Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical Characterization of the Electronic Properties of Heterogeneous Vertical Stacks of 2D Metal Dichalcogenides Containing one Doped Layer

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Systems	a(A°)	d (A°)	E_b (eV)	X-S / X-Se length
MoS_2	**15.58**			**$L_{(Mo—S)}$:2.39**
WS_2	**15.64**			**$L_{(W—S)}$: 2.40**
WSe_2	**16.26**			**$L_{(W—Se)}$: 2.51**
WS_2/MoS_2	**15.62**	**2.86**	**-2.83**	**$L_{(W—S)}$: 2.40** **$L_{(Mo—S)}$: 2.39**
WSe_2/MoS_2	**15.95**	**2.89**	**-3.05**	**$L_{(W—Se)}$: 2.51** **$L_{(Mo—S)}$: 2.41**

Table S1: Optimized lattice constant a (in Å) of the super cell, interlayer distance d (in Å), binding energy E_b (in eV) and bond lengths (in Å).

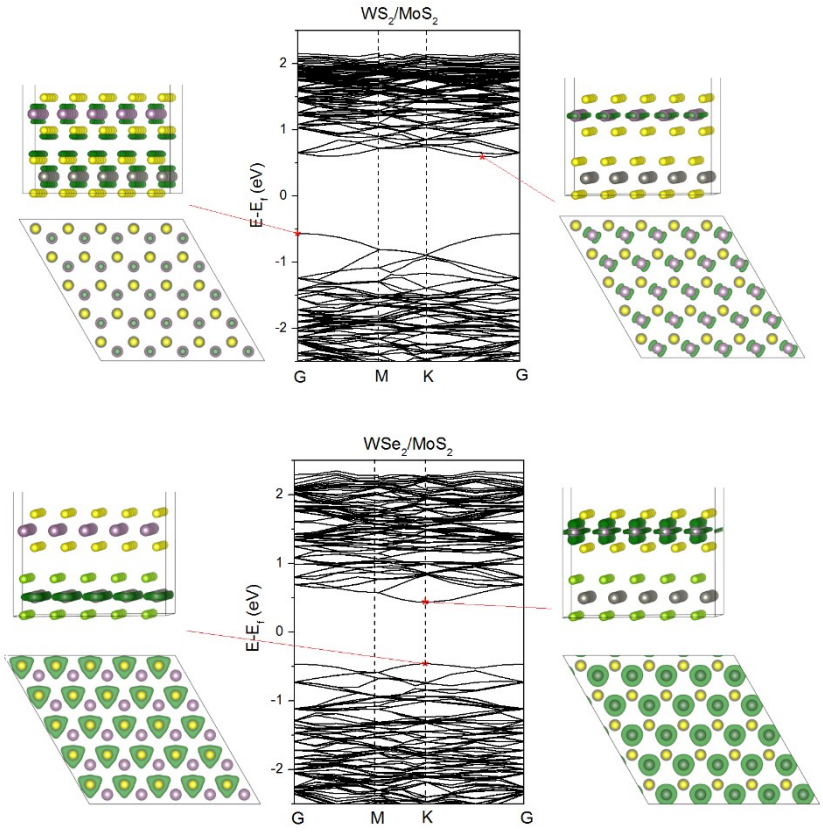


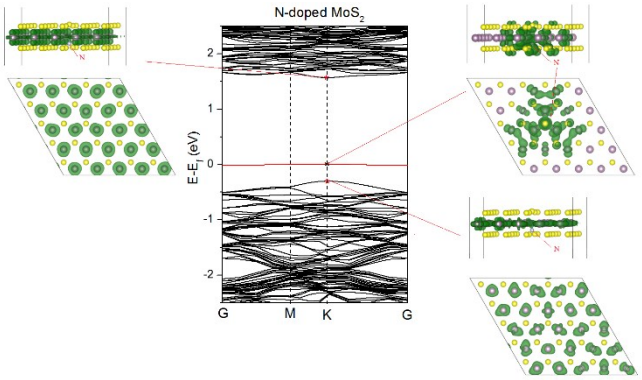
Figure S1: Band structure of the hetero-bilayers with band-decomposed charge density isosurfaces of the valence band maximum (VBM) and conduction band minimum (CBM).

