Electronic Supporting Information

Combined Healing and Doping of Transition Metal Dichalcogenides Through Molecular Functionalization

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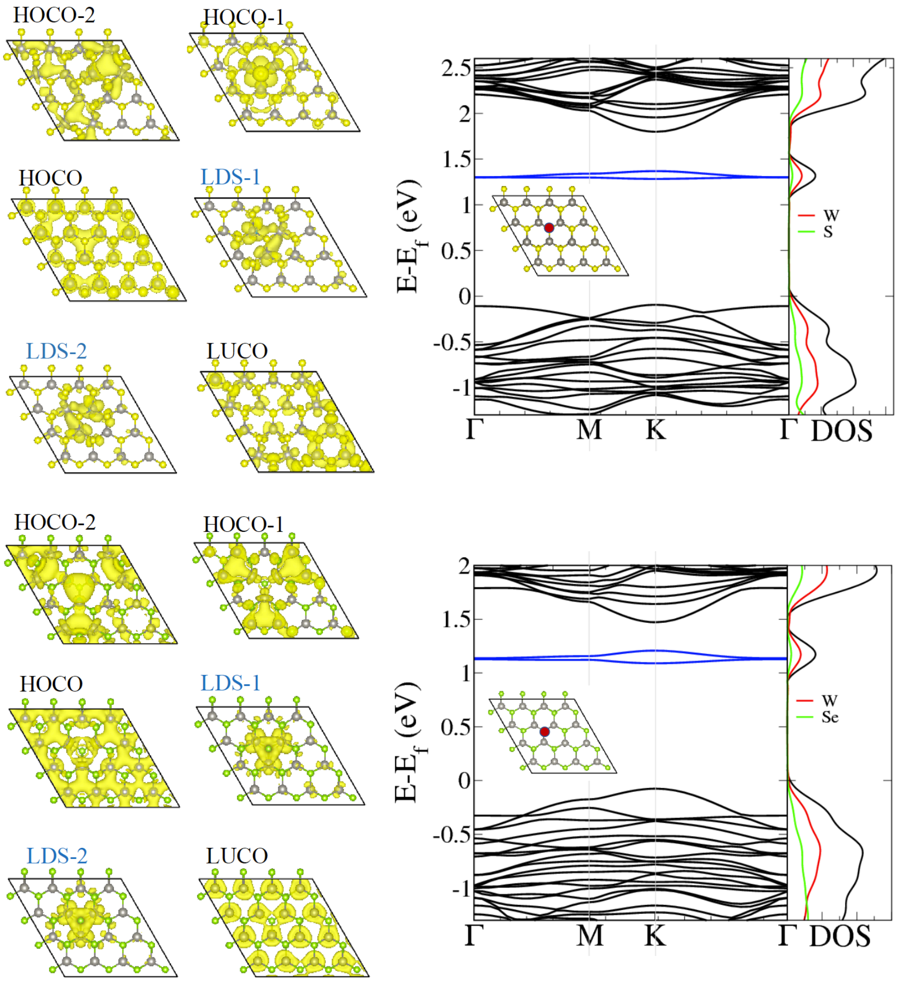


Figure SI-1 Electronic band structure of (a) top: WS_2 and (b) bottom: WSe_2 monolayers in their defective forms with one chalcogen vacancy on a unit cell replicated 4x4x1 times (corresponding to -3% vacancy concentration), along with their band decomposed charge density maps; HOCO (-1/-2) and LUCO correspond to charge density maps of the highest occupied (with -1/-2) and lowest unoccupied crystalline orbitals at the VBM (-1/-2) and CBM, respectively. Localized (mid-gap) defect states are shows with blue lines in the electronic band structure, and the corresponding band decomposed charge density maps of these crystalline orbitals are represented as LDS-1 and LDS-2, for clarity. Inset correspond to the 4x4x1 cell of defective WX_2; X=S & Se surfaces with chalcogen vacancy indicated with a red dot.

Table SI-1: Table: SI-1: Adsorption energy and work function (φ) of different molecular units on defective WS2 and WSe2 monolayers, in the vicinity of vacancy sites calculated by setting E_f=E_{mBG}, wherein E_{mBG} correspond to the middle of the electronic band gap at GGA/PBE (HSE06) level of theory. The axial component of dipole moment induced by the functional molecules (in units of Dby). Negative (positive) sign indicates the induced dipole moment towards (away) from the basal plane of WX_2, X=S/Se, monolayers. Change in work function ($\Delta \phi$) is reported with respective to the defective WX$_2$, X=S/Se, monolayers with -3 % X vacancy concentration.

System	Work function (ϕ)	$\Delta\phi$	Dipole (Dby)	E_{Ads} (kcal/mol)
		WS2		
Pristine	4.79, 4.86 (HSE)	-na-	-na-	-na-
1D-3% Sv	4.71, 4.75 (HSE)	0.0	-na-	-na-
ThH	4.58, 4.62 (HSE)	-0.35	-1.38	11.9
		WSe2		
Pristine	4.31, 4.38 (HSE)	-na-	-na-	-na-
1D-3% SeV	4.25, 4.30 (HSE)	0.0	-na-	-na-
ThH	4.10, 4.11 (HSE)	-0.16	-0.80	19.1

