Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Electronic Structure of iron dinitrogen complex $[(TPB)FeN_2]^{2-/-1/0}$: correlation to Mössbauer parameters

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Table S1: Optimized parameters and energies (a.u.) of all complexes **[(TPB)FeN$_2$]$^{2-/-1/0}$** at B3LYP level of theory using LANL2DZ/6-31G(d) basis set (distances in Å and angles in degree). Experimental values are in small bracket & blue colour.

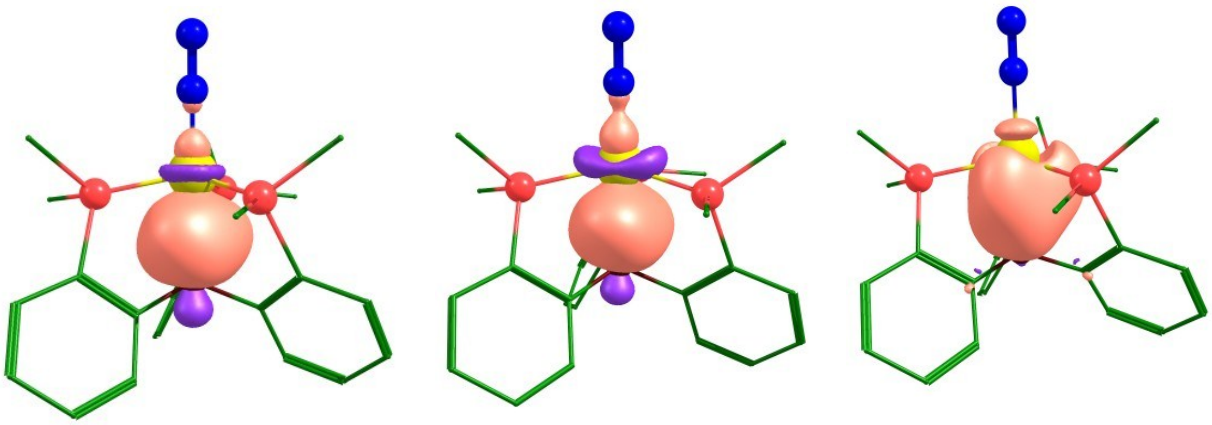
Species		Fe-B	Fe-N1	Fe-P	N1-N2	∠P-Fe-P	∠B-Fe-N1	∠Fe-N1-N2	Energies (a.u.)
Fe^{2-}	S=0	2.369 **(2.34)**	1.779 **(1.772)**	2.137,2.137,2.137	1.145 **(1.16)**	116.3,116.2,116.2	179.9	179.9	-3355.014752
Fe^{1-}	S=1/2	2.345 **(2.293)**	1.807 **(1.776)**	2.254,2.224,2.242	1.136 **(1.149)**	106.8,107.1,134.0	178.4	179.3 **(179.5)**	-3354.976925
Fe^{0}	S=1	2.28	1.973	2.404,2.404,2.404	1.121	117.7,117.7,117.7	179.9	179.9	-3354.8936
	S=0	2.237	1.826	2.194,2.254,2.265	1.127	157.1,96.9,101.2	173.7	176.3	-3354.8752

Table S2: Nature of Fe-N, Fe→B bonds, APT charges and HOMO-LUMO gap (eV) in complexes **[(TPB)FeN$_2$]$^{2-/-1/0}$.**