systems	a (A°)	d (A°)	E_b (eV)	$L_{(X\text{-}S) \text{ or } (X\text{-}Se)}$ bond length (Ang)
MoS_{N2}	15.58	-	-	$L_{(Mo—N)}$: 1.98
$Mo_{Nb}S_2$	15.61	-	-	$L_{(Nb—S)}$: 2.42
WS_{F2}	15.63	-	-	$L_{(W—F)}$: 2.59
$W_{Re}S_2$	15.58	-	-	$L_{(Re—S)}$: 2.44
WSe_{F2}	16.21	-	-	$L_{(W—F)}$: 2.24
$W_{Re}Se_2$	16.28	-	-	$L_{(Re—Se)}$: 2.52
WS_{F2}/MoS_2	15.61 (↓0.1%)	2.80 (↓2.1%)	-2.75 (↓2.73%)	$L_{(W—F)}$: 2.54, $L_{(Mo—S)}$: 2.39
WSe_{F2}/MoS_2	15.92 (↑0.1%)	2.86 (↓1.05%)	-3.21 (↑5.08%)	$L_{(W—F)}$: 2.18, $L_{(Mo—S)}$: 2.40
$W_{Re}S_2/MoS_2$	15.62 (↓0.001%)	2.79 (↓2.45%)	-2.94 (↑4.0%)	$L_{(Re—S)}$: 2.44, $L_{(Mo—S)}$: 2.39
$W_{Re}Se_2/MoS_2$	15.95 (↑0.3%)	2.88 (↓0.7%)	-3.37 (↑9.7%)	$L_{(Re—Se)}$: 2.53, $L_{(Mo—S)}$:2.41
WS_2/MoS_{N2}	15.62 (↓0.001%)	2.78 (↓2.88%)	-2.92 (↑3.32)	$L_{(W—S)}$ 2.40, $L_{(Mo—N)}$ 1.98
WSe_2/MoS_{N2}	15.93 (↑0.19%)	2.86 (↓1.40%)	-3.25 (↑6.10%)	$L_{(W—Se)}$: 2.50, $L_{(Mo—N)}$: 2.00
$WS_2/Mo_{Nb}S_2$	15.65 (↑0.17%)	2.79 (↓2.51%)	-3.13 (↑9.70%)	$L_{(W—S)}$: 2.40, $L_{(Nb—S)}$: 2.42
$WSe_2/Mo_{Nb}S_2$	15.96 (↑0.39%)	2.88 (↓0.7%)	-3.52 (↑13.30%)	$L_{(W—Se)}$:2.51 , $L_{(Nb—S)}$: 2.44

Table S2: Lattice constant, interlayer distance, binding energy of substitutionally doped hetero-structures. We report between parentheses the relative shifts with respect to the pristine systems.

System	Q_{bader} (|e|)	μ (D)
WS_2/MoS_2	+0.03/-0.03	0.25
WSe_2/MoS_2	+0.37/-0.37	1.18
WS_{F2}/MoS_2	+0.06/-0.06 (↑100%)	1.36 (↑444%)
WSe_{F2}/MoS_2	+0.63/-0.63 (↑71%)	3.03 (↑156.8%)
$W_{Re}S_2/MoS_2$	+0.23/-0.23 (↑666%)	1.62 (↑548%)
$W_{Re}Se_2/MoS_2$	+0.67/-0.67 (↑82%)	3.13 (↑165.26)
WS_2/MoS_{N2}	+0.16/-0.16 (↑433%)	1.05 (↑320%)
WSe_2/MoS_{N2}	+0.55/-0.55 (↑49%)	2.05 (↑73.73%)
$WS_2/Mo_{Nb}S_2$	+0.24/-0.24 (↑700%)	1.70 (↑580%)
$WSe_2/Mo_{Nb}S_2$	+0.62/-0.62 (↑68%)	2.65 (↑124.58%)

Table S3: Bader charge on the individual sheets and total dipole moment along the z direction in the bilayer with substitutional doping. We report between parentheses the relative changes with respect to the pristine systems.


