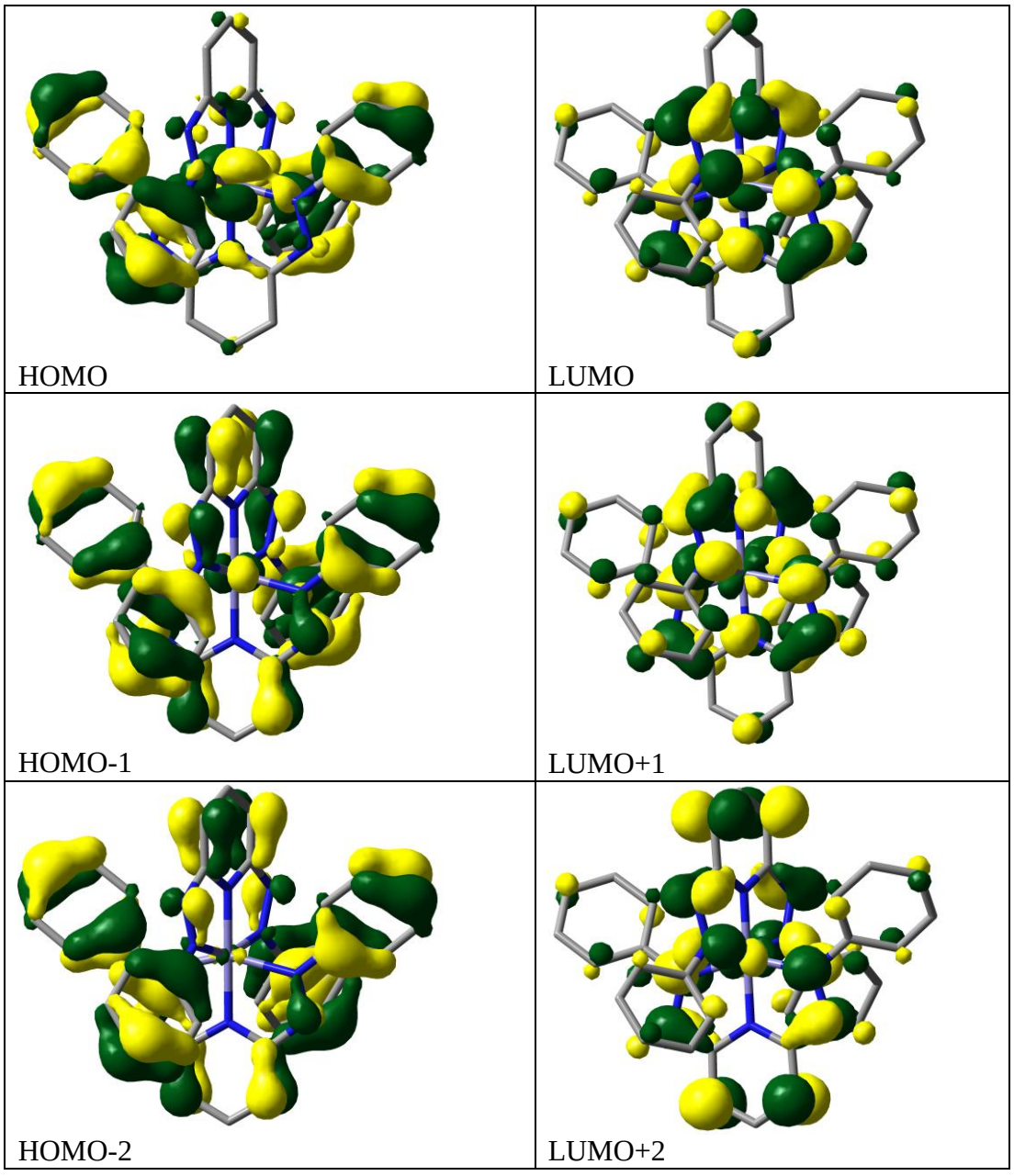

Figure S11: Frontier molecular orbitals of the oxidized complex, [**2**]$^{2+}$.

Table S1: Selected experimental and calculated bond distances for L, $[L^{\bullet}]^{1-}$ and $[L^{\bullet\bullet}]^{2-}$.

	Experimental (Å)	Calculated(Å)		
	L	L	$[L^{\bullet}]^{1-}$	$[L^{\bullet\bullet}]^{2-}$
N1 -N2	1.239(8)	1.259	1.292	1.337
N4 -N5	1.219(7)	1.259	1.292	1.337
N2 -C7	1.438(9)	1.427	1.395	1.385
N3 -C7	1.310(10)	1.336	1.342	1.355
N3 -C11	1.324(10)	1.336	1.342	1.355
N4 -C11	1.440(9)	1.427	1.396	1.385
N5 -C12	1.423(9)	1.418	1.400	1.365
C7 -C8	1.391(14)	1.404	1.424	1.426
C8 -C9	1.376(11)	1.391	1.390	1.390
C9 -C10	1.367(11)	1.391	1.390	1.390
C10 -C11	1.392(14)	1.404	1.424	1.426

Table S2: Selected experimental and calculated bond distances for **1**.

