Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

DFT Study on a Fluorine-Functionalized Nitrogen- and Boron-doped Triangulene as an Electrocatalyst for the Oxygen Reduction Reaction

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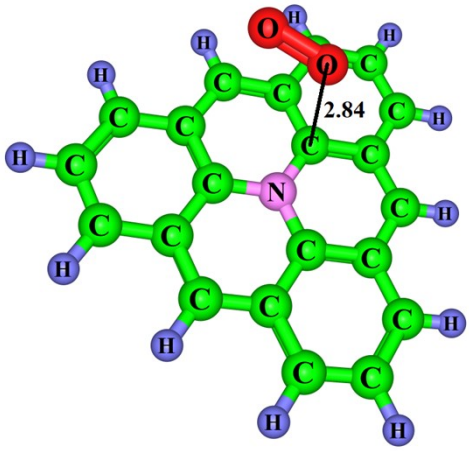
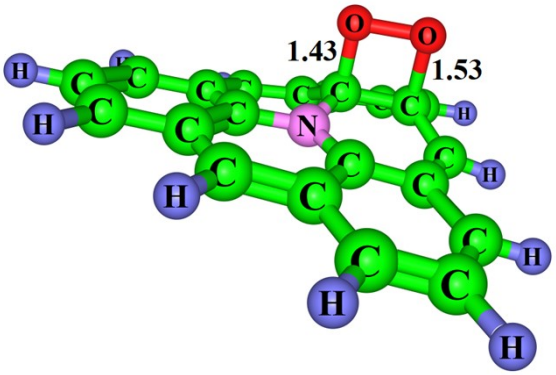
Table S1. Thermodynamic properties of the N- and B-doped triangulene (N-tri and B-tri) of ORR at calculated B3LYP-D3(BJ) level of theory/eV.

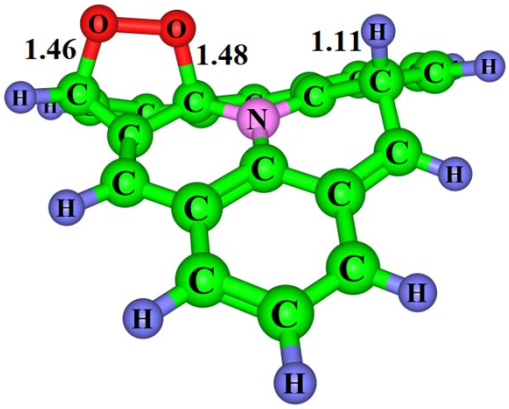
STRUCTURE	N-tri			B-tri		
	ΔE	**ΔH**	**ΔG**	**ΔE**	**ΔH**	**ΔG**
R1	0	0	0	0	0	0
I1	1.51	1.46	1.63	0.41	0.38	0.46
R2	0	0	0	0	0	0
I2	-2.35	-2.33	-2.37	0.61	0.64	0.59
R3	0	0	0	0	0	0
I3	-4.58	-4.54	-4.64	-1.38	-1.36	-1.42
R4	0	0	0	0	0	0
I4	-3.09	-3.12	-3.06	-0.09	-0.07	-0.12
R5	0	0	0	0	0	0
P1	-2.82	-2.78	-2.91	-2.90	-2.85	-3.02



R1



I1



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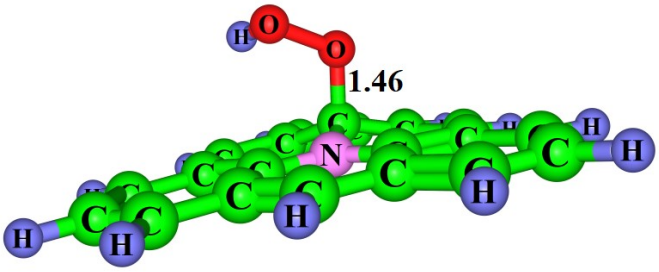
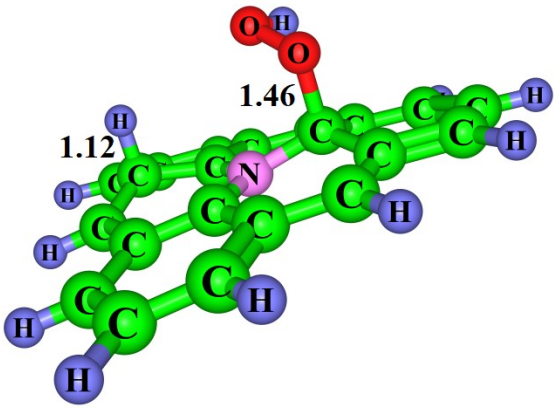


I2

Fig S1. The optimized geometry of N-doped triangulene (N-tri) with *OO, *OOH, *O+H_2O, *OH and H_2O molecules in reactants (R), intermediates (I) and the final product (P).



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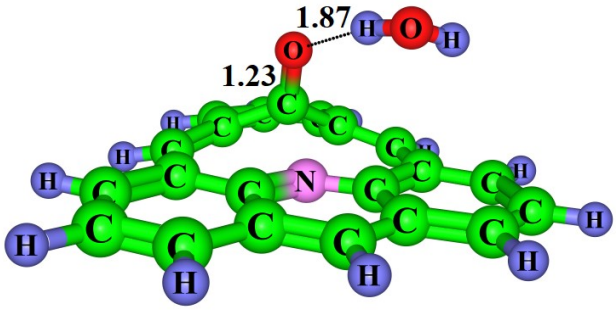

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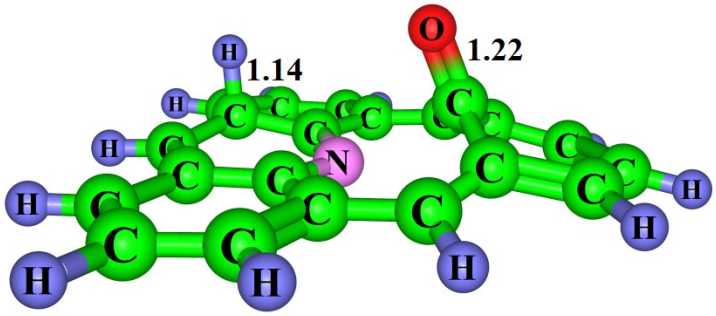