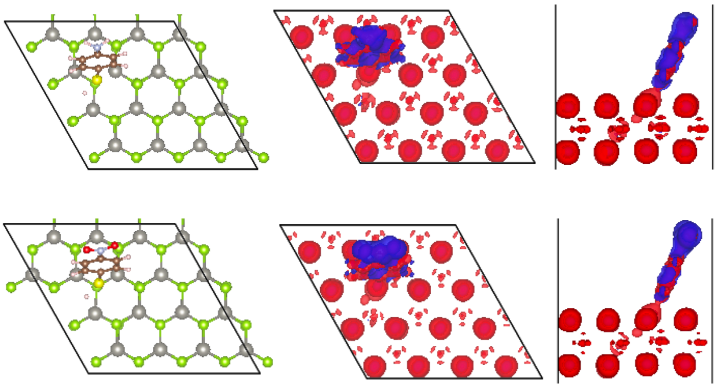


Figure SI-2: Laplacian of charge density maps, showing subtle variations in electron density within the WSe2 surface due to electron donating nature of NH2 unit (top) and electron withdrawing nature of NO2 unit (bottom) of the thiophenol molecule.

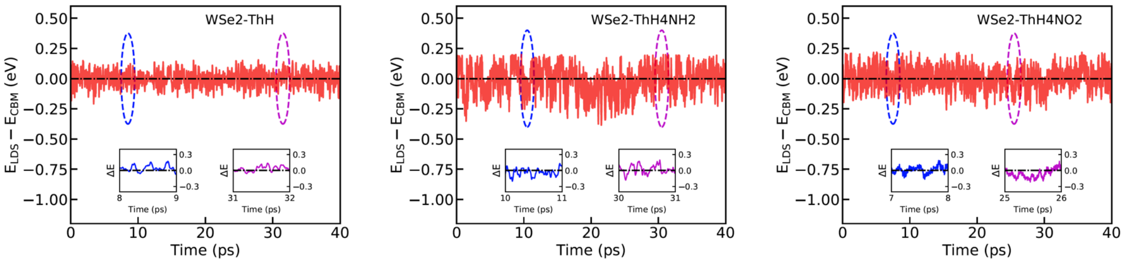


Figure SI-3 Energy difference ($E_{LDS} - E_{CBM}$) between partially recovered localized mid-gap defect state (E_{LDS}) and conduction band minimum (E_{CBM}) for (a) left: thiophenol molecule (ThH), (b) middle: NH2 decorated thiophenol molecule (ThH4NH2) and (c) right: NO2 decorated thiophenol molecule (ThH4NO2) adsorbed on WSe2-3%SeV surface. If the energy difference is close to zero (farther from zero), the LDS state merges (moves away from) with CBM giving complete (partial) recovery of electronic structure . Fluctuations of $E_{LDS} - E_{CBM}$, used as a proxy for the recovery of the pristine electronic structure, indeed occur on a sub-ps timescale, as indicated by the insets. Zero of the energy difference ($E_{LDS} - E_{CBM}$) is indicated with a (dotted) black line, for clarity.

