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SUPPORTING INFORMATION

Unravelling Single Atom Electrocatalytic Activity of Transition Metal Doped Phosphorene

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Table S1: Structural details of transition metal doped phosphorene SACs.

System	Bond Distance (Å)					Magnetic Moment
	TM-P1	**TM-P2**	**TM-P4**	**P1-P3**	**P1-P2**	
Pristine	-	-	-	2.261	3.518	0
Fe-Ph	2.393	2.567	2.198	2.261	3.085	1
Co-Ph	2.357	2.512	2.193	2.26	3.052	0
Ni-Ph	2.173	3.343	2.171	2.249	3.386	1
Cu-Ph	2.181	3.634	2.245	2.244	3.427	0
Ru-Ph	2.468	2.641	2.272	2.264	3.154	0
Rh-Ph	2.47	2.637	2.297	2.261	3.127	0
Pd-Ph	2.325	3.235	2.317	2.25	3.383	0
Ag-Ph	2.454	3.162	2.492	2.241	3.363	0
Os-Ph	2.439	2.579	2.296	2.275	3.136	0
Ir-Ph	2.431	2.543	2.309	2.266	3.09	0
Pt-Ph	2.305	3.086	2.303	2.253	3.276	0
Au-Ph	2.318	3.678	2.387	2.25	3.432	0

Table S2: Dissolution potential calculation of TM-Ph SACs**.** ΔG_1 and ΔG_2 correspond to free energies of equations (TM-Ph + $n(H^+ + e^-)$ → nH-Ph + TM) and (TM → $ne^- + TM^{n+}$), respectively. $\Delta G/nH$ indicates the sum of ΔG_1 and ΔG_2 divided by the number of protons. pH_{min} denotes the minimum pH required to achieve $\Delta G/nH=0$ calculated as $pH_{min} = (\Delta G/0.0591*n)$. The standard dissolution potentials are taken from reference 41 in manuscript.

System	Standard dissolution potential(vs. SHE)	Number of electrons(n)	ΔG_1	ΔG_2	$\Delta G/nH$ (pH=0)	pH_{min}
Fe-Ph	-3.030	2	5.796	-0.900	2.448	0.145
Co-Ph	-1.321	2	6.680	-0.560	3.060	0.181
Ni-Ph	-0.407	2	6.025	-0.520	2.752	0.163
Cu-Ph	-0.241	2	4.143	0.680	2.411	0.143
Ru-Ph	-0.272	2	9.837	0.920	5.379	0.318
Rh-Ph	-1.262	2	7.837	1.200	4.518	0.267
Pd-Ph	-1.468	2	4.914	1.900	3.407	0.201
Ag-Ph	-0.197	1	1.881	0.800	2.681	0.158
Os-Ph	-2.790	2	8.698	1.700	5.199	0.307
Ir-Ph	-1.283	3	9.468	3.480	4.316	0.255
Pt-Ph	-0.572	2	6.837	2.360	4.599	0.272
Au-Ph	-0.184	3	3.904	4.500	2.801	0.166

Table S3: O_2 adsorption details on TM-Ph systems

System	Adsorption Mode	Binding Energy (eV)	O-O frequency(cm^{-1})	Magnetic Moment (μ_B)
Fe-Ph	linear	-1.77	1291	2.99
Co-Ph	linear	-0.85	1210	1.81
Ni-Ph	linear	-1.01	1272	0.99
Cu-Ph	linear	-0.45	1272	1.99
Ru-Ph	linear	-1.09	1179	1
Rh-Ph	linear	-0.22	1249	0.48
Pd-Ph	di-sigma	-0.91	1136	1
Ag-Ph	linear	-0.36	1318	0.65
Os-Ph	linear	-1.40	1105	0.99
Ir-Ph	linear	-0.43	1255	1.77
Pt-Ph	linear	-0.89	1189	1
Au-Ph	top	-0.13	1485	2