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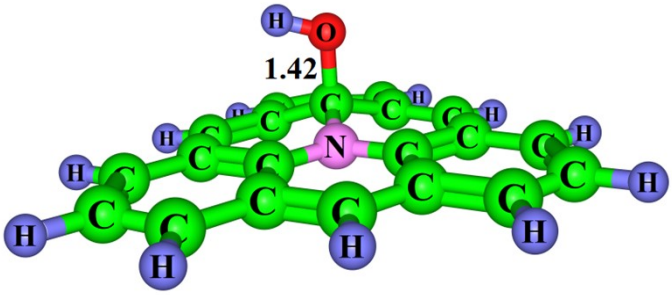

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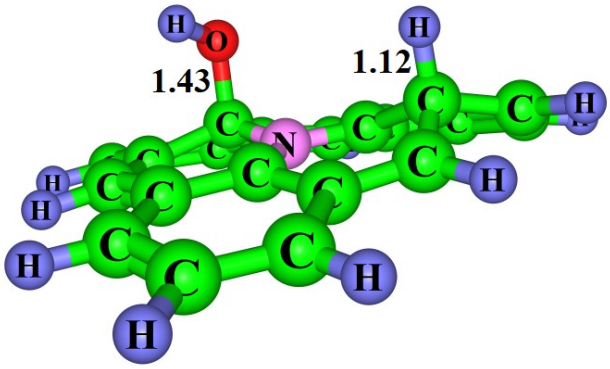

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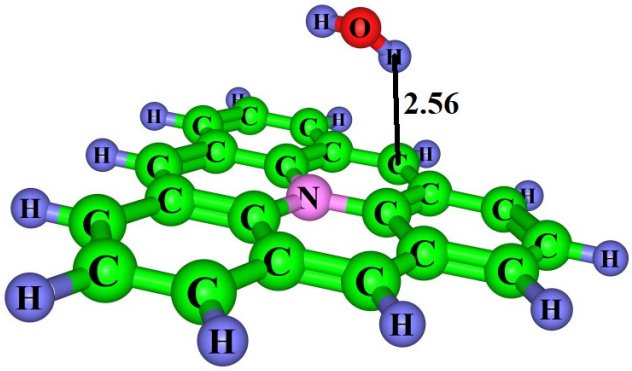

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Fig S1 contd…

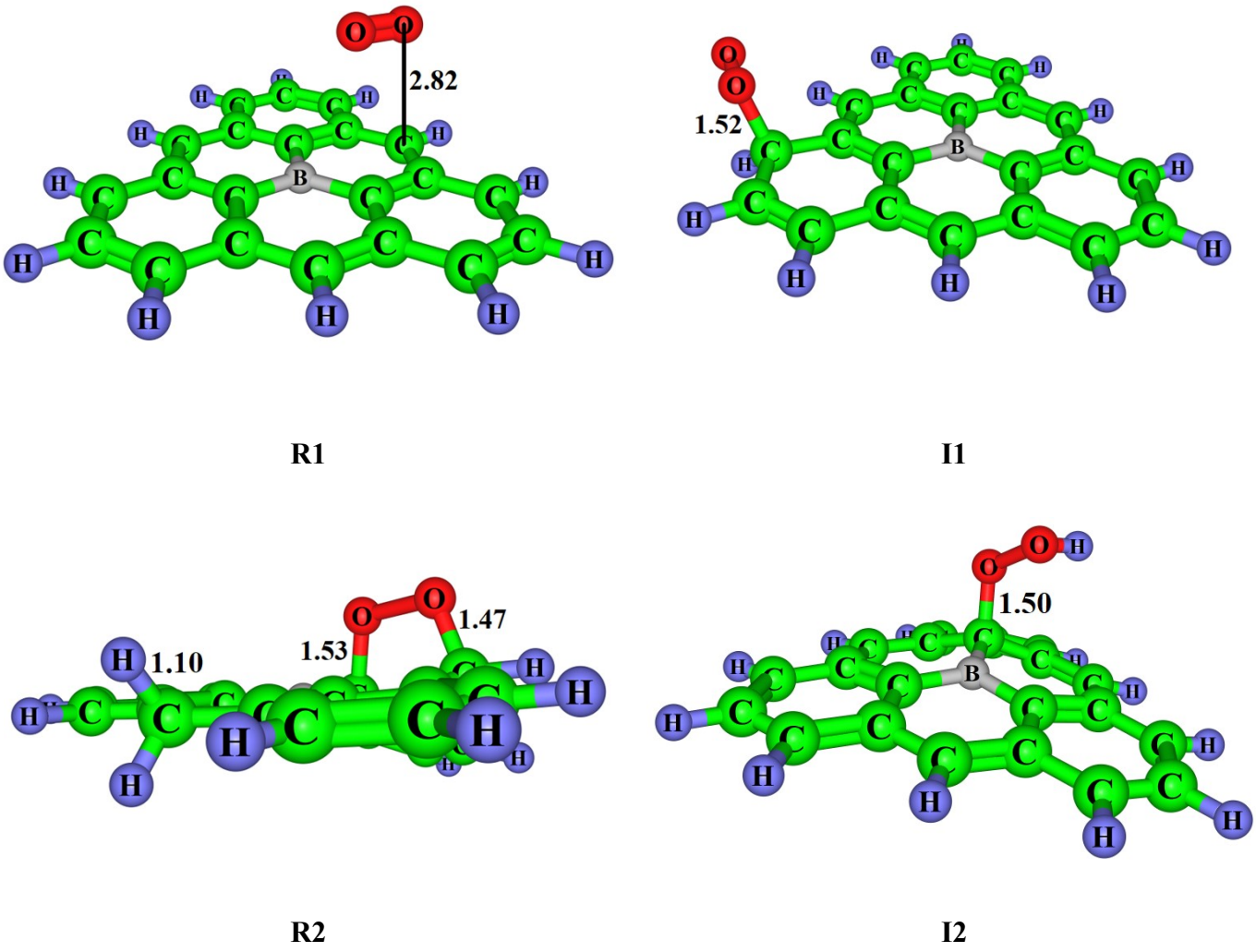
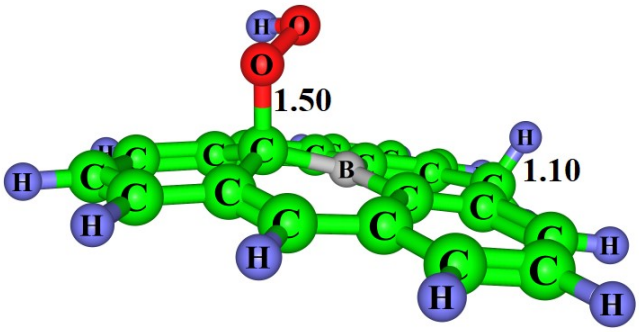


Fig S2. The optimized geometry of B-doped triangulene (B-tri) with *OO, *OOH, *O+H_2O, *OH and H_2O molecules in reactants (R), intermediates (I) and the final product (P).