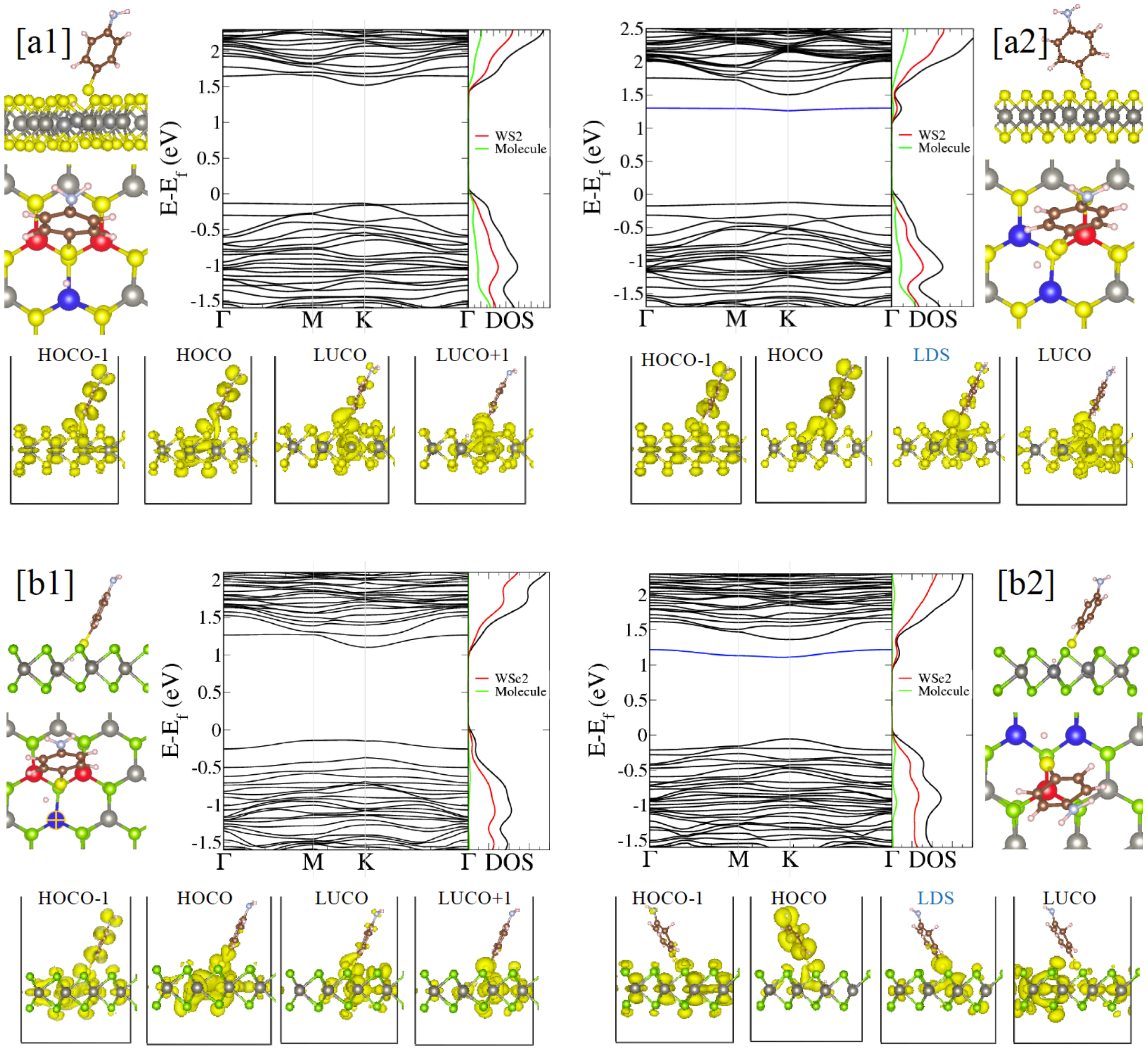


Figure SI-4 Electronic band structure of (i) top: WS2 and (ii) bottom: WSe2 defective monolayers functionalized with NH$_2$ substituted thiophenol molecules (ThH-4NH$_2$) extracted at different abMD times steps, along with their band decomposed charge density maps; HOCO (-1) and LUCO (+1) correspond to charge density maps of the highest occupied (with -1) and lowest unoccupied (+1) crystalline orbitals at the VBM (-1) and CBM (+1), respectively. Partially recovered localized (mid-gap) defect state, in configurations [a2] and [b2], is show with blue line in the electronic band structure and the corresponding band decomposed charge density map (crystalline orbitals) are represented as LDS, for clarity.