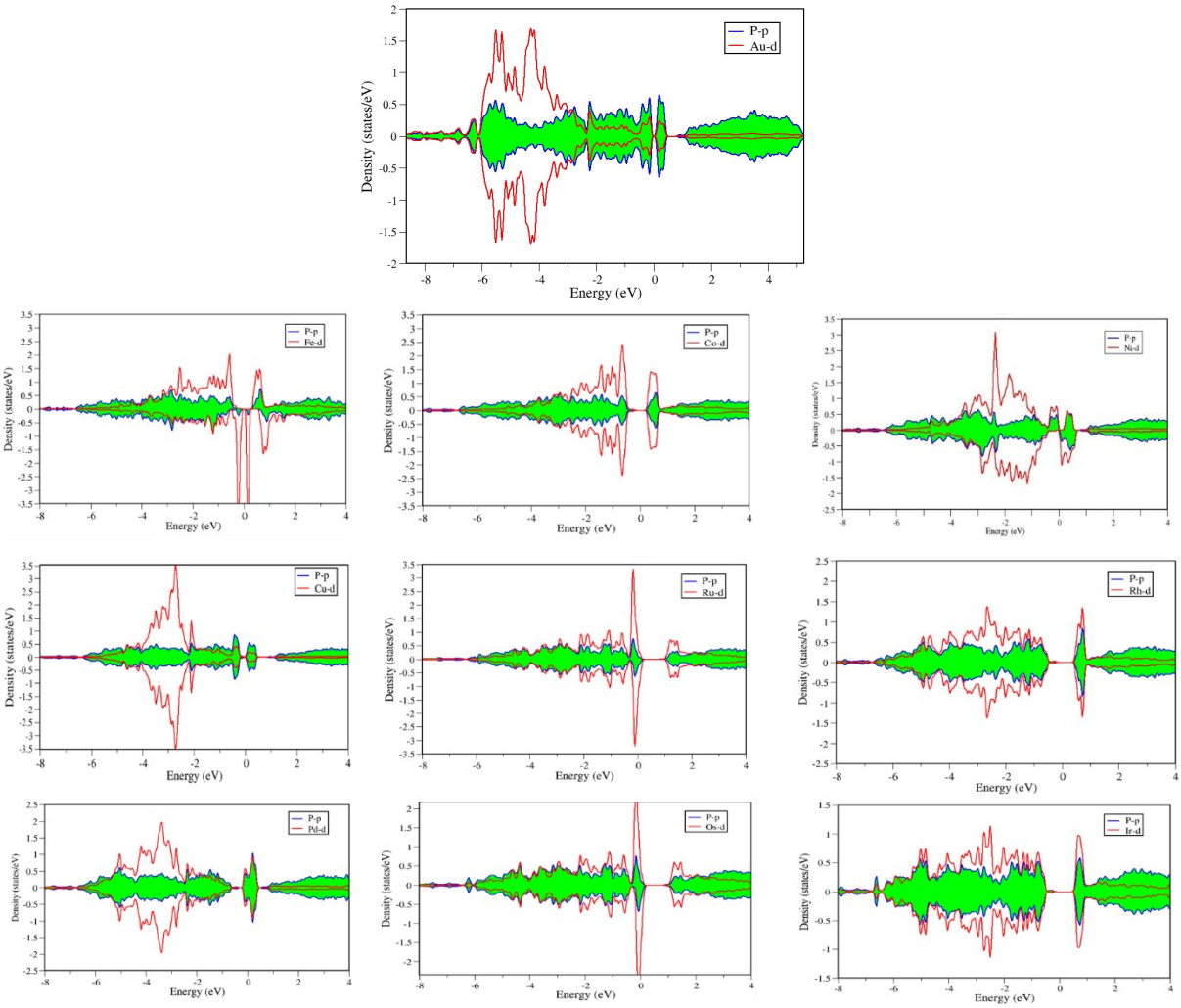

Fig. S1: Projected density of states (PDOS) analysis of TM-d and P-p states in TM-Ph SACs except Pt-Ph. The transition metals are given in insets.