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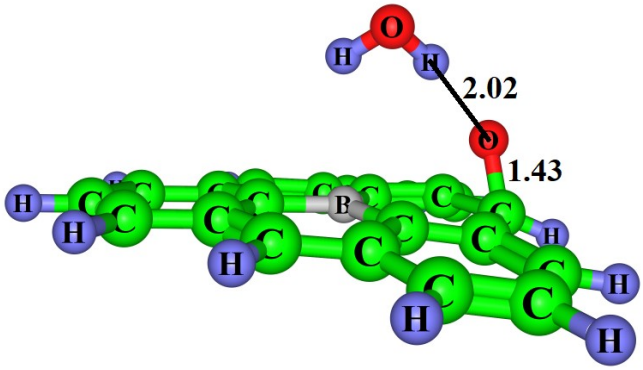

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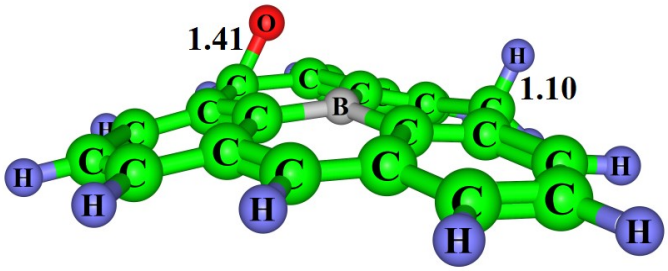

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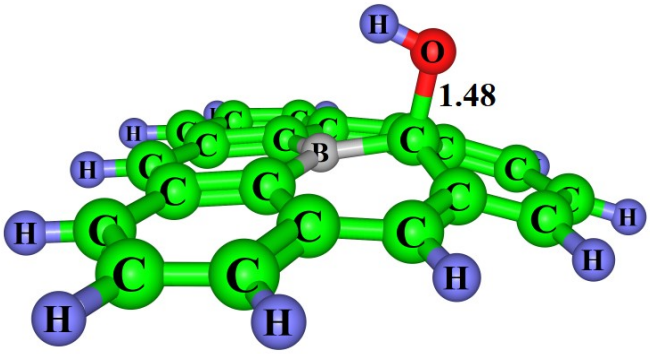

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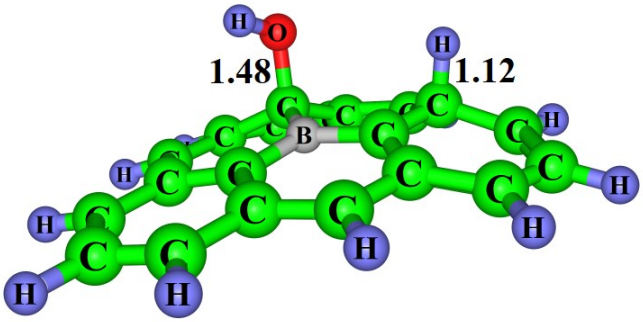

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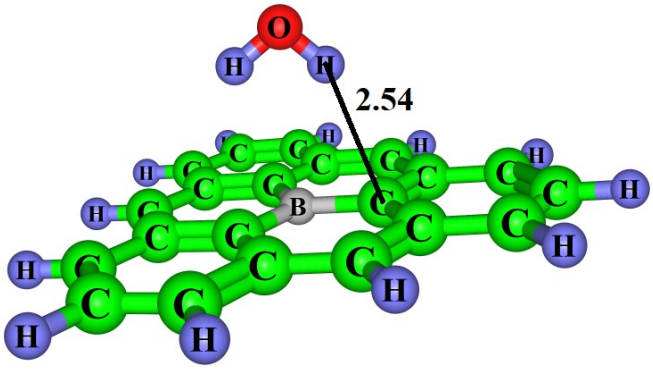

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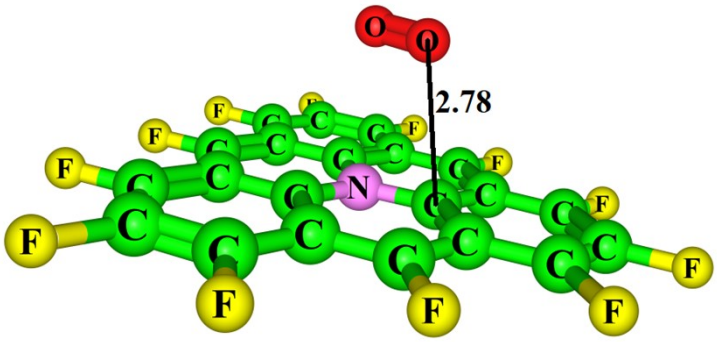