N-doped MoS2
E-EF (eV)
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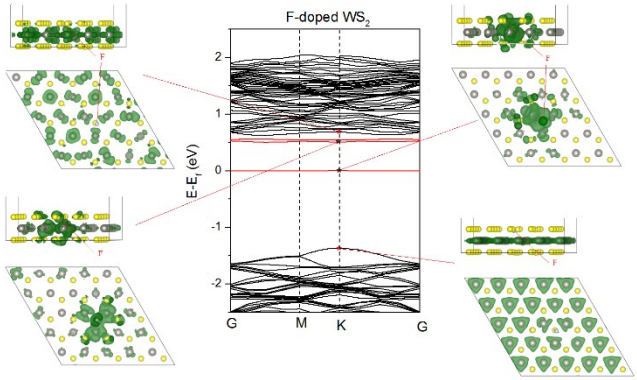
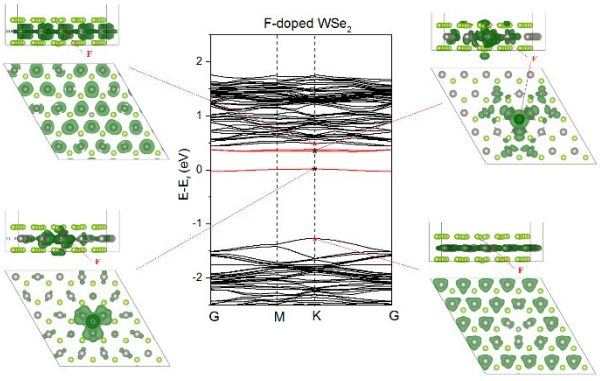
1
0
-1
-2
G
M
K
G


F-doped WS2
E-EF (eV)
2
1
0
-1
-2
G
M
K
G


F-doped WSe2
E-EF (eV)
2
1
0
-1
-2
G
M
K
G

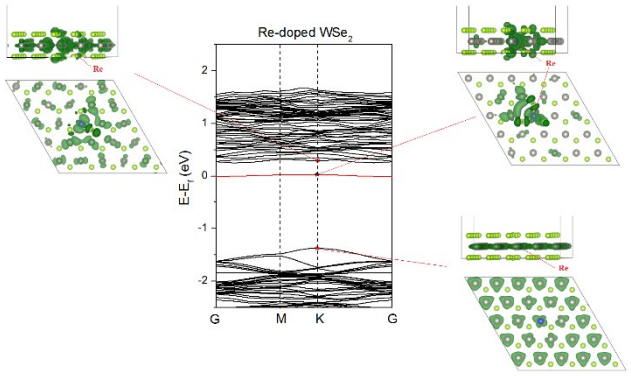


Figure S2: Band structure of substitutionally doped monolayers, showing the half-filled occupied trap states within the gap, with relevant band-decomposed charge density isosurfaces. The total contribution of the dopant in the trap levels is ~15% for N, ~7% for F, and ~48% for Re.