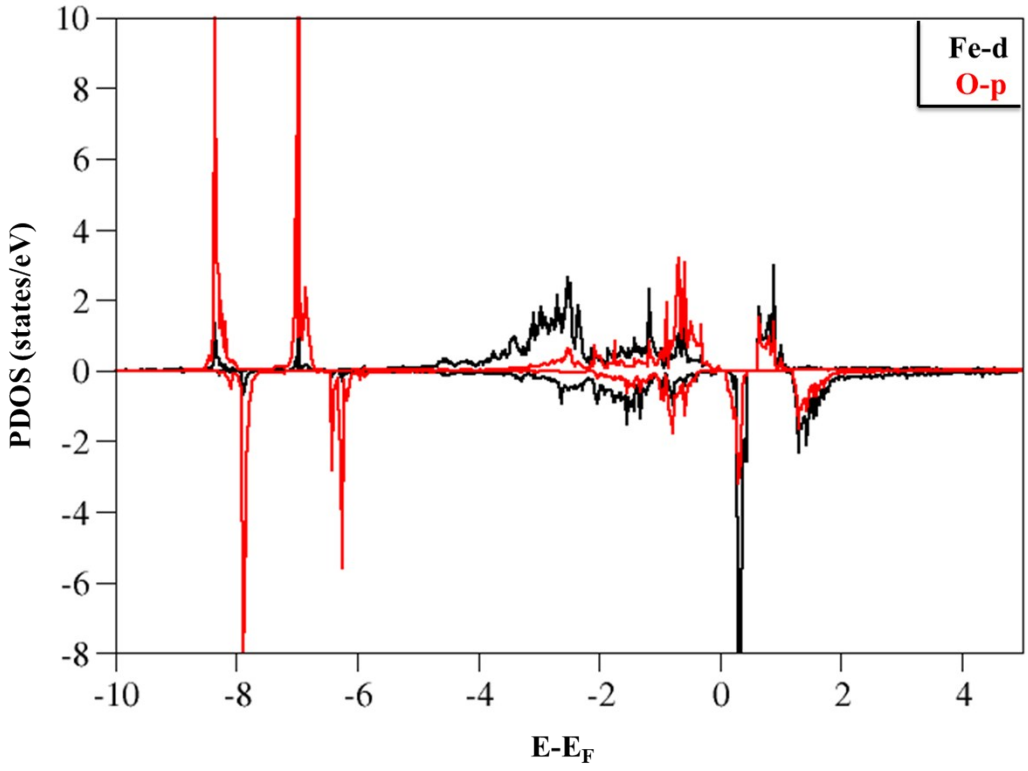

Fig. S2: Projected Density of States (PDOS) of O_2 binding to Fe-Ph SAC.

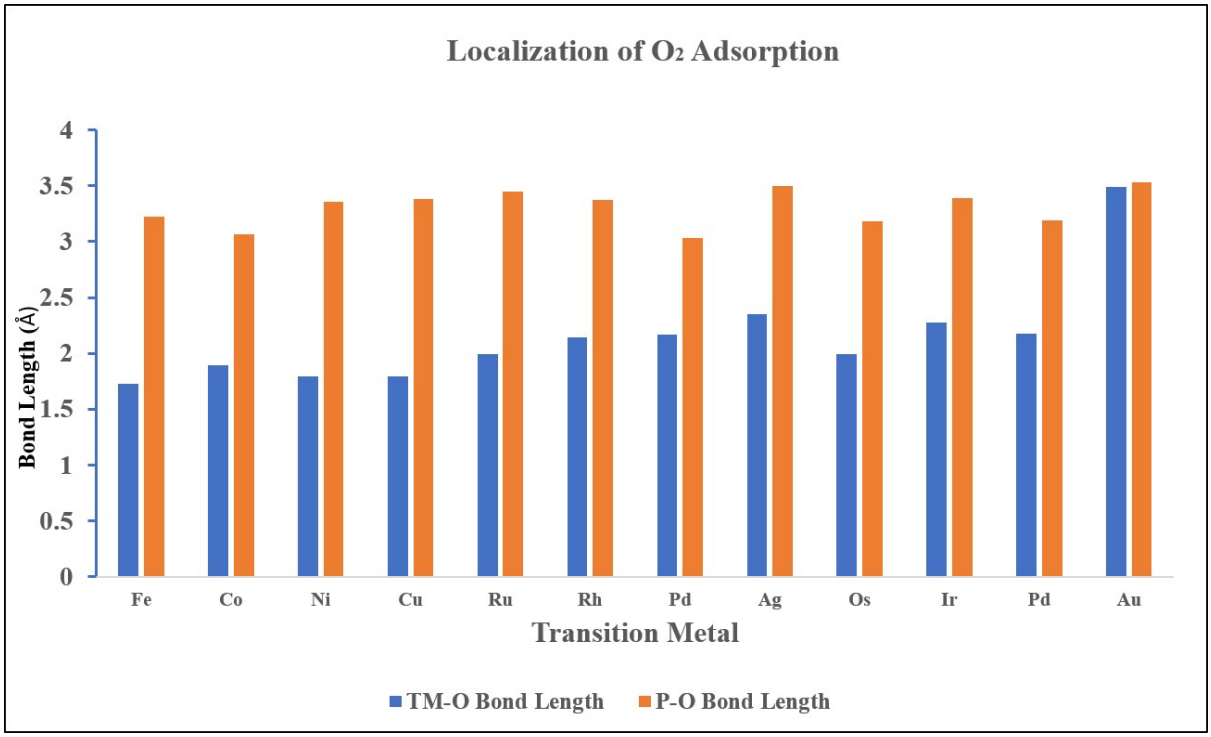

Fig. S3: The comparison of TM-O* and P-O* bond lengths during O_2 binding to TM-Ph SACs. A relatively higher P-O* bond lengths except for Au-Ph confirms localization of O_2 bonding on TM atom.