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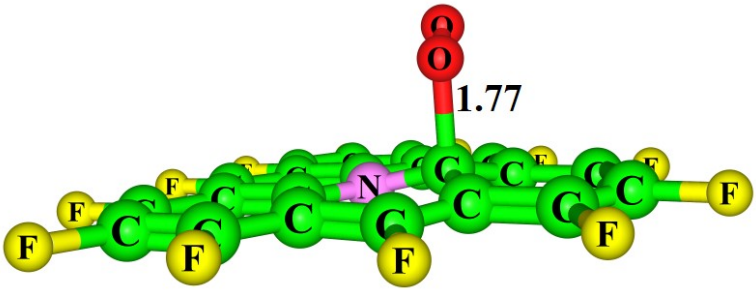
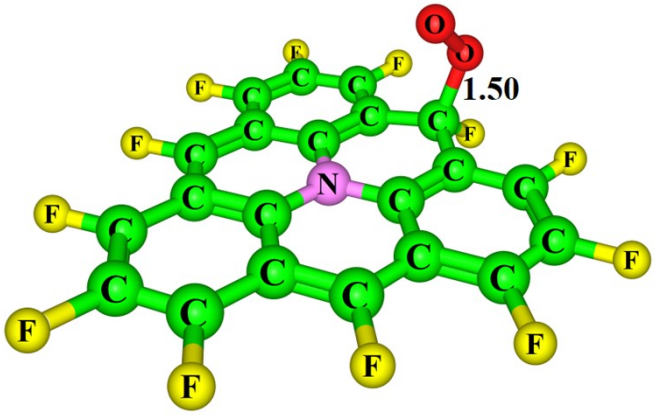
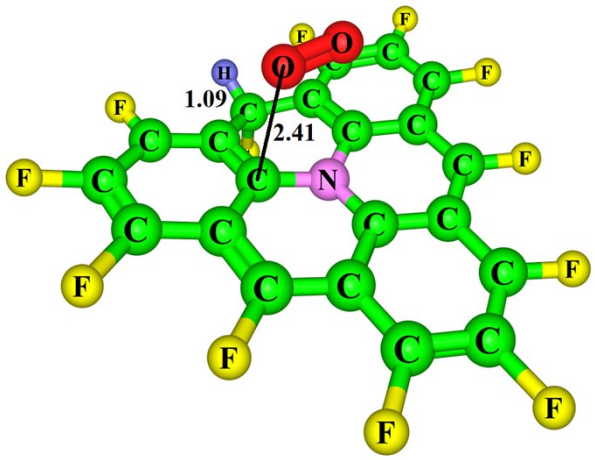


TS1



I1

Fig S3. The optimized structures of reactants (R), transition states (TS), intermediates (I) and the final product (P) of ORR with F-N-tri.



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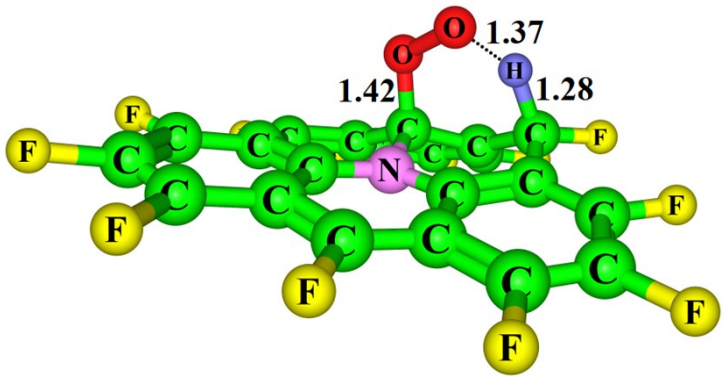

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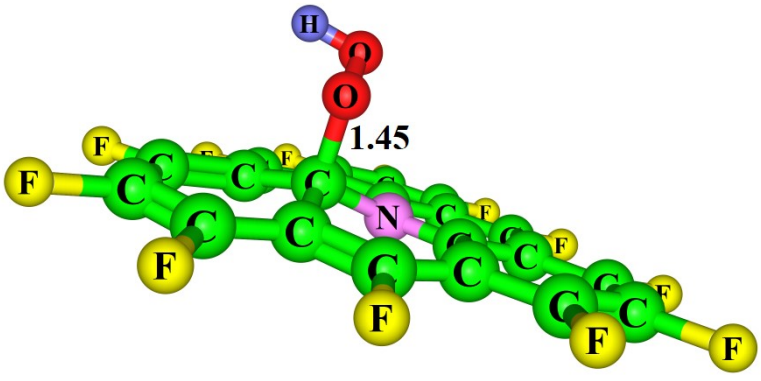

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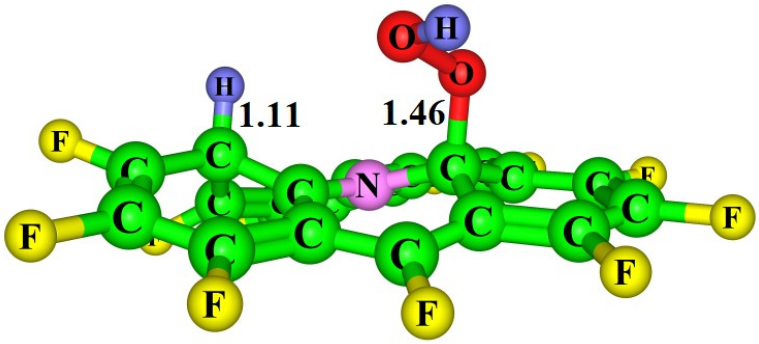

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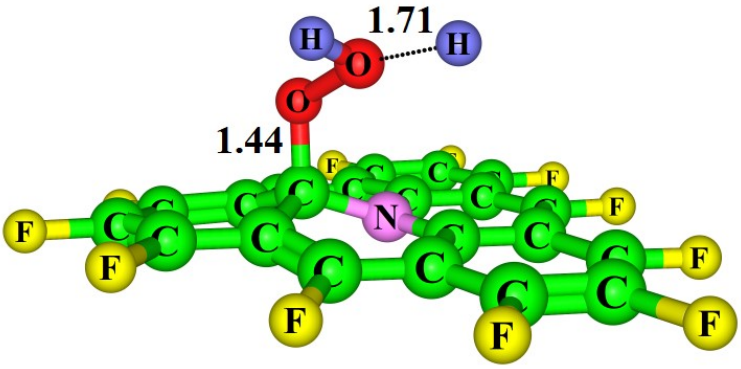

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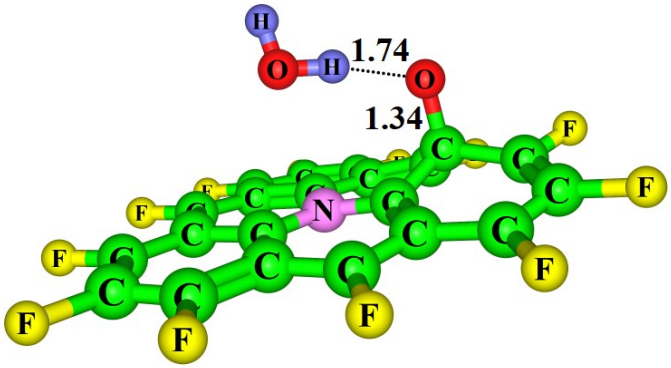