Complex	**Bond**	**Orbitals**	**% Contribution**	**APT Charges**				**HOMO-LUMO gap(eV)**	**ν(N ≡ N) cm^{-1}**
				Fe	B	Nα	Nβ		2079
Fe^{2-}	Fe-N	$sp^{2.21}d^{2.47}$(Fe) $sp^{0.70}$(N)	21.55%(Fe), 78.45% (N)	-2.180	0.18	1.31	-1.12	2.76	
	Fe-B	$sp^{68.64}d^{54.37}$(Fe) $sp^{3.29}$ (B)	53.79% (Fe), 46.21% (B)						
Fe^{1-}	Fe-N	$sp^{4.07}d^{2.77}$(Fe) $sp^{0.72}$(N)	18.65% (Fe), 81.35% (N)	-1.438	0.29	1.20	-1.02	3.59	2142
	Fe-B	$sp^{99.99}d^{99.99}$(Fe) $sp^{4.18}$ (B)	67.70% (Fe), 32.30% (B)						
Fe^{0}	Fe-N	$sp^{2.73}d^{0.11}$(Fe) $sp^{0.66}$(N)	11.13% (Fe), 88.87% (N)	-0.44	0.41	0.85	-0.74	4.43	2246
	Fe-B	$sp^{0.45}d^{0.12}$(Fe) $sp^{1.81}$(B)	55.93% (Fe), 44.07% (B)						

Table S3: Topological parameters corresponds to the Fe-B and Fe-N bonds

Species	BCP	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-3})	G(r) (hartree Å^{-3})	V(r) (hartree Å^{-3})	H(r) (hartree Å^{-3})
Fe^{2-}-AIM	Fe- B	0.059	0.033	0.022	-0.036	-0.014
	Fe- N	0.133	0.833	0.262	-0.315	-0.053
Fe^{1-}-AIM	Fe- B	0.061	0.024	0.021	-0.035	-0.014
	Fe- N	0.124	0.787	0.244	-0.291	-0.047
Fe^{0} -AIM	Fe- B	0.063	0.020	0.021	-0.037	-0.016
	Fe- N	0.081	0.546	0.148	-0.160	-0.012



53.79% (Fe)-46.21% (B) **67.70% (Fe)-32.30% (B)** **55.93% (Fe)- 44.07% (B)**

(a) **(b)** **(c)**

Figure S1: NBO computed Fe–B σ-bond in $[(TPB)Fe]^{2-}$ (a), $[(TPB)Fe]^{1-}$ (b), and $[(TPB)Fe]^{0}$, and. The hybridizations of the iron and boron orbitals involved in the overlap are noted along with the percentage contributions of the constituent atoms to the Fe-B bond.

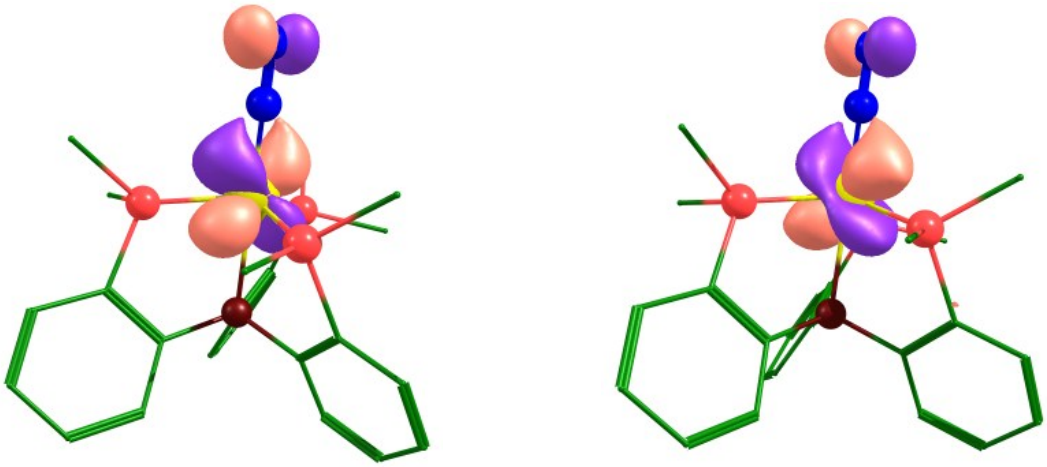


Figure S2: Fe-N bonding molecular orbitals ($d_{yz}\_\pi_{y*}$ and $d_{xz}\_\pi_{z*}$) of $[(TPB)FeN_2]^{2-}$

