## **Supporting Information**

## for

## Reaction of a non-heme iron-nitrosyl with dioxygen: Decomposition of the

## ligand through NOD-like activity

Riya Ghosh, Rakesh Mazumdar, Bapan Samanta, Shankhadeep Saha, and Biplab Mondal

Department of Chemistry, Indian Institute of Technology Guwahati, Assam – 781039, India. Email: biplab@iitg.ac.in; Phone: (+)91-361-258-2317; Fax: (+)91-361-258-2339

Sl	Description	Page
No.		No.
1	<b>Figure S1:</b> FT-IR spectrum of 1-(hydroxymethyl)-3,5-dimethyl-1-pyrazole in	S3
	KBr.	
2	Figure S2: <sup>1</sup> H NMR spectrum of 1-(hydroxymethyl)-3, 5-dimethyl-1-	S3
	pyrazole in CDCl <sub>3</sub> .	
3	<b>Figure S3:</b> <sup>13</sup> C NMR spectrum of 1-(hydroxymethyl)-3,5-dimethyl-1-pyrazole	S4
	in CDCl <sub>3</sub> .	
4	Figure S4: FT-IR spectrum of TPz in KBr.	S4
5	Figure S5: <sup>1</sup> H NMR spectrum of TPz in CDCl <sub>3</sub> .	S5
6	Figure S6: <sup>13</sup> C NMR spectrum of Tpz in CDCl <sub>3</sub> .	S5
7	Figure S7: ESI-mass spectrum of ligand TPz in acetonitrile.	S6
8	Figure S8: FT-IR spectrum of complex 1 in KBr.	S6
9	Figure S9: UV-visible spectrum of complex 1 in acetonitrile at RT.	S7
10	Figure S10: X-band EPR spectrum of complex 1 in acetonitrile at 77 K.	<b>S</b> 7
11	Figure S11: ESI-mass of complex 1 in acetonitrile. [Inset: (a) experimental	S8
	and (b) simulated isotopic distribution pattern].	
12	Figure S12: ORTEP diagram of complex 1 (30% thermal ellipsoid plot, H	S8
	atoms are omitted for clarity).	
13	Figure S13: FT-IR spectrum of complex 2 in KBr pellet.	S9
14	<b>Figure S14</b> : UV-visible spectrum of complex <b>2</b> in acetonitrile at RT.	S9
15	Figure S15: X-band EPR spectrum of complex 2 in methanol at 77K.	S10
16	Figure S16: X-band EPR Spectra of reaction of complex 2 with O <sub>2</sub> at 77 K in	S10
	methanol.	
17	Figure S17: FT-IR spectrum of complex 3 in KBr.	S11
18	Figure S18: UV-visible spectrum of complex 3 in acetonitrile at RT.	S11
19	Figure S19: X-band EPR spectrum of complex 3 in DMSO at 77 K.	S12