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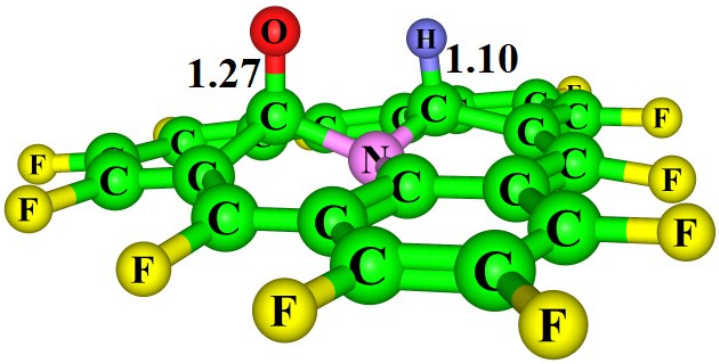

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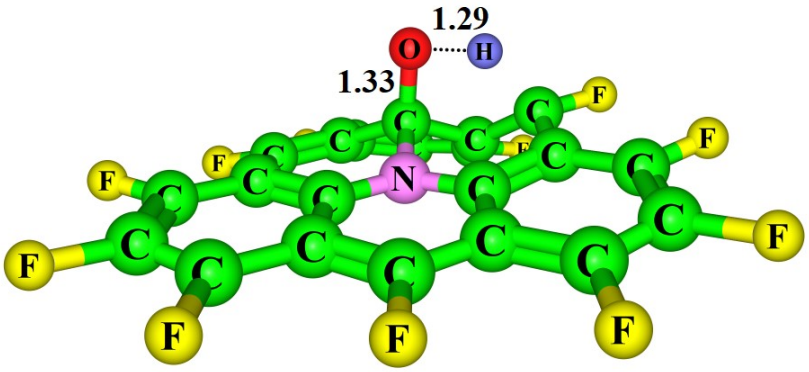

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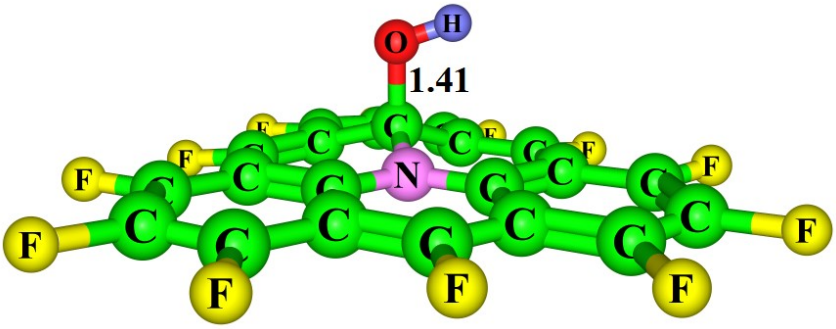

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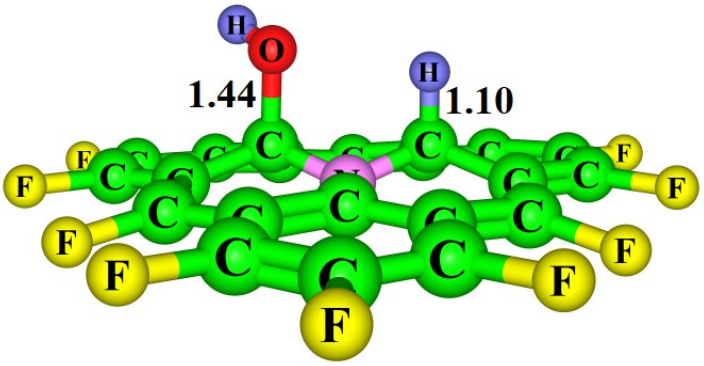

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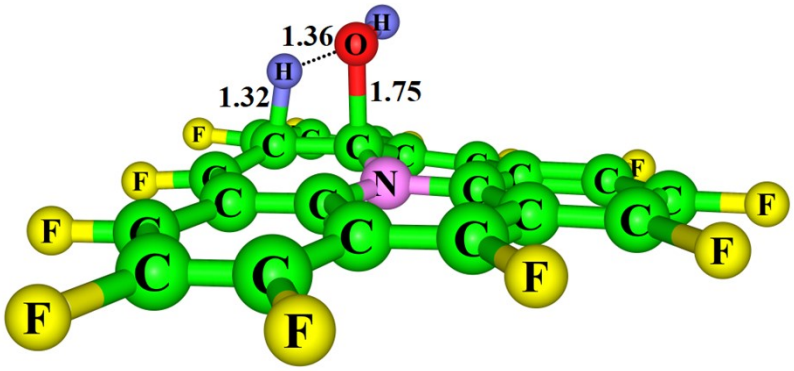

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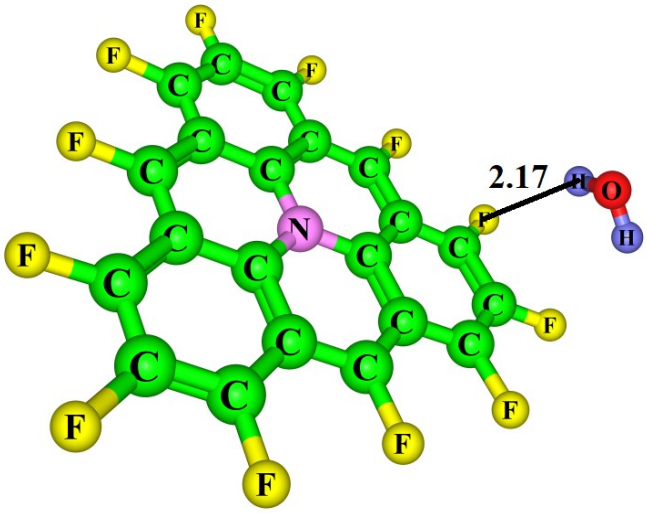

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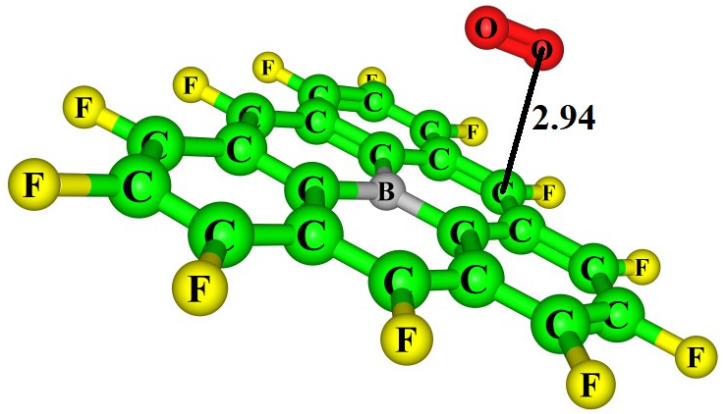