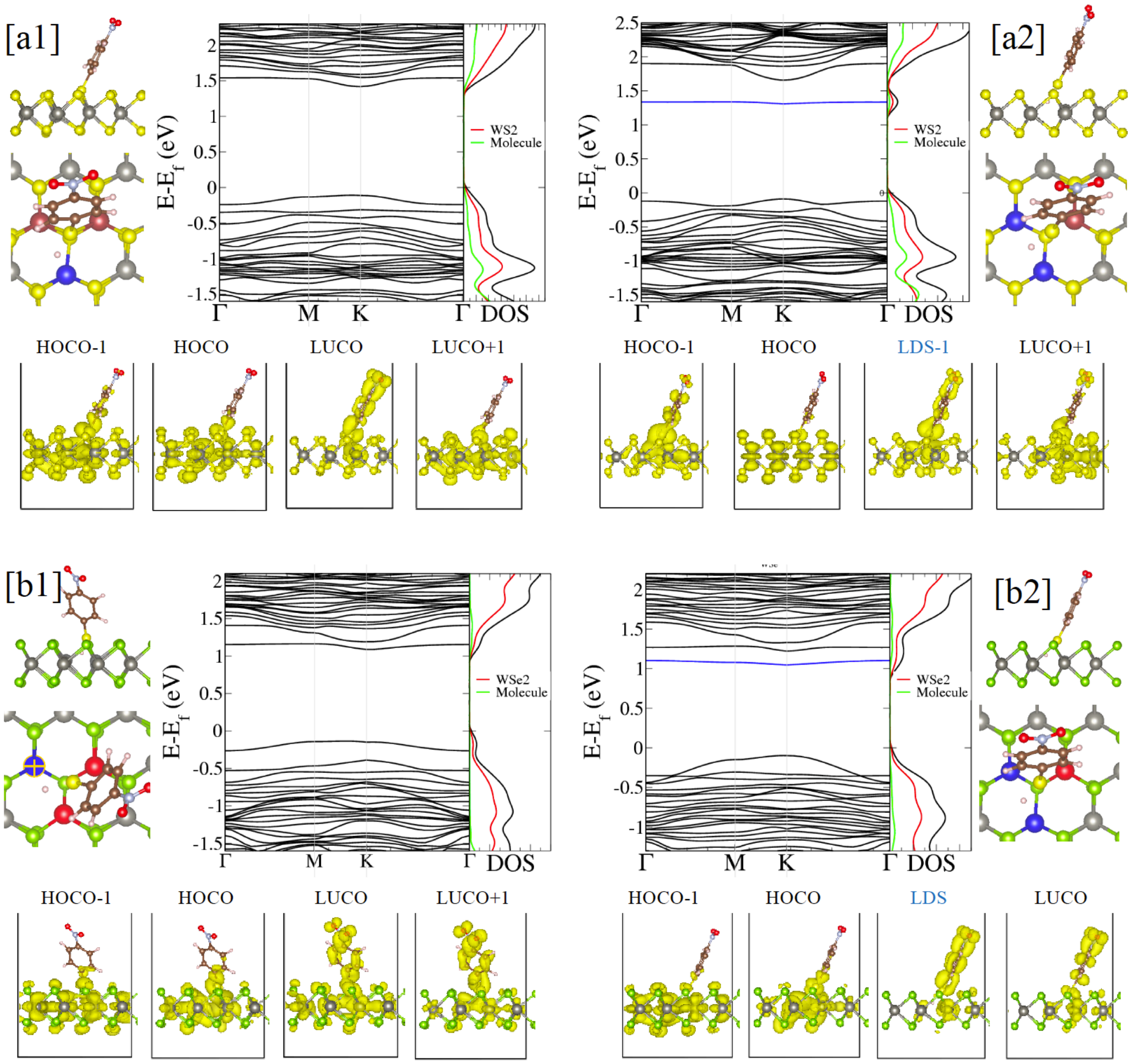


Figure SI-5 Electronic band structure of (i) top: WS2 and (ii) bottom: WSe2 defective monolayers functionalized with NO_2 substituted thiophenol molecules (ThH-4NO_2) extracted at different abMD times steps, along with their band decomposed charge density maps; HOCO (-1) and LUCO (+1) correspond to charge density maps of the highest occupied (with -1) and lowest unoccupied (+1) crystalline orbitals at the VBM (-1) and CBM (+1), respectively. Partially recovered localized (mid-gap) defect state, in configurations [a2] and [b2], is show with blue line in the electronic band structure and the corresponding band decomposed charge density map (crystalline orbitals) are represented as LDS, for clarity.

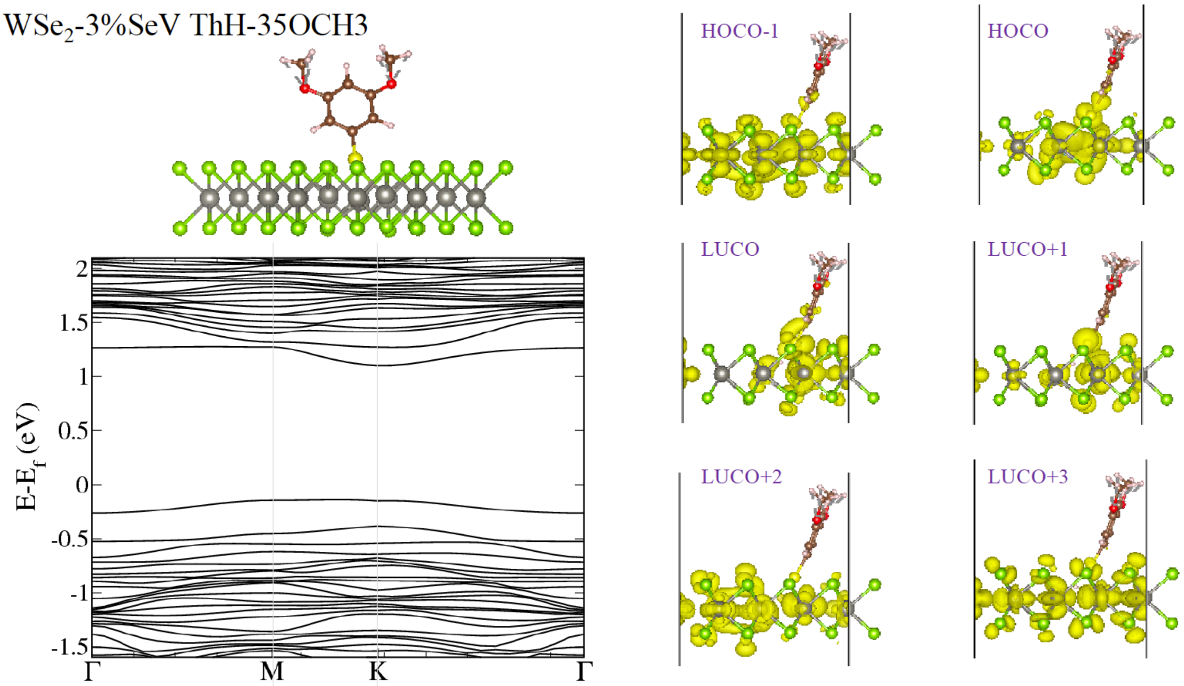


Figure SI-*6*: Electronic band structure of defective WSe2 monolayers functionalized with Th35OCH3 thiophenol molecules extracted at the abMD times steps where thiol (hydrogen) atom is close to two (one) of the neighboring tungsten atoms in the vicinity of chalcogen vacancy, along with their band decomposed charge density maps; HOCO (-1) and LUCO (+3) correspond to charge density maps of the highest occupied (with -1) and lowest unoccupied (+3) crystalline orbitals at the VBM (-1) and CBM (+1), respectively. A complete recovery of the mid-gap defect states could be observed from the electronic band structure, with electron density delocalized along the basal WSe2 monolayer.