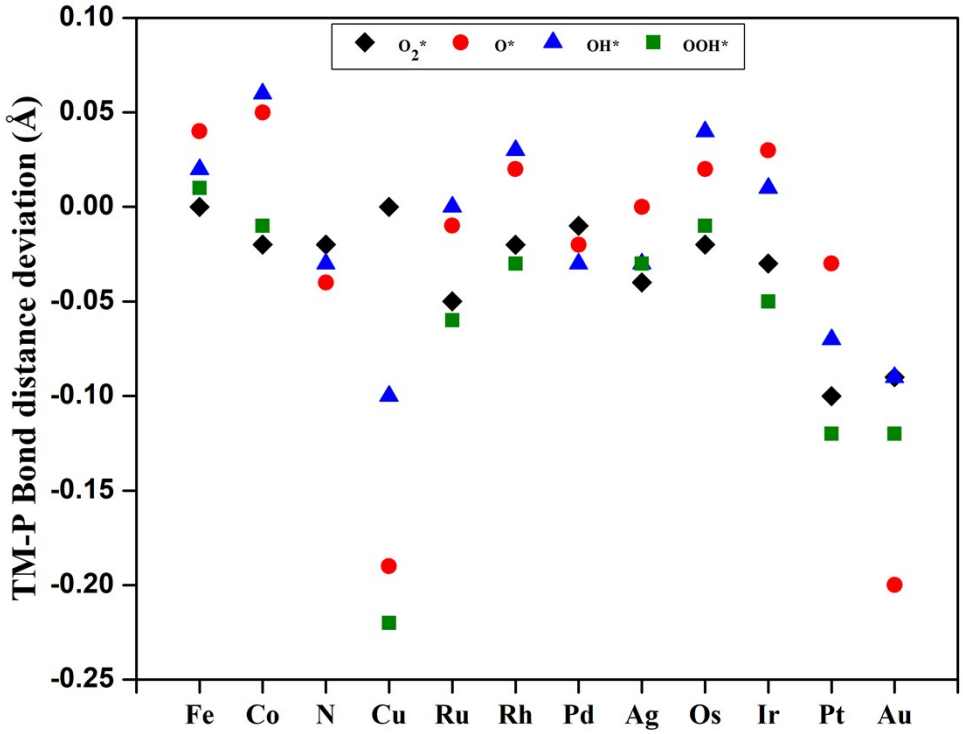

Fig. S4: ORR intermediate adsorption induced bond length variation across the TM-Ph SACs