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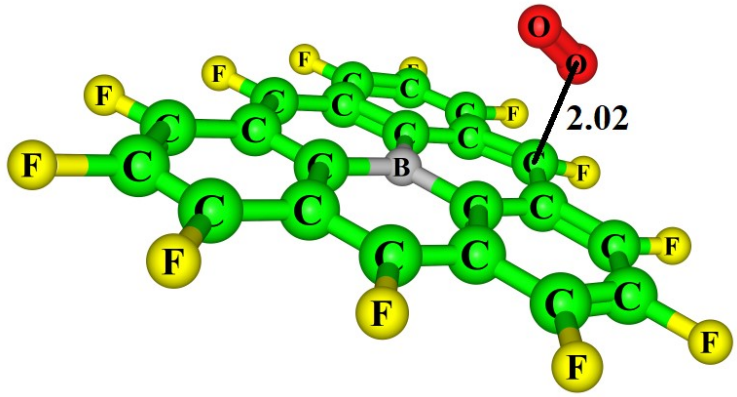

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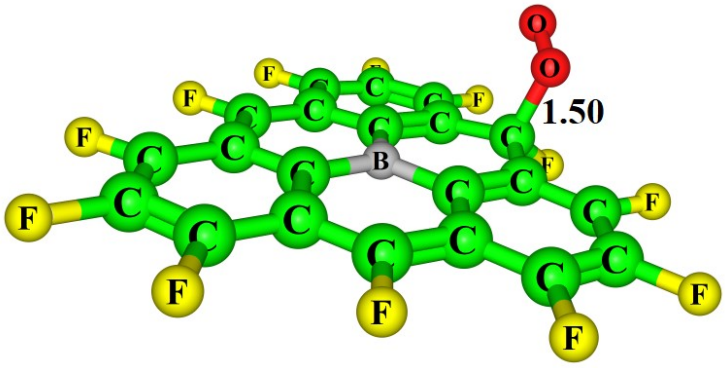
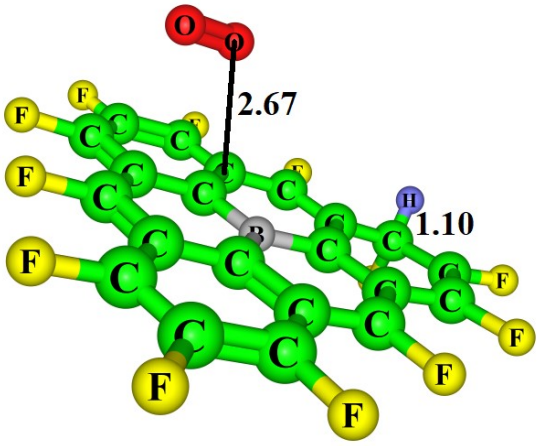


I1

Fig S4. The optimized structures of reactants (R), transition states (TS), intermediates (I) and the final product (P) of ORR with F-B-tri.



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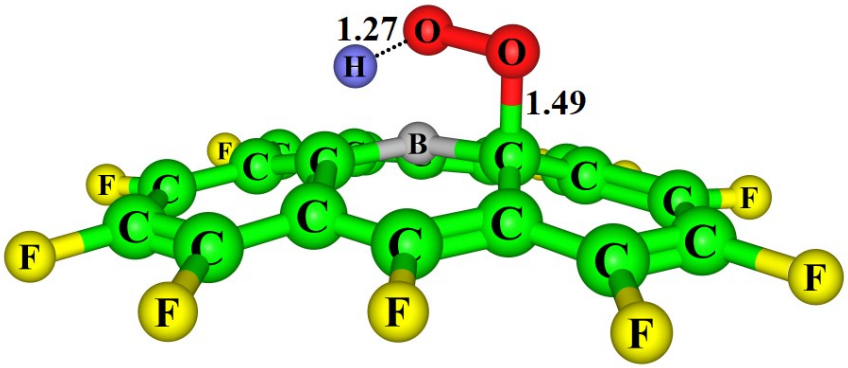

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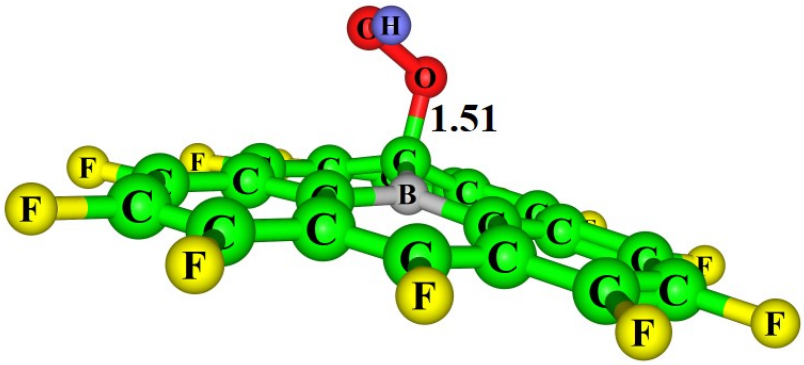

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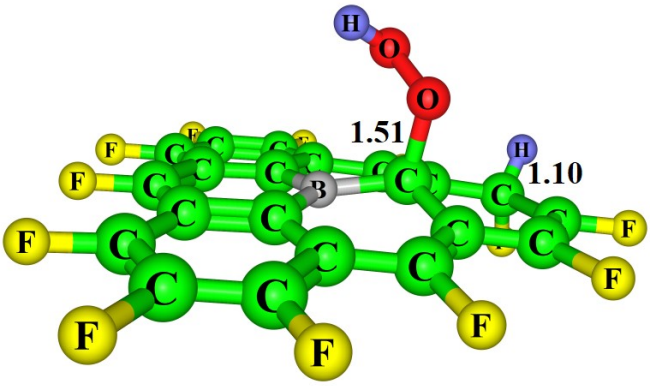