Parameter	Experimental (Å)	Calculated (S = 2)	
	1	$Fe^{II}(L)Cl_2$	$Fe^{III}(L^{\bullet-})Cl_2$
Fe1 -N1	2.198(3)	2.234	2.240
Fe1 -N3	1.995(3)	1.985	1.991
Fe1 -N5	2.246(3)	2.234	2.240
Fe1 -Cl1	2.2444(13)	2.241	2.207
Fe1 -Cl2	2.2370(13)	2.241	2.207
N1 -N2	1.283(4)	1.285	1.299
N4 -N5	1.278(4)	1.285	1.299
N2 -C7	1.388(5)	1.377	1.363
N3 -C7	1.352(5)	1.355	1.361
N3 -C11	1.341(5)	1.355	1.361
N4 -C11	1.395(5)	1.377	1.363
N5 -C12	1.421(5)	1.410	1.403
C7 -C8	1.375(6)	1.399	1.400
C8 -C9	1.377(5)	1.396	1.397
C9 -C10	1.375(6)	1.396	1.387
C10 -C11	1.383(6)	1.399	1.400
Cl1 -Fe1 -Cl2	116.43(4)	119.67	120.38
N1 -Fe1 -N5	143.53(11)	145.84	145.45
Relative energy/eV	-	0	0.12

Table S3: Selected experimental and calculated bond distances for $[\mathbf{2}]^{+}$, $[\mathbf{2}]^{2+}$ and $[\mathbf{2}]^{0}$.

parameter	Expt	Calc						
		$[\mathbf{2}]^{+}$, (S = ½)		$[\mathbf{2}]^{2+}$, (S = 0)		$[\mathbf{2}]^{0}$, (S = 1 or 0)		
	$[\mathbf{2}]^{+}$	$[Fe^{II}(L^{\bullet-})(L)]^{+}$	$[Fe^{III}(L^{\bullet-})_2]^{+}$	$[Fe^{II}(L)_2]^{2+}$	$[Fe^{III}(L)(L^{\bullet-})]^{2+}$	BS(1, 1) S = 0	S = 1	S = 0
Fe1 -N1	1.971(2)	2.023	2.011	2.054	2.082	2.015	2.011	2.017
Fe1 -N3	1.848(2)	1.864	1.861	1.866	1.872	1.851	1.842	1.848
Fe1 -N5	1.980(2)	2.023	2.018	2.054	2.039		2.018	2.017
N1 -N2/ N6 -N7	1.302(3)	1.299	1.303	1.282	1.293	1.316	1.315	1.317
N4 -N5/ N9 -N10	1.311(3)	1.299	1.997	1.282	1.297	1.318	1.319	1.316
N2 -C7	1.380(3)	1.376	1.362	1.389	1.374	1.367	1.363	1.364
N3 -C11	1.353(3)	1.349	1.361	1.343	1.351	1.352	1.355	1.354
N3 -C7	1.353(3)	1.349	1.360	1.342	1.352	1.351	1.356	1.354
N4 -C11	1.375(3)	1.376	1.369	1.389	1.369	1.365	1.364	1.364
N5 -C12	1.419(3)	1.420	1.411	1.417	1.411	1.414	1.416	1.418
N1-Fe1-N5	154.03(8)	154.20	153.92	154.10	153.8	153.45	154.29	154.11
Dihedral angle	81.98	82.50	82.85	83.14	81.89	80.67	85.31	82.51
Relative energy/eV	-	0	0.29	0	0.21	0.03	0	0.23

Table S4: Cartesian coordinates of the optimized structures.

[**2**]$^{+}$ in native state (S = ½)