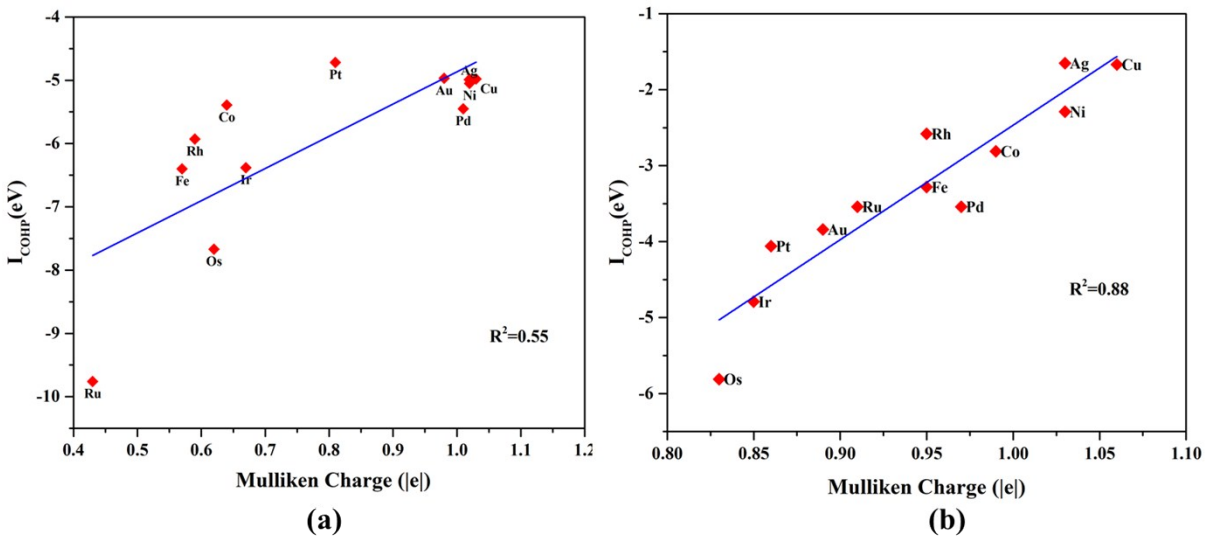

Fig. S5: Correlation between Mulliken's charge transfer and integrated COHP of (a) TM-O* interaction, (b) TM-OH* interaction

Table S4: Layer dependent ORR and HER activity of selected TM-Ph SACs

System	Thickness	Overpotential (V)
Ir-Ph (ORR)	1ML	0.39
	2ML	0.66
	3ML	0.73
Pt-Ph (HER)	1ML	0.01
	2ML	0.11
	3ML	0.08