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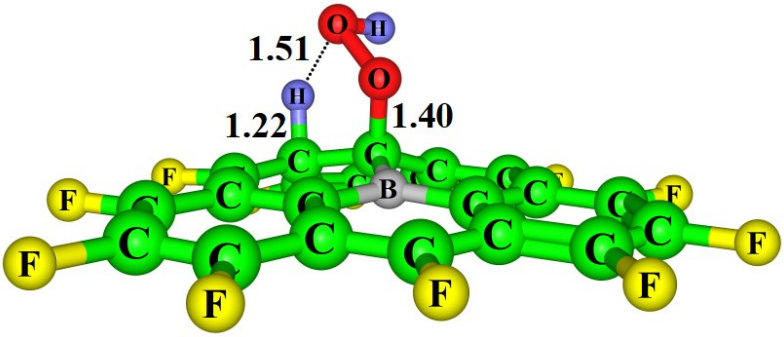

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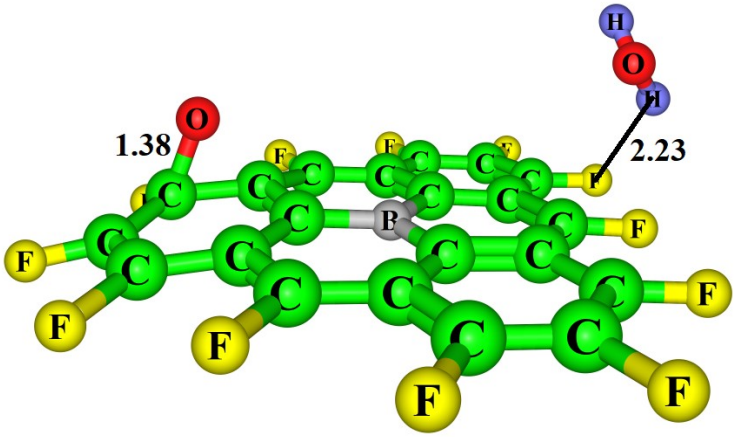

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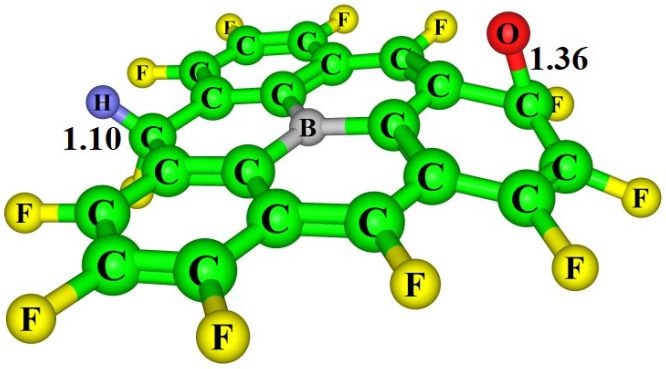

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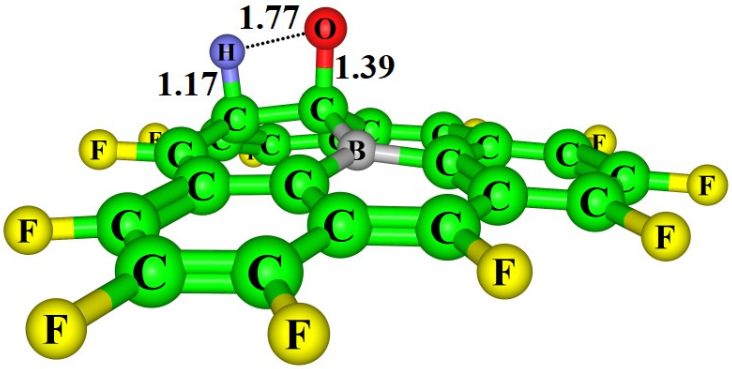

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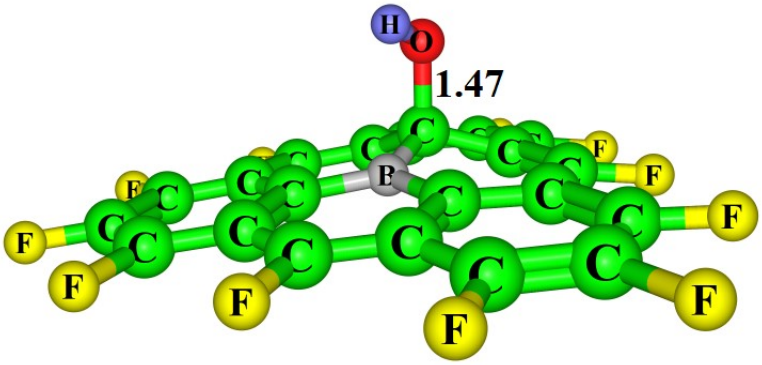

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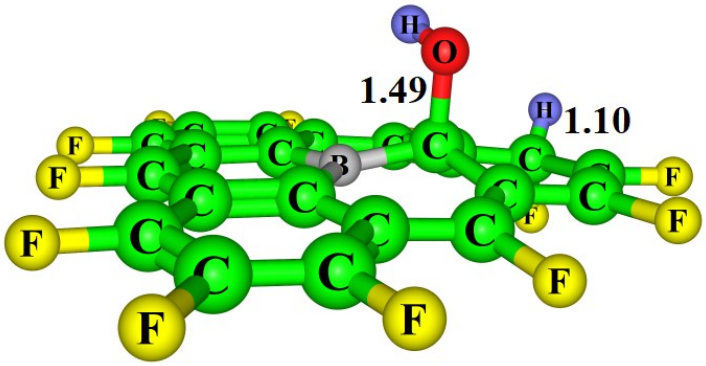

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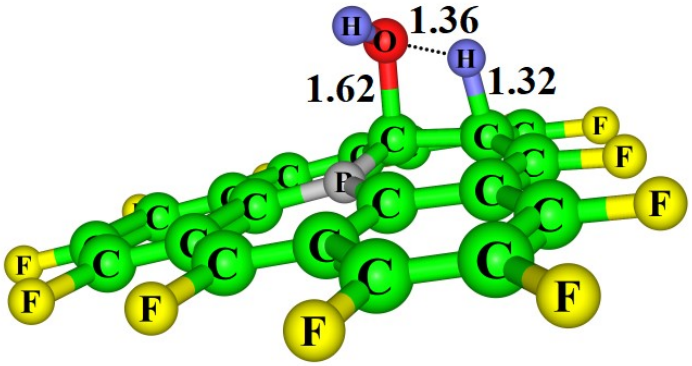