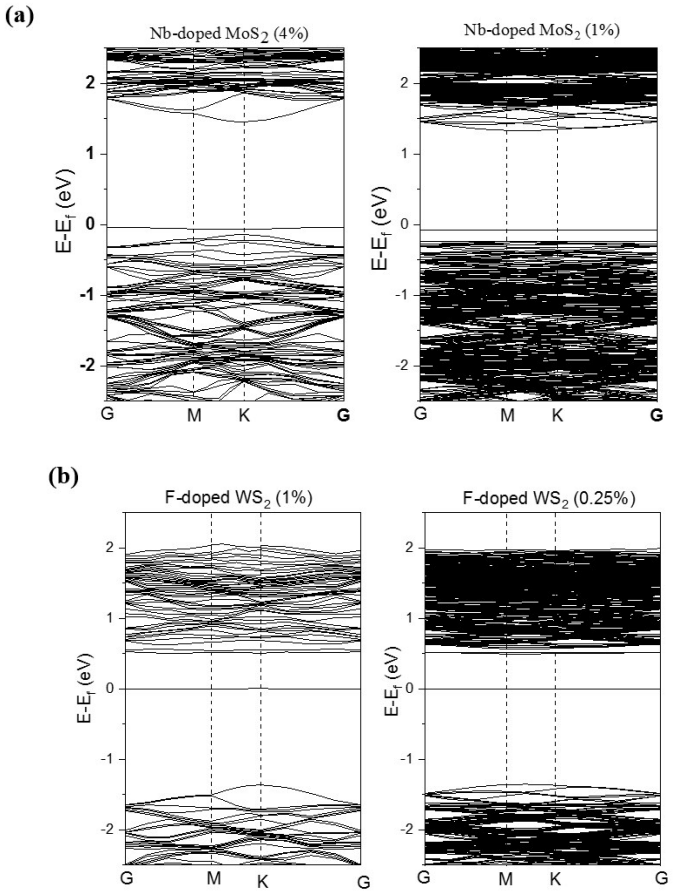
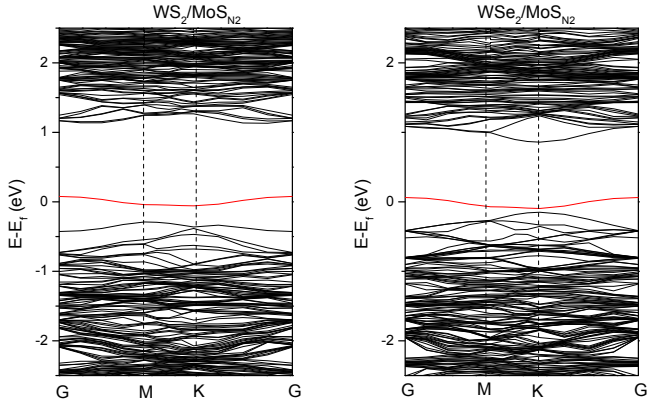
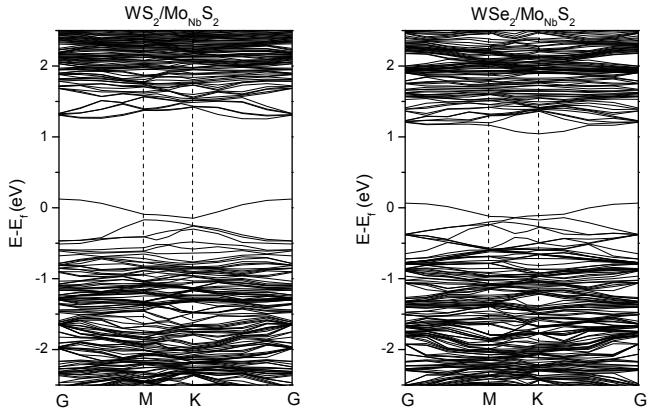


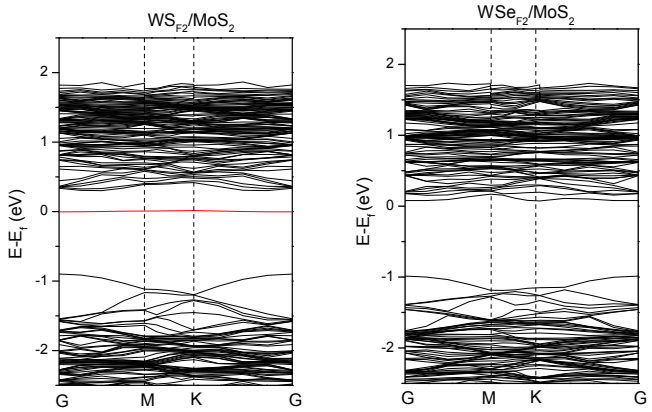
Figure S3: Band structure of substitutionally doped monolayers with two different concentrations for : (a) Nb-doped MoS_2 and (b) F-doped WS_2, showing the negligible effect of the variation in the doping concentration on the sharp/localization of the defect states within the band gap.