20	Figure S20: FT-IR spectrum of L' in KBr.	S12
21	Figure S21: <sup>1</sup> H NMR spectrum of L' in CD <sub>3</sub> CN.	S13
22	Figure S22: <sup>13</sup> C NMR spectrum of L' in CD <sub>3</sub> CN.	S13
23	Figure S23: COSY NMR spectrum of L' in CD <sub>3</sub> CN.	S14
24	Figure S24: FT-IR spectrum of complex 4 in KBr.	S14
25	Figure S25: UV-visible spectrum of complex 4 in DMSO at RT.	S15
26	Figure S26: X-band EPR spectrum of complex 4 in DMSO at 77 K.	S15
27	<b>Figure S27:</b> <sup>1</sup> H NMR spectrum of 2,4-di- <i>tert</i> -butyl-6-nitrophenol in CDCl <sub>3</sub> .	S16
28	Figure S28. <sup>13</sup> C NMR spectrum of 2,4-di- <i>tert</i> -butyl-6-nitrophenol in CDCl <sub>3</sub> .	S16
29	Figure S29. ESI-mass spectrum of 2,4-di- <i>tert</i> -butyl-6-nitrophenol in	S17
	methanol.	
30	Figure S30: FT-IR spectrum of complex 5 in KBr.	S17
31	Figure S31: UV-visible spectrum of complex 5 in DMSO at RT.	S18
32	Figure S32: X-band EPR spectrum of complex 5 in DMSO at 77 K.	S18
33	Figure S33: <sup>1</sup> H NMR spectrum of (tmpH <sub>2</sub> <sup>+</sup> )(NO <sub>3</sub> <sup>-</sup> )in CDCl <sub>3</sub> .	S19
34	Figure S34: <sup>13</sup> C NMR spectrum of (tmpH <sub>2</sub> <sup>+</sup> )(NO <sub>3</sub> <sup>-</sup> ) in CDCl <sub>3</sub> .	S19
35	Table A1: Crystallographic data for complexes 1, 2, L' and (tmpH <sub>2</sub> <sup>+</sup> )(NO <sub>3</sub> <sup>-</sup> )	S20
36	Table A2: Selected bond lengths (Å) of complexes 1, 2, L' and	S20
	$(tmpH_2^+)(NO_3^-)$	
37	<b>Table A3:</b> Selected bond angles (°) of complexes 1, 2, L' and $(tmpH_2^+)(NO_3^-)$	S21
38	<b>Figure S35</b> : ESI-mass spectrum of complex <b>3</b> in acetonitrile. [Inset: (a)	S22
20	experimental and (b) simulated isotopic distribution pattern].	622
39	Figure 836: ESI-mass spectrum of modified ligand (L') in acetonitrile.	823
40	Figure S37. ESI-mass spectrum of complex 5 in acetonitrile. [Inset: (a)	S23
	experimental and (b) simulated isotopic distribution pattern].	
41	Figure S38: FT-IR spectra of reaction of complex I with NO gas (black line)	S24
42	and "NO gas (blue line) in acctonitrile medium at room temperature.	524
42	Figure S39: F1-IK spectra of $\{Fe(NO)\}$ of formed in the reaction of complex 2 with O2. Bed trace represents with NO and green trace for it's 15NO labelled	524
	analogue	
43	<b>Figure S40:</b> FT-IR spectral monitoring of the reaction of complex $2(^{15}NO)$	S25
	labeled) with $O_2$ in acetonitrile medium. [complex 2 (blue), after $O_2$ addition	~=0
	(green)].	
44	Figure S41: FT-IR spectral monitoring of the reaction complex 2 with AgClO <sub>4</sub>	S25
	in acetonitrile medium.	
45	Figure S42: FT-IR spectral monitoring of the decomposition of {Fe(NO)} <sup>6</sup>	S26
	intermediate in acetonitrile solution.	



Figure S1: FT-IR spectrum of 1-(hydroxymethyl)-3,5-dimethyl-1-pyrazole in KBr.



Figure S2: <sup>1</sup>H NMR spectrum of 1-(hydroxymethyl)-3,5-dimethyl-1-pyrazole in CDCl<sub>3</sub>.



Figure S3: <sup>13</sup>C NMR spectrum of 1-(hydroxymethyl)-3,5-dimethyl-1-pyrazole in CDCl<sub>3</sub>.



Figure S4: FT-IR spectrum of TPz in KBr.



Figure S5: <sup>1</sup>H NMR spectrum of TPz in CDCl<sub>3</sub>.



Figure S6: <sup>13</sup>C NMR spectrum of Tpz in CDCl<sub>3</sub>.



Figure S7: ESI-mass spectrum of ligand TPz in acetonitrile.



Figure S8: FT-IR spectrum of complex 1 in KBr.



Figure S9: UV-visible spectrum of complex 1 in acetonitrile at RT.



Figure S10: X-band EPR spectrum of complex 1 in acetonitrile at 77 K.



**Figure S11:** ESI-mass of complex 1 in acetonitrile. [Inset: (a) experimental and (b) simulated isotopic distribution pattern].



Figure S12. ORTEP diagram of complex 1 (30% thermal ellipsoid plot, H atoms are omitted for clarity).



Figure S13: FT-IR spectrum of complex 2 in KBr pellet.



Figure S14: UV-visible spectrum of complex 2 in acetonitrile at RT.



Figure S15: X-band EPR spectrum of complex 2 in methanol at 77K. [Note: a very small amount impurity (< 0.5%) accounting for the isotropic signal near g = 2 in the EPR spectrum]



Figure S16: X-band EPR Spectra of reaction of complex 2 with  $O_2$  at 77 K in methanol medium. [Complex 2 (black) at  $g \sim 4.11$  and 2.04, after  $O_2$  addition final product (red) at  $g \sim 5.05$ ].