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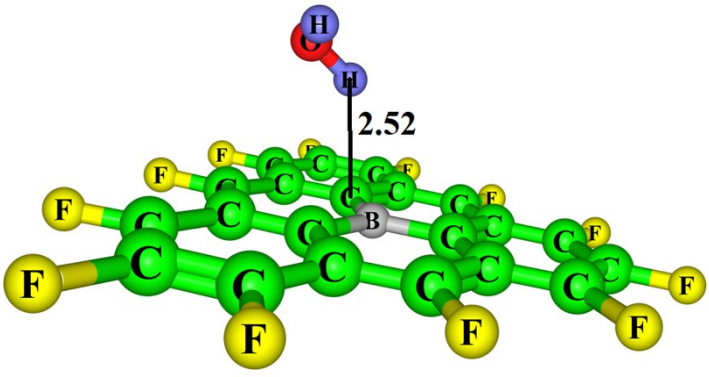

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Fig S4 contd…

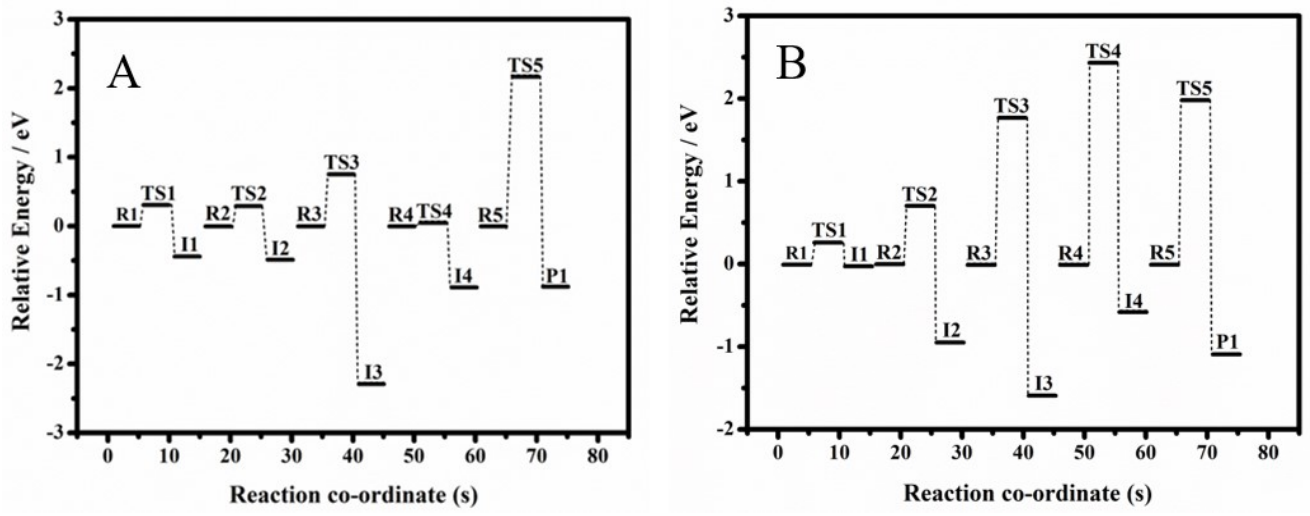

Fig S5. The relative energy profile of 4e$^-$ reduction pathway in the ORR steps are calculated at B3LYP-D3(BJ) level of theory for **A**) F-N-tri **B**) F-B-tri.

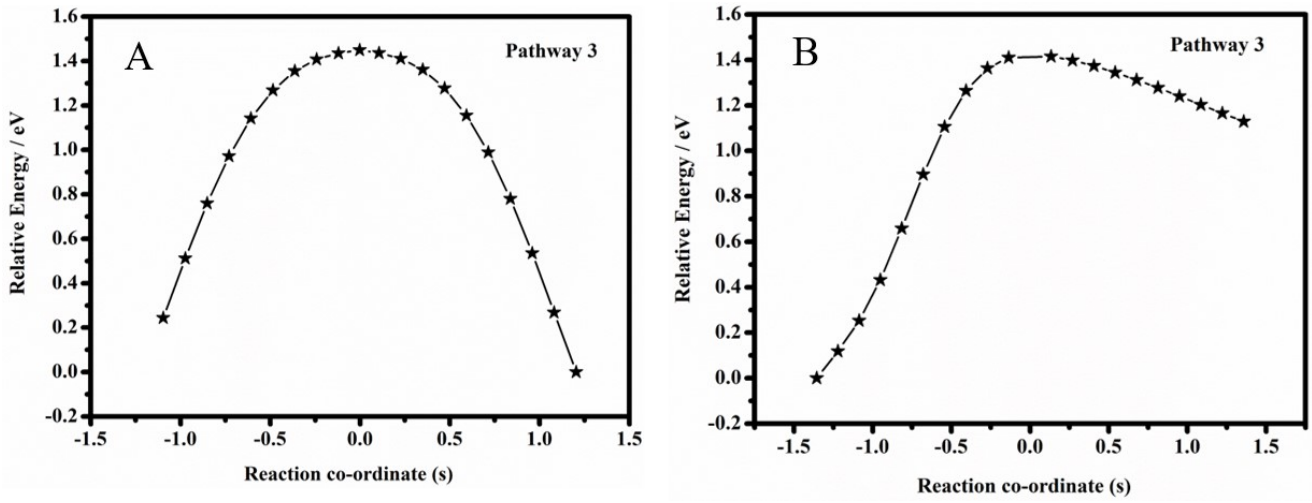

Fig S6. The intrinsic reaction coordinate (IRC) plots of ORR reaction calculated at B3LYP-D3(BJ) level of theory for **A**) F-N-tri **B**) F-B-tri.

Table S2. The rate limiting step (ΔG_1, ΔG_2, ΔG_3, ΔG_4), maximum free energy (G^{ORR}) and overpotential (η^{ORR}) are calculated for F-N-tri and F-B-tri molecules.

Molecules	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	G^{ORR} (eV)	η^{ORR} (V)
F-N-tri	-0.81	-2.59	-0.28	-1.24	-0.28	1.16
F-B-tri	-0.53	-2.81	-0.06	-1.52	-0.06	1.21