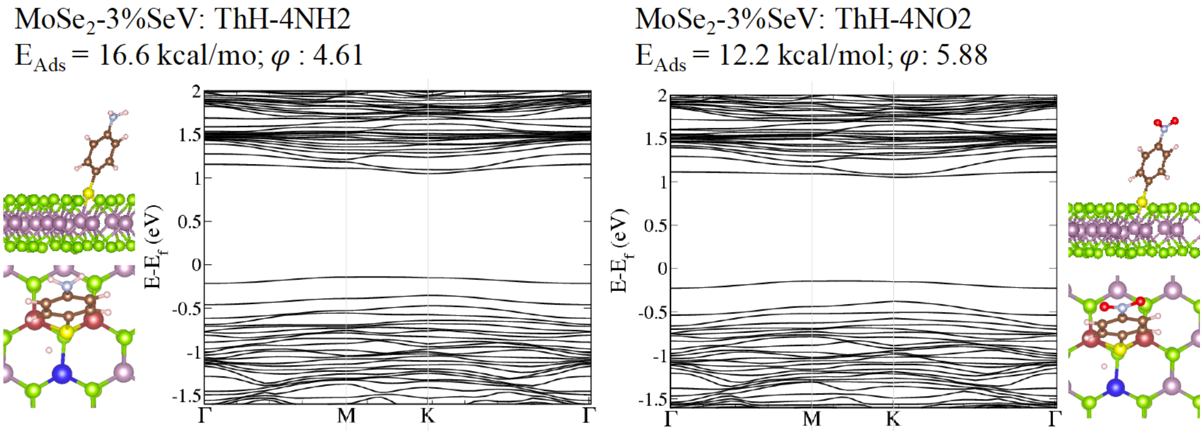


Figure SI-7: Electronic band structure of defective $MoSe_2$-3% SeV monolayers functionalized with (a) left: ThNH2 and (b) right: ThNO2 units, with calculated work function and adsorption energies. The work function of defective $MoSe_2$-3%SeV monolayers is found to be 5.31. The atomic configuration, extracted from abMD simulation trajectory, corresponds to the case where thiol (hydrogen) atom is close to two (one) of the neighboring tungsten atoms in the vicinity of chalcogen vacancy, thereby generating full-recovery of mid-gap defect states in the electronic structure.

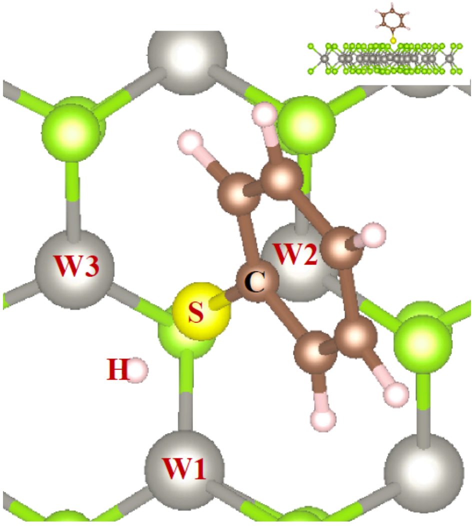


Figure SI-8 Atoms considered in the vicinity of chalcogen vacancy to characterize the interaction strength between defective WX_2; X=S/Se monolayers and the passivating (functionalized) thiophenol molecules.

For the first atomic configuration where the thiol atom is in the vicinity of two tungsten atoms, as reported in Figures 4, SI-3 and SI-4: a1 & b1, the bond order and overlap populations of hydrogen atom with the remaining tungsten atom in defective WS_2 monolayers are ≤ 0.62 and ≤ 0.51, respectively; these are ≤ 0.70 and ≤ 0.55, respectively, in WSe_2 monolayers (Figures , SI3- and SI-4: a1 & b1, W atoms in blue). For the alternative atomic configurations, where the thiol atom from the passivating molecule is in the vicinity of only one tungsten atom as reported in Figures 4, SI-3 and SI-4: a2 & b2, the bond order and overlap populations of hydrogen atom with the remaining two tungsten atoms in defective WS_2 monolayers are ≤ 0.50 and ≤ 0.38, respectively; they are ≤ 0.58 and ≤ 0.45, respectively, for WSe_2 monolayers (Figures 4, SI-3 and SI-4: a2 & b2, W atoms in blue).

Table SI-2: DDEC6 - bond order and overlap population parameters pertaining to different configurations of (functionalized) thiophenol adsorbed WS2 and WSe2 monolayers, reported in Figs. 4, 5 and 6, respectively.

Config.	Parameter	W1-H	W2-H	W3-H	W1-S	W2-S	W3-S	S-H	S-C
WS2: ThH									
Config: a1	Bond Order	0.13	0.02	0.57	0.45	0.51	0.08	0.23	1.01
	Overlap Pop.	0.11	0.01	0.42	0.38	0.42	0.05	0.19	0.68
Config: a2	Bond order	0.46	0.47	0.05	0.10	0.09	0.51	0.23	1.05
	Overlap Pop.	0.35	0.37	0.03	0.07	0.07	0.40	0.18	0.71
WS2: ThH-4NH2									
Config: a1	Bond Order	0.12	0.03	0.62	0.49	0.57	0.05	0.36	1.08
	Overlap Pop.	0.10	0.03	0.51	0.39	0.47	0.03	0.28	0.69
Config: a2	Bond Order	0.49	0.40	0.03	0.07	0.13	0.54	0.24	1.07
	Overlap Pop.	0.38	0.30	0.03	0.07	0.10	0.41	0.18	0.70
WS2: ThH-4NO2									
Config: a1	Bond Order	0.03	0.03	0.62	0.35	0.40	0.05	0.36	1.08
	Overlap Pop.	0.02	0.03	0.51	0.27	0.31	0.03	0.27	0.72
Config: a2	Bond Order	0.50	0.39	0.03	0.07	0.15	0.54	0.24	1.07
	Overlap Pop.	0.38	0.30	0.03	0.07	0.11	0.40	0.19	0.71
WSe2: ThH									
Config: b1	Bond order	0.03	0.09	0.70	0.60	0.55	0.05	0.34	1.04
	Overlap Pop.	0.02	0.07	0.55	0.45	0.42	0.04	0.29	0.72
Config: b2	Bond Order	0.49	0.46	0.03	0.10	0.11	0.55	0.31	0.71
	Overlap Pop.	0.37	0.35	0.02	0.08	0.10	0.41	0.21	0.71
WSe2: ThH-4NH2									
Config: b1	Bond Order	0.30	0.02	0.58	0.57	0.63	0.08	0.24	1.02
	Overlap Pop.	0.24	0.02	0.43	0.48	0.51	0.06	0.19	0.69
Config: b2	Bond Order	0.58	0.48	0.03	0.09	0.13	0.64	0.21	0.14
	Overlap Pop.	0.45	0.39	0.02	0.08	0.11	0.47	0.16	0.73
WSe2: ThH-4NO2									
Config: b1	Bond Order	0.12	0.02	0.58	0.45	0.64	0.08	0.24	1.02
	Overlap Pop.	0.10	0.02	0.43	0.36	0.52	0.07	0.19	0.68
Config: b2	Bond Order	0.53	0.48	0.03	0.09	0.13	0.64	0.21	1.14
	Overlap Pop.	0.45	0.40	0.02	0.08	0.11	0.47	0.19	0.73