Fe	-0.000000	-0.000000	-0.000000
N	1.799000	-1.713000	1.412000
N	-1.800000	-1.699000	-1.427000
N	-1.483000	-0.445000	-1.303000
N	-0.000000	-1.865000	-0.009000
C	-1.929000	1.595000	-2.551000
H	-0.864000	1.790000	-2.579000
N	1.483000	-0.458000	1.298000
C	-0.932000	-2.514000	-0.738000
C	-4.188000	2.169000	-3.198000
H	-4.881000	2.843000	-3.693000
C	0.930000	-2.521000	0.715000
C	-2.409000	0.435000	-1.925000
C	-4.666000	1.016000	-2.567000
H	-5.730000	0.796000	-2.567000
C	3.784000	0.121000	1.939000
H	4.137000	-0.775000	1.441000
C	4.667000	0.988000	2.576000
H	5.731000	0.767000	2.575000
C	-2.819000	2.450000	-3.195000
H	-2.443000	3.333000	-3.702000
C	-0.963000	-3.912000	-0.763000
H	-1.719000	-4.423000	-1.349000
C	-3.784000	0.142000	-1.938000
H	-4.137000	-0.757000	-1.447000
C	0.960000	-3.920000	0.728000
H	1.715000	-4.436000	1.309000
C	-0.002000	-4.608000	-0.021000
H	-0.002000	-5.693000	-0.025000
C	2.410000	0.416000	1.928000
C	4.191000	2.136000	3.217000
H	4.884000	2.805000	3.718000
C	1.931000	1.571000	2.564000
H	0.866000	1.767000	2.593000
C	2.822000	2.419000	3.216000
H	2.447000	3.299000	3.730000
N	1.799000	1.713000	-1.412000
N	-1.801000	1.699000	1.427000
N	-1.483000	0.445000	1.303000
N	-0.001000	1.864000	0.009000
C	-1.929000	-1.595000	2.552000
H	-0.863000	-1.790000	2.580000
N	1.483000	0.458000	-1.298000
C	-0.932000	2.514000	0.738000
C	-4.188000	-2.169000	3.198000
H	-4.880000	-2.844000	3.693000
C	0.930000	2.521000	-0.715000

C	-2.409000	-0.435000	1.925000
C	-4.666000	-1.016000	2.566000
H	-5.730000	-0.797000	2.566000
C	3.784000	-0.121000	-1.939000
H	4.136000	0.775000	-1.441000
C	4.668000	-0.987000	-2.576000
H	5.731000	-0.766000	-2.575000
C	-2.819000	-2.450000	3.196000
H	-2.443000	-3.333000	3.703000
C	-0.964000	3.912000	0.763000
H	-1.720000	4.423000	1.348000
C	-3.784000	-0.143000	1.937000
H	-4.137000	0.757000	1.447000
C	0.960000	3.920000	-0.728000
H	1.715000	4.437000	-1.309000
C	-0.003000	4.608000	0.020000
H	-0.003000	5.693000	0.025000
C	2.410000	-0.415000	-1.928000
C	4.191000	-2.135000	-3.217000
H	4.884000	-2.805000	-3.718000
C	1.931000	-1.571000	-2.564000
H	0.866000	-1.767000	-2.592000
C	2.823000	-2.419000	-3.215000
H	2.448000	-3.299000	-3.730000

[**2**]$^{2+}$ in oxidized state (S = 0)

Fe	0.003000	0.000000	0.000000
N	1.805000	-1.483000	1.651000
N	-1.796000	-1.889000	-1.169000
N	-1.495000	-0.645000	-1.250000
N	0.005000	-1.848000	0.264000
C	-1.886000	1.201000	-2.785000
H	-0.829000	1.434000	-2.758000
N	1.501000	-0.267000	1.381000
C	-0.934000	-2.595000	-0.339000
C	-4.093000	1.575000	-3.698000
H	-4.759000	2.146000	-4.338000
C	0.946000	-2.395000	1.050000
C	-2.386000	0.109000	-2.055000
C	-4.592000	0.494000	-2.961000
H	-5.644000	0.232000	-3.023000
C	3.746000	0.375000	2.142000
H	4.124000	-0.589000	1.822000
C	4.584000	1.319000	2.721000
H	5.636000	1.091000	2.858000
C	-2.740000	1.919000	-3.616000
H	-2.350000	2.740000	-4.210000
C	-0.971000	-3.982000	-0.163000
H	-1.737000	-4.570000	-0.655000
C	-3.746000	-0.249000	-2.149000
H	-4.116000	-1.089000	-1.572000
C	0.986000	-3.776000	1.268000
H	1.754000	-4.202000	1.905000
C	0.008000	-4.565000	0.650000