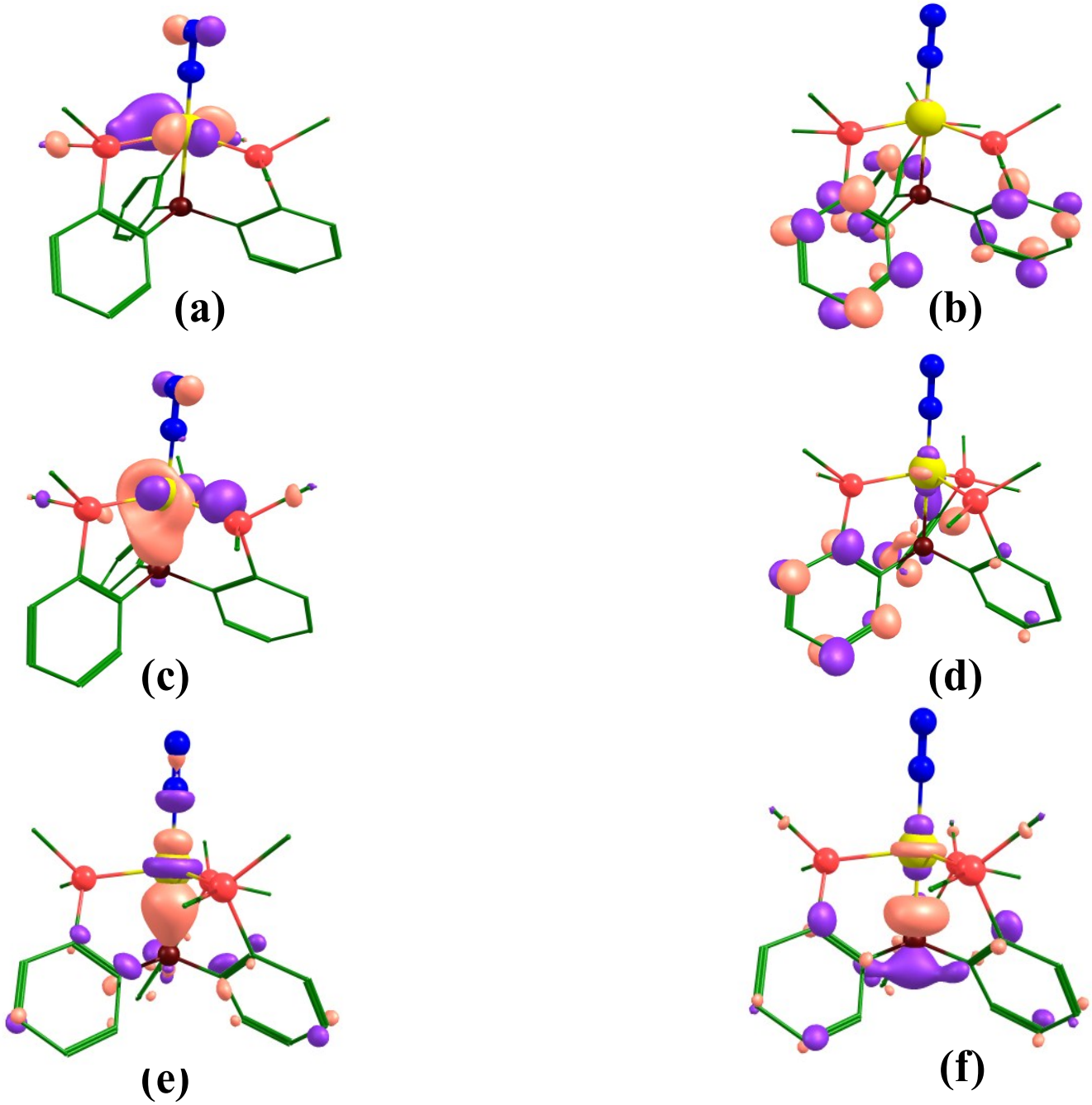


Figure S3: HOMO (a),(c) and (e), LUMO (b), (d) and (f) of the **[(TPB)Fe]$^{2-/-1/0}$** respectively.