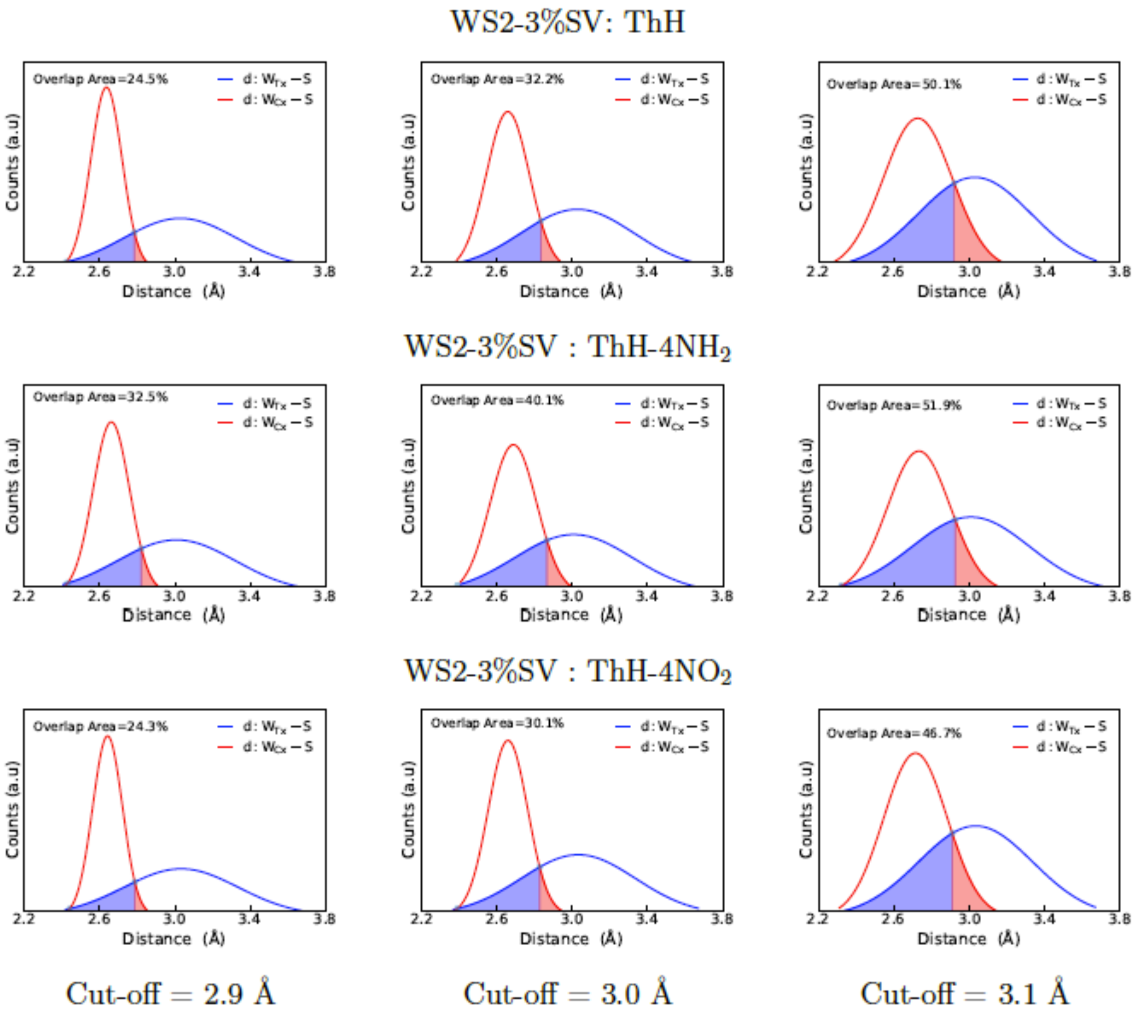
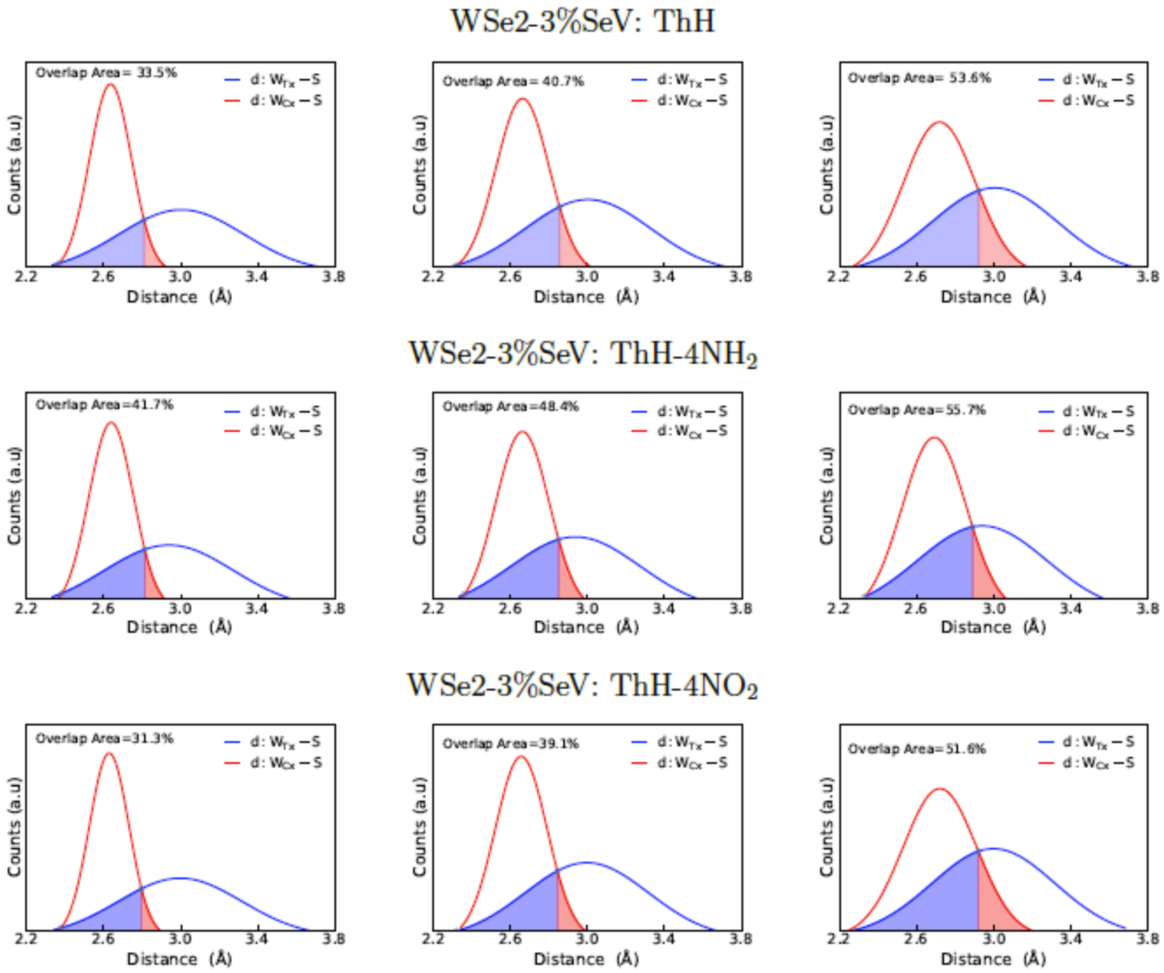