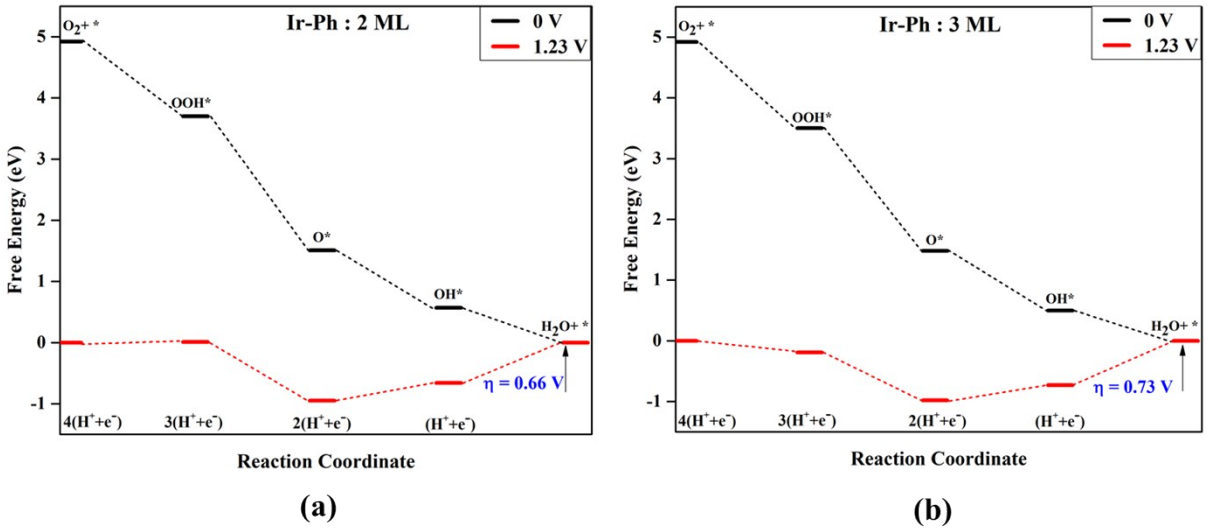

Fig. S6: ORR free energy diagrams of (a) 2ML thick Ir-Ph, (b) 3ML thick Ir-Ph

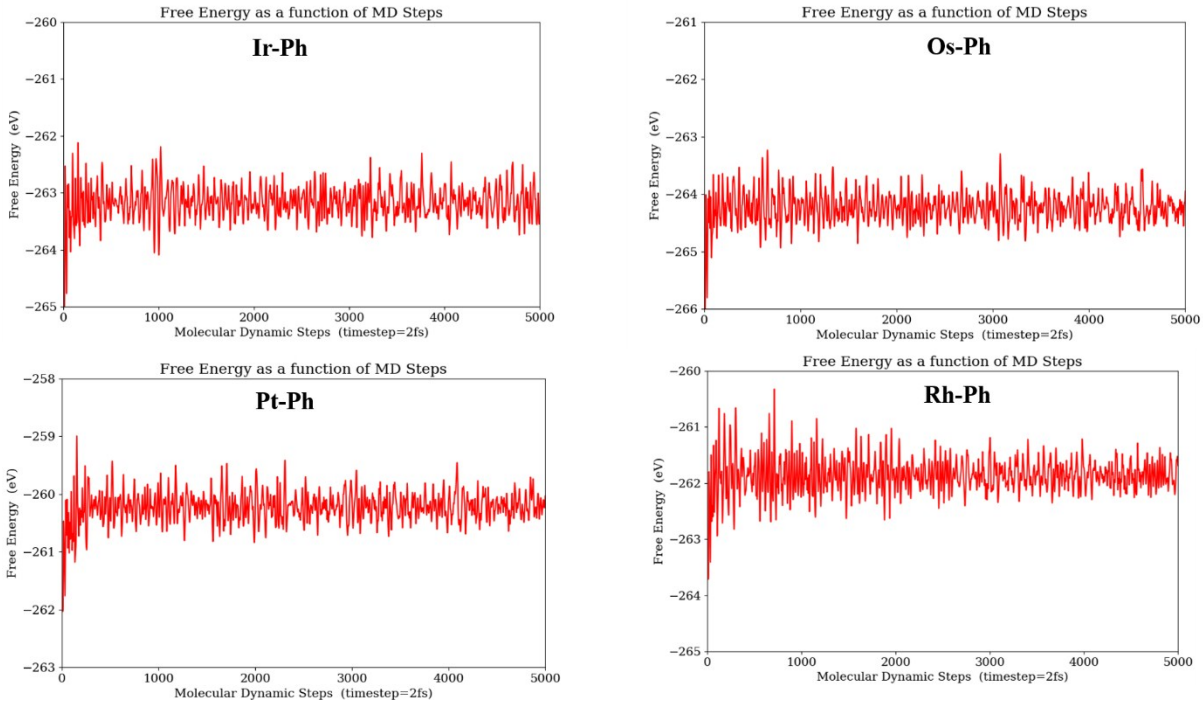

Fig. S7: AIMD simulation of active TM-Ph SACs at 300K for 10 ps.

Table S5: Structural details of O_2 interaction with P atoms of TM-Ph SACs. Pristine phosphorene is given as reference

System	O_2-Physisorbed			O_2-chemisorbed			O_2-dissociated		
	O-O bond length (Å)	P-O bond length(Å)	Magnetic Moment(μ_B)	O-O bond length (Å)	P-O bond length(Å)	Magnetic Moment(μ_B)	O-O bond length (Å)	P-O bond length (Å)	Magnetic Moment(μ_B)
Pristine-Ph	1.24	3.31	2	1.47	1.78	0	2.83	1.50	0
Rh-Ph	1.26	2.73	0	1.48	1.77	0	2.61	1.51	0
Os-Ph	1.24	3.17	1.44	1.48	1.77	0.72	2.59	1.51	0.95
Ir-Ph	1.24	3.25	2	1.48	1.77	0	2.90	1.50	0
Pt-Ph	1.24	3.21	1.08	1.47	1.78	0	2.64	1.50	0

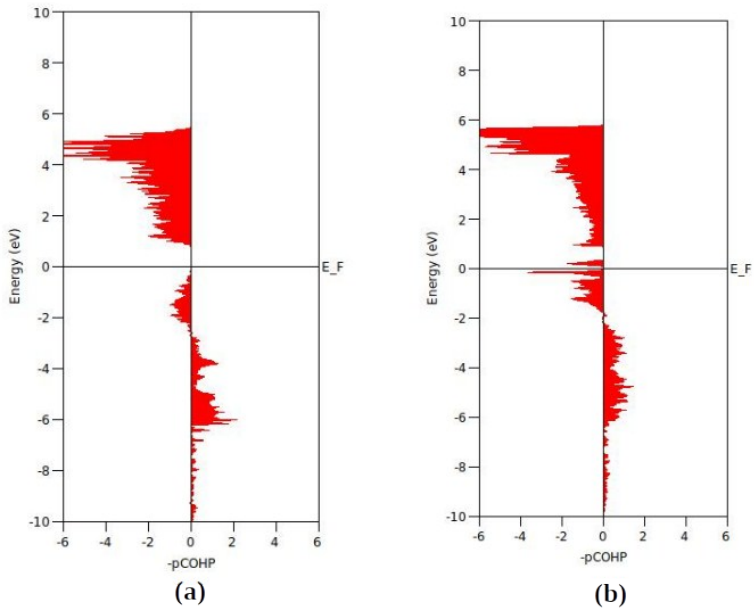

Fig. S8: Projected COHP analysis of (a) O* interaction with pristine Ph, (b) O* interaction with Ir-Ph