System	K_{VBM}	K_{CBM}	K_{Traps}
MoS_{N2}	35.16%Mo-d_{xy} 35.16%Mo-d_{x2-y2} 6.94%S-p_x 6.94%S-p_y	85.91%Mo-d_{z2} 5.57%Mo-s 3.76%S-p_x 3.76%S-p_y	42.24%Mo-d_{z2} 7.58% Mo-d_{x2-y2} 7.58%Mo-d_{xy} 5.6%S-p_x , 5.6%S-p_y 14.90%N-p_z
$Mo_{Nb}S_2$	38.30%Mo-d_{xy} 38.30%Mo-d_{x2-y2} 2.2%Nb-d_{xy} 2.2%Nb-d_{x2-y2} 8.05%S-p_x 8.05%S-p_y	85.77%Mo-d_{z2} 5.70%Mo-s 3.76%S-p_x 3.76%S-p_y	53.77%Mo-d_{z2} 11.75%Nb-d_{z2} 5.75%Mo-d_{x2-y2} 5.75% Mo-d_{xy} 14.96%S-p_z
WS_{F2}	39.83%W-d_{x2-y2} 39.58%W-d_{xy} 9.93%S-p_x 9.93%S-p_y	56.45%W-d_{z2} 9.45%W-d_{x2-y2} 9.45%W-d_{xy} 7.54%S-p_x 7.54%S-p_y 6.65%S-s	18.43%W-d_{xy} 21.52%W-d_{xz} 11.73%W-d_{x2-y2} 11.70%W-d_{z2} 11%W-dyz 3.5% F-p_z , 3.2%F-p_x , 5.15%S-p_x , 5.15%S-p_y , 5.15%S-p_z
$W_{Re}S_2$	39.80%W-d_{x2-y2} 39.80%W-d_{xy} 9.95%S-p_x 9.95%S-p_y	52.36%W-d_{z2} 12.81%W-d_{x2-y2} 12.83%W-d_{xy} 7.07%S-p_x 7.07%S-p_y 5.37%S-s	23.53%W-d_{z2} 26.28%Re-d_{z2} 13.35%W-d_{x2-y2} 12.35%W-d_{xy} 8.94%S-p_x , 8.8%S-p_y
WSe_{F2}	40.16% W-d_{xy} 40.16%W-d_{x2-y2} 9.16%Se-p_x 9.16%Se-p_y	80.83%W-d_{z2} 9.14%W-s 2.74%Se-p_x 2.74%Se-p_y	19.03%W-d_{xy} 19.80%W-d_{z2} 19.03%W-d_{x2-y2} 8.95%W-d_{xz} 8.95%W-d_{yz} 4.6%Se-p_x , 4.60%Se-p_y, 5.11%Se-p_z 6.4%F-p_z
$W_{Re}Se_2$	40.28% W-d_{xy} 40.28%W-d_{x2-y2} 9.16%Se-p_x 9.16%Se-p_y	44.88%W-d_{z2} 8.88%Re-d_{z2} 5.88%W-s 8.13%Se-p_x 8.13%Se-p_y 6.5 %W-dxy 6.5%Re-dxy	31.05%W-d_{xy} 14.71%W-d_{x2-y2} 23.02%W-d_{z2} 7.70%W-d_{xy} 12.15%Re-d_{z2}, 4.35%Re-d_{x2-y2} , 13.04%Re-d_{xy} 9.47%Se-p_x , 7.42%Se-p_y

Table S4: Orbital characters of the VBM and CBM at the K point in the four isolated monolayers.


WS2/MoSN2
WSe2/MoSN2
E-Ef (eV)
2
1
0
-1
-2
G
M
K
G


WS2/MoNbS2
WSe2/MoNbS2
E-Ef (eV)
2
1
0
-1
-2
G
M
K
G


WSF2/MoS2
WSeF2/MoS2
E-Ef (eV)
2
1
0
-1
-2
G
M
K
G

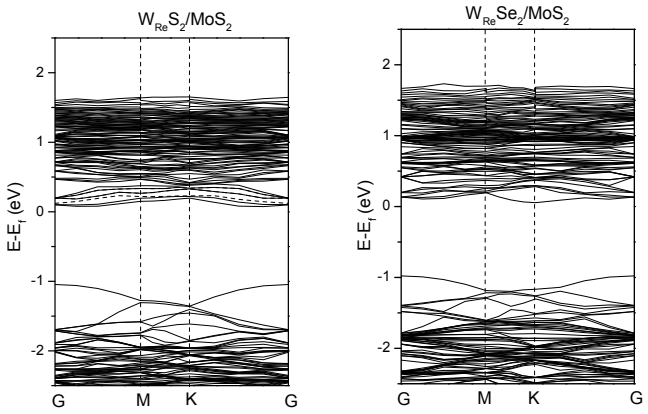


Figure S4: Band structures of the bilayers doped by substitutional doping with the trap levels in the gap highlighted in red