Figure SI-9: WS2-3%SV with Thiophenol molecule; Distribution of distances between thiol atom and 3 tungsten atoms in the vicinity of chalcogen vacancy extracted from abMD configurations over 40 ps of simulation time is indicated with red curves. W-Thiol distances within the arbitrarily defined (maximum) cut-off distance set to 2.9 Å, 3.0 Å and 3.1 Å, reported from left to right respectively, is indicated in blue. Overlap area between the red and blue curves correspond to the percentage (fraction) of abMD configurations when the thiol atom is in the vicinity of two tungsten atoms within the specified cut-off distance. Top, Middle and Bottom images correspond to ThH, ThH-4NH2 and ThH-4NO2 molecules passivating the chalcogen vacancy in WS2-3%SV monolayers.



Cut-off = 2.9 Å Cut-off = 3.0 Å Cut-off = 3.1 Å

Figure SI-10: WSe2-3%SeV with Thiophenol molecule; Distribution of distances between thiol atom and 3 tungsten atoms in the vicinity of chalcogen vacancy extracted from abMD configurations over 40 ps of simulation time is indicated with red curves. W-Thiol distances within the arbitrarily defined (maximum) cut-off distance set to 2.9 Å, 3.0 Å and 3.1 Å, reported from left to right respectively, is indicated in blue. Overlap area between the red and blue curves correspond to the percentage (fraction) of abMD configurations when the thiol atom is in the vicinity of two tungsten atoms within the specified cut-off distance. Top, Middle and Bottom images correspond to ThH, ThH-4NH2 and ThH-4NO2 molecules passivating the chalcogen vacancy in WSe2-3%SeV monolayers.