H	0.010000	-5.640000	0.803000
C	2.385000	0.685000	1.948000
C	4.075000	2.558000	3.130000
H	4.734000	3.288000	3.591000
C	1.875000	1.933000	2.346000
H	0.817000	2.142000	2.251000
C	2.720000	2.858000	2.951000
H	2.323000	3.808000	3.293000
N	1.805000	1.483000	-1.651000
N	-1.796000	1.889000	1.169000
N	-1.495000	0.645000	1.250000
N	0.005000	1.848000	-0.264000
C	-1.886000	-1.201000	2.785000
H	-0.829000	-1.434000	2.759000
N	1.501000	0.267000	-1.381000
C	-0.934000	2.595000	0.339000
C	-4.093000	-1.575000	3.698000
H	-4.759000	-2.146000	4.338000
C	0.946000	2.395000	-1.050000
C	-2.386000	-0.109000	2.055000
C	-4.592000	-0.494000	2.961000
H	-5.644000	-0.232000	3.023000
C	3.746000	-0.375000	-2.142000
H	4.124000	0.589000	-1.822000
C	4.584000	-1.319000	-2.721000
H	5.636000	-1.091000	-2.858000
C	-2.740000	-1.919000	3.616000
H	-2.350000	-2.740000	4.210000
C	-0.971000	3.982000	0.163000
H	-1.737000	4.570000	0.655000
C	-3.746000	0.249000	2.149000
H	-4.116000	1.089000	1.572000
C	0.986000	3.776000	-1.268000
H	1.754000	4.202000	-1.905000
C	0.008000	4.565000	-0.650000
H	0.010000	5.640000	-0.803000
C	2.385000	-0.685000	-1.948000
C	4.075000	-2.558000	-3.130000
H	4.734000	-3.288000	-3.591000
C	1.875000	-1.933000	-2.346000
H	0.817000	-2.142000	-2.251000
C	2.720000	-2.858000	-2.951000
H	2.323000	-3.808000	-3.293000

One electron reduced complex, (S = 1), [**2**]^{0}

Fe	-0.005000	0.000000	0.000000
N	1.755000	-1.915000	1.217000
N	-1.771000	-1.498000	-1.698000
N	-1.455000	-0.258000	-1.387000
N	-0.009000	-1.847000	-0.259000
C	-1.820000	1.931000	-2.389000
H	-0.758000	2.126000	-2.312000
N	1.447000	-0.633000	1.260000
C	-0.941000	-2.389000	-1.082000
C	-4.034000	2.609000	-3.099000

H	-4.696000	3.353000	-3.535000
C	0.921000	-2.598000	0.383000
C	-2.329000	0.695000	-1.965000
C	-4.543000	1.376000	-2.678000
H	-5.603000	1.161000	-2.782000
C	3.700000	-0.203000	2.138000
H	4.067000	-1.045000	1.562000
C	4.555000	0.560000	2.926000
H	5.612000	0.311000	2.965000
C	-2.671000	2.877000	-2.958000
H	-2.263000	3.826000	-3.297000
C	-0.970000	-3.773000	-1.289000
H	-1.720000	-4.200000	-1.946000
C	-3.700000	0.420000	-2.120000
H	-4.080000	-0.540000	-1.788000
C	0.944000	-3.986000	0.200000
H	1.692000	-4.580000	0.714000
C	-0.014000	-4.564000	-0.640000
H	-0.016000	-5.640000	-0.791000
C	2.332000	0.120000	2.067000
C	4.064000	1.644000	3.661000
H	4.736000	2.237000	4.276000
C	1.841000	1.207000	2.806000
H	0.781000	1.429000	2.788000
C	2.704000	1.958000	3.601000
H	2.310000	2.787000	4.181000
N	1.755000	1.915000	-1.217000
N	-1.771000	1.498000	1.698000
N	-1.455000	0.258000	1.387000
N	-0.009000	1.847000	0.259000
C	-1.820000	-1.932000	2.389000
H	-0.758000	-2.126000	2.312000
N	1.447000	0.633000	-1.260000
C	-0.941000	2.389000	1.082000
C	-4.034000	-2.609000	3.099000
H	-4.695000	-3.353000	3.535000
C	0.921000	2.598000	-0.383000
C	-2.329000	-0.695000	1.965000
C	-4.543000	-1.377000	2.678000
H	-5.603000	-1.161000	2.782000
C	3.700000	0.203000	-2.138000
H	4.067000	1.045000	-1.562000
C	4.555000	-0.560000	-2.926000
H	5.613000	-0.310000	-2.965000
C	-2.671000	-2.877000	2.958000
H	-2.263000	-3.826000	3.297000
C	-0.971000	3.773000	1.289000
H	-1.720000	4.200000	1.946000
C	-3.700000	-0.420000	2.120000
H	-4.080000	0.540000	1.788000
C	0.944000	3.986000	-0.200000
H	1.692000	4.580000	-0.714000
C	-0.014000	4.564000	0.640000
H	-0.017000	5.640000	0.791000
C	2.332000	-0.120000	-2.067000
C	4.065000	-1.644000	-3.661000
H	4.736000	-2.237000	-4.276000

C	1.841000	-1.207000	-2.806000
H	0.781000	-1.429000	-2.788000
C	2.705000	-1.957000	-3.601000
H	2.310000	-2.787000	-4.181000