[Note: a very small amount impurity (< 0.5%) accounting for the isotropic signal near g = 2 in the EPR spectrum]



Figure S17: FT-IR spectrum of complex 3 in KBr.



Figure S18: UV-visible spectrum of complex 3 in DMSO at RT.



Figure S19: X-band EPR spectrum of complex 3 in DMSO at 77 K ( $g \sim 5.05$ ).



Figure S20: FT-IR spectrum of L' in KBr.



Figure S21: <sup>1</sup>H NMR spectrum of modified crystal L' in CDCl<sub>3</sub>. (\* for solvent)



Figure S22: <sup>13</sup>C NMR spectrum of L' in CD<sub>3</sub>CN.

.

S13



Figure S23: COSY NMR spectrum of L' in CD<sub>3</sub>CN.



Figure S24: FT-IR spectrum of complex 4 in ATR.



Figure S25: UV-visible spectrum of complex 4 in DMSO at RT.



Figure S26: X-band EPR spectrum of complex 4 in DMSO at 77 K ( $g \sim 5.04$ ).



Figure S28: <sup>13</sup>C NMR spectrum of 2, 4-di-*tert*-butyl-6-nitrophenol in CDCl<sub>3</sub>.



**Figure S29:** ESI-mass spectrum of 2, 4-di-*tert*-butyl-6-nitrophenol in methanol.



Figure S30: FT-IR spectrum of complex 5 in KBr.



Figure S31: UV-visible spectrum of complex 5 in DMSO at RT.



Figure S32: X-band EPR spectrum of complex 5 in DMSO at 77 K (g ~5.06).



Figure S33: <sup>1</sup>H NMR spectrum of (tmpH<sub>2</sub><sup>+</sup>)(NO<sub>3</sub><sup>-</sup>) in CDCl<sub>3</sub>.



Figure S34: <sup>13</sup>C NMR spectrum of (tmpH<sub>2</sub><sup>+</sup>)(NO<sub>3</sub><sup>-</sup>) in CDCl<sub>3</sub>.

	1	2	L'	(tmpH <sub>2</sub> <sup>+</sup> )(NO <sub>3</sub> <sup>-</sup> )
Formulae	$C_{20}H_{34}Cl_2N_8O_{10}Fe$	C <sub>20</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>9</sub> O <sub>9</sub> Fe	C <sub>15</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>7</sub> O <sub>10</sub>	$C_9H_{20}N_2O_3$
Mol. wt.	673.30	667.28	532.30	204.27
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P -1	P 21/n	P 21	Pca21
Temperature /K	296(2)	101(2)	293(2)	293(2)
Wavelength /Å	0.71073	0.71073	0.71073	0.71073
a /Å	11.9018(6)	10.4501(6)	8.3825(5)	15.56(4)
b /Å	11.9774(6)	19.7521(12)	9.5056(5)	9.90(2)
c /Å	12.2326(6)	15.8247(9)	15.3798(8)	15.75(4)
α/°	84.555(3)	90	90	90
β/°	74.331(3)	91.422(4)	94.911(5)	90
$\gamma/^{\circ}$	68.652(2)	90	90	90
V/ Å <sup>3</sup>	1563.78(14)	3265.4(3)	1220.97(12)	2426(10)
Ζ	2	4	2	8
Density/Mgm <sup>-3</sup>	1.430	1.357	1.448	1.118
Abs. Coeff. /mm <sup>-1</sup>	0.714	0.682	0.328	0.083
Abs. correction	none	none	multi-scan	none
F(000)	700	1380	552	896
Total no. of reflections	5502	5764	3475	4258
Reflections, $I > 2\sigma(I)$	4355	3822	2853	2392
Max. 20/°	25.000	24.999	24.993	24.990
Ranges (h, k, l)	$-14 \le h \le 14$ $-14 \le k \le 14$ $-14 \le l \le 14$	$\begin{array}{c} -12 \leq h \leq 12 \\ -23 \leq k \leq 23 \\ -18 \leq 1 \leq 18 \end{array}$	$-9 \le h \le 7$ $-10 \le k \le 11$ $-17 \le l \le 18$	$-18 \le h \le 18$ $-11 \le k \le 11$ $-18 \le 1 \le 18$
Complete to 2θ (%)	1.000	1.000	1.000	0.999
Refinement method	Full-matrix least- squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on $F^2$	Full-matrix least- squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on $F^2$
$Goof(F^2)$	1.012	1.024	1.026	1.023
R indices $[I > 2\sigma(I)]$	0.0564	0.0770	0.0641	0.0725
R indices (all data)	0.0723	0.1158	0.0780	0.1360