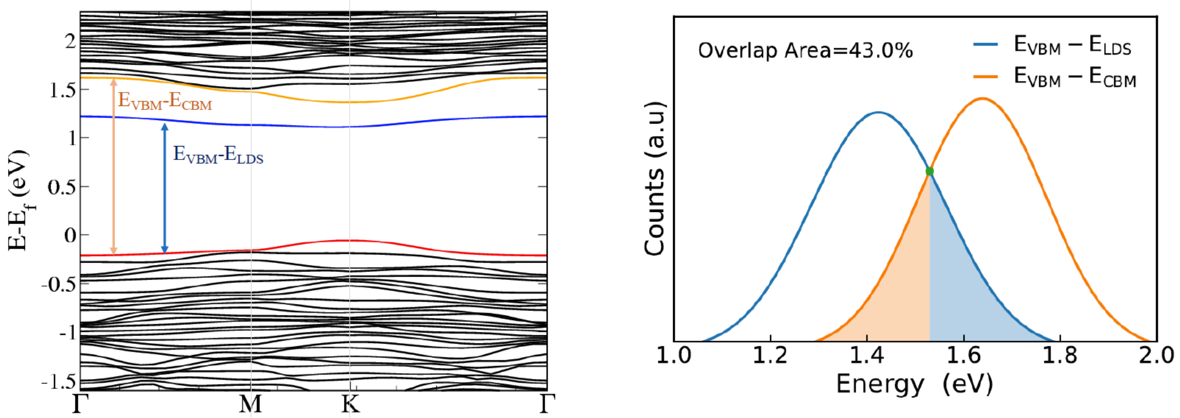


Figure SI-11: Distribution pertaining to the energy difference between VBM and localized defect state (LDS, in blue) and the difference between VBM and CBM (in orange). The overlap (shaded) region is when LDS merges with CBM and correspond to the atomic conformation when thiol atom is in the vicinity of two tungsten atom, generating full recovery of electronic band structure. The VBM, LDS and CBM are indicated as red, blue and orange curves, respectively, in the corresponding electronic band structure of WSe2-3%SeV with ThH-4NH2 molecule.

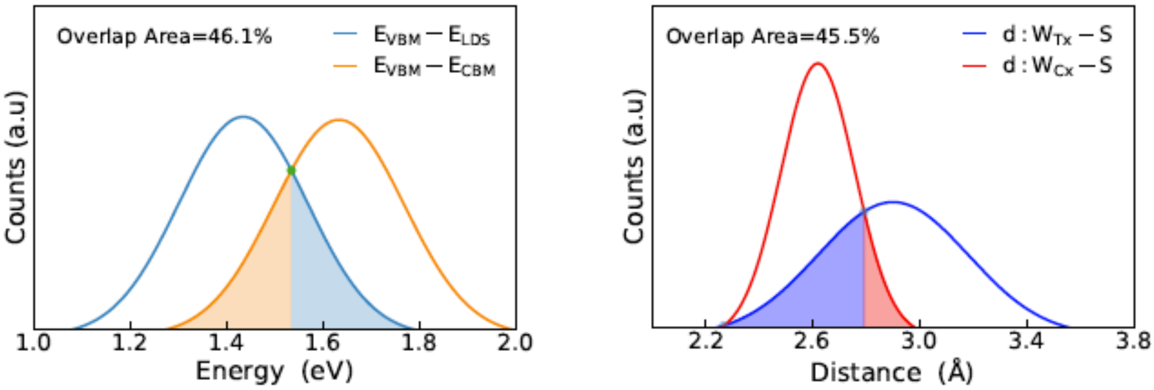


Figure SI-12: Distribution analysis of WSe2-3% SeV with ThH-35OCH3 molecule pertaining to (a) left: the energy difference between VBM and localized defect state (LDS, in blue) and the difference between VBM and CBM (in orange) and (b) the distance between passivating thiol atom and all the three tungsten atoms in the vicinity of chalcogen vacancy (in blue) and the distribution obtained by arbitrarily selecting a cut-off distance of 2.9 Å (in red). The overlap (shaded) region on the left image is when LDS merges with CBM and correspond to the atomic conformation when thiol atom is in the vicinity of two tungsten atom, whereas the overlap (shaded) region on the right image is the distance dependent distribution which indicates the percentage of atomic configurations when thiol atom is close to two of the three tungsten atoms with a mean distance of ≈ 2.6 Å generating full recovery of electronic band structure.

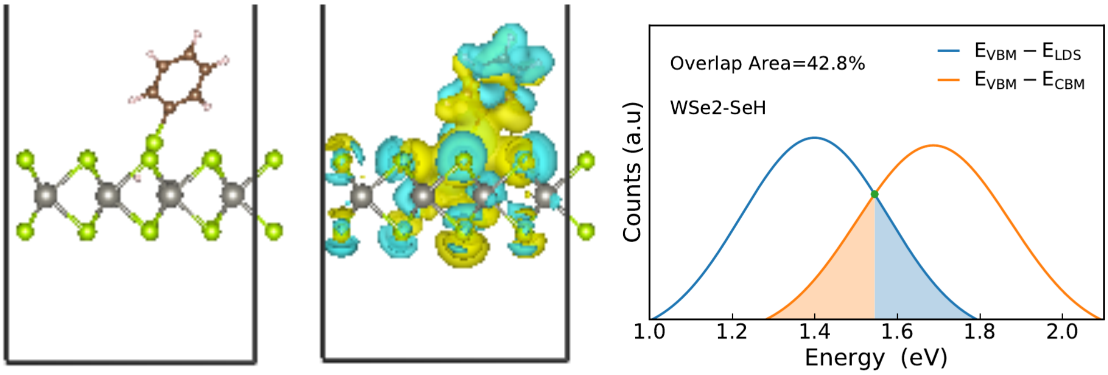


Figure SI-13 Distributions pertaining to the energy difference between VBM and localized defect state (LDS): E_{VBM}-E_{LDS} (in blue) and the energy difference between VBM and CBM: E_{VBM}-E_{CBM} (in orange) for benzeneselenol adsorbed WSe_2-3% SeV monolayers. The overlap (shaded) region is when LDS merges with CBM and correspond to the atomic conformation when thiol atom is in the vicinity of two tungsten atom, generating a full recovery of electronic band structure. Left and middle images correspond to the atomic configuration and the charge density difference plot.