Systems	a (A°)	d (A°)	D(A°)	E_b (eV)	Ea (eV)	$L_{(X-S)}$ bond length
MoS_2-H	15.60	-	1.43	-	-1.62	$L_{(S—H)}$: 1.43
MoS_2-F	15.60	-	1.81	-	-2.60	$L_{(S—F)}$:1.81
MoS_2-O	15.60	-	1.52	-	-5.90	$L_{(S—O)}$: 1.50
MoS_2-CH_3	15.60	-	1.82	-	-1.617	$L_{(S—C)}$: 1.82
MoS_2-CF_3	15.60	-	1.95	-	-0.63	$L_{(S-C)}$: 1.95
WS_2/MoS_2-H	15.62 ()	2.79	1.43	-2.81	-1.65	$L_{(W—S)}$: 2.40 $L_{(Mo—S)}$: 2.41 $L_{(S—H)}$: 1.43
WS_2/MoS_2-F	15.62 ()	2.84	1.81	-2.825	-2.61	$L_{(W—S)}$: 2.40 $L_{(Mo—S)}$: 2.40 $L_{(S—F)}$: 1.81
WS_2/MoS_2-O	15.62	2.82	1.51	-2.799	-5.92	$L_{(W—S)}$ 2.40 $L_{(Mo—S)}$ 2.40 $L_{(S—O)}$ 1.51
WS_2/MoS_2-CH_3	15.621	2.81	1.82	-2.86	-1.67	$L_{(W—S)}$ 2.40 $L_{(Mo—S)}$ 2.41 $L_{(S—C)}$ 1.82
WS_2/MoS_2-CF_3	15.62	2.79	1.94	-2.795	-0.65	$L_{(W—S)}$ 2.4 $L_{(Mo—S)}$ 2.41 $L_{(S—C)}$ 1.94
WSe_2/MoS_2-H	15.95	2.88	1.39	-3.08	-1.86	$L_{(W—Se)}$: 2.51 $L_{(Mo—S)}$: 2.43 $L_{(S—H)}$: 1.39
WSe_2/MoS_2-F	15.94	2.86	1.81	-3.06	-2.62	$L_{(W—Se)}$ 2.50 $L_{(Mo—S)}$ 2.42 $L_{(S—F)}$ 1.81
WSe_2/MoS_2-O	15.94	2.88	1.51	-3.03	-5.92	$L_{(W—Se)}$ 2.51 $L_{(Mo—S)}$ 2.42 $L_{(S—O)}$ 1.51
WSe_2/MoS_2-N	15.95	2.87	1.52	-3.08	-1.63	$L_{(W—Se)}$ 2.51 $L_{(Mo—N)}$ 2.40 $L_{(S—N)}$ 1.52
WSe_2/MoS_2-CH_3	15.96	2.88	1.78	-3.19	-1.80	$L_{(W—Se)}$ 2.51 $L_{(Mo—S)}$ 2.43 $L_{(S—C)}$ 1.79
WSe_2/MoS_2-CF_3	15.96	2.88	1.86	-3.19	-0.80	$L_{(W—Se)}$ 2.51 $L_{(Mo—S)}$ 2.44 $L_{(S—C)}$ 1.86

Table S5: Lattice constants, Mo-R bond lengths, interlayer distances d, binding energies between top and bottom layer and adhesion energies of the ad-atoms for the various structures considered.