Table A1: Crystallographic data for complexes 1, 2, L' and  $(tmpH_2^+)(NO_3^-)$ 

Table A2: Selected bond lengths (Å) of complexes 1, 2, L' and  $(tmpH_2^+)(NO_3^-)$ 

Atoms	1	2	L'	$(tmpH_2^+)(NO_3^-)$
Fe1-N1	2.161(4)	2.101(5)		
N1-N2	1.365(6)	1.354(6)	1.370(8)	
Fe1-N3	2.293(4)	2.330(4)		
Fe1-N8	2.118(5)	1.732(6)		
N8-01		1.13(1)		

Fe1-N9		2.195(5)		
Fe1-O1	2.100(3)			
C1-C2	1.48(1)	1.476(9)	1.49(1)	1.549(1)
C2-C3	1.40(1)	1.395(9)	1.36(1)	
C3-C4	1.358(9)	1.379(9)	1.36(1)	
N1-C2	1.332(6)	1.343(8)		
N2-C2			1.357(9)	
Cl1-O3	1.417(7)	1.424(9)	1.36(1)	
Cl2-07	1.412(5)	1.378(8)	1.372(7)	
N2-01			1.50(1)	1.226(8)
N3-01			1.442(9)	
N1-C1				1.552(1)
C1-C2				1.549(1)
C4-C5				1.563(13)
C5-C6				1.533(14)
C6-C7				1.511(11)
N2-O2				1.250(9)

Table A3: Selected bond angles (°) of complexes 1, 2, L' and  $(tmpH_2^+)(NO_3^-)$ 

Atoms	1	2	L'	(tmpH <sub>2</sub> <sup>+</sup> )(NO <sub>3</sub> <sup>-</sup> )
N1-Fe1-N3	76.8(1)	76.0(2)		
N3-Fe1-N5	76.4(1)	75.3(2)		
N3-Fe1-N7	77.6(1)	77.1(2)		
N1-Fe1-N8	103.9(2)	104.3(2)		
Fe1-N8-O1		174.2(6)		
N1-Fe1-N9		86.2(2)		
N1-Fe1-O1	87.4(1)			
O3-Cl1-O4	106.6(4)	96.6(6)	109.2(7)	
O7-Cl2-O8	112.6(4)	116.5(7)	112.2(5)	
O1-N3-O2			117.9(6)	
N3-C7-N6			113.9(6)	
C6-N6-C8			118.3(6)	
N1-C1-C4				107.8(7)
C1-C4-C5				112.8(8)
C4-C5-C6				109.9(8)
01-N2-O2				124.0(9)
O1-N2-O3				119.0(9)



**Figure S35**. ESI-mass spectrum of complex **3** in acetonitrile. [Inset: (a) experimental and (b) simulated isotopic distribution pattern].



**Figure S36**: ESI-mass spectrum of modified ligand (L') in acetonitrile. ESI-mass of modified ligand: [L'(ClO<sub>4</sub>)]<sup>+</sup> unit: calculated: 391.113; found: 391.283.



**Figure S37**. ESI-mass spectrum of complex **5** in acetonitrile. [Inset: (a) experimental and (b) simulated isotopic distribution pattern].



**Figure S38:** FT-IR spectra of reaction of complex **1** with NO gas (black line) and <sup>15</sup>NO gas (blue line) in acetonitrile medium at room temperature.



Figure S39: FT-IR spectra of  $\{Fe(NO)\}^6$  formed in the reaction of complex 2 with O<sub>2</sub>. Red trace represents with NO and green trace for it's <sup>15</sup>NO labelled analogue.



Figure S40: FT-IR spectral monitoring of the reaction of complex 2 ( $^{15}$ NO labeled) with O<sub>2</sub> in acetonitrile medium. [complex 2 (blue), after O<sub>2</sub> addition (green)].



**Figure S41:** FT-IR spectral monitoring of the reaction complex **2** with AgClO<sub>4</sub> in acetonitrile medium.



**Figure S42:** FT-IR spectral monitoring of the decomposition of  $\{Fe(NO)\}^6$  intermediate in acetonitrile solution.