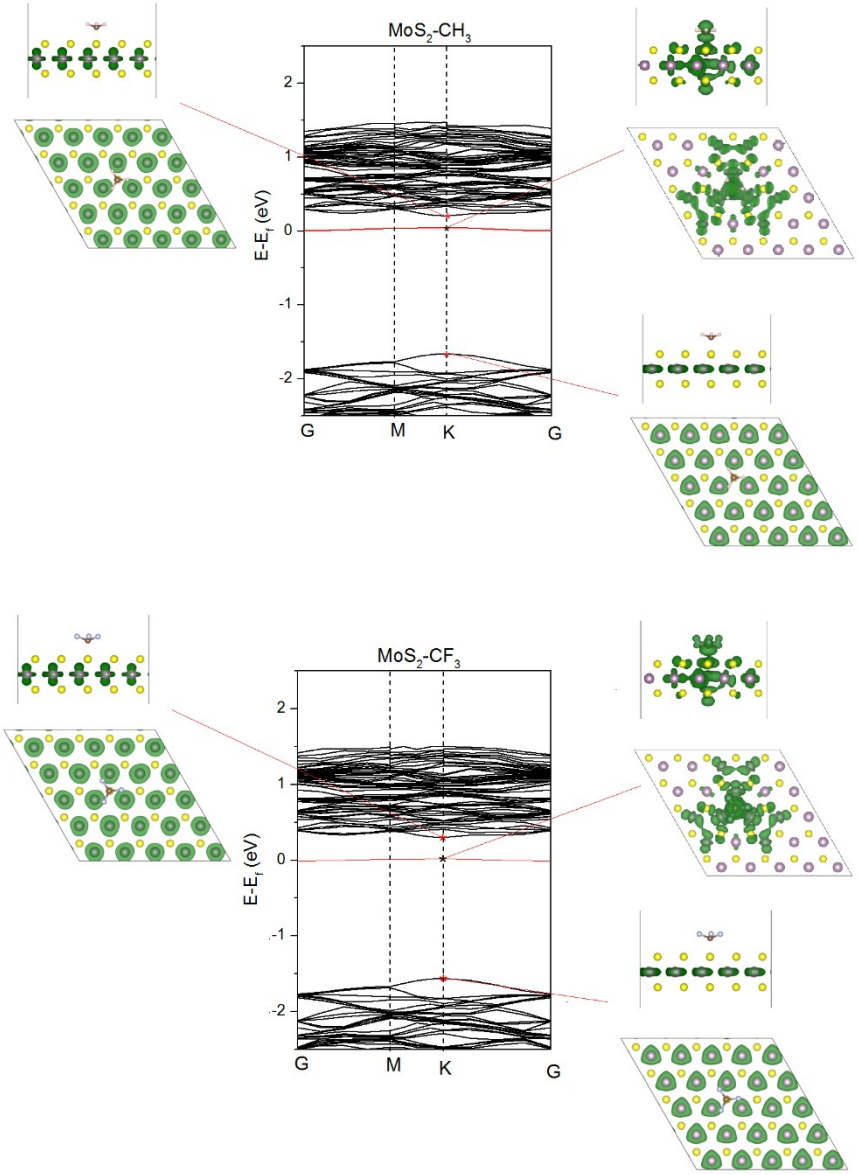


Figure S5: Band structure of an isolated MoS_2 monolayer with covalently bounded CF_3- and CH_3-groups showing the appearance of half-filled trap states in the gap. The total contributions of the dopants in trap levels are 11% for CH_3 and 7.3% for CF_3.

System	K_{VBM}	K_{CBM}	K_{Traps}
MoS_2-H	41.72%Mo-d_{xy} 41.72%Mo-d_{x2-y2} 8.35%S-p_x 8.35%S-p_y	86.01%Mo-d_{z2} 5.76%Mo-s 4.07%S-p_x 4.07%S-p_y	Mo-d_{xy} (24.10%) Mo-d_{z2} (21.46 %) Mo-d_{x2-y2} (18.62 %) Mo-d_{xz} (10%), Mo-d_{yz} (10%), S-p_y (5.7%), S-px (7.03 %) S-s (5.80%) H-s (5%)
MoS_2-F	41.72%Mo-d_{xy} 41.72%Mo-d_{x2-y2} 8.35%S-p_x 8.35%S-p_y	86.01%Mo-d_{z2} 5.76%Mo-s 4.07%S-p_x 4.07%S-p_y	Mo-d_{z2} (11.38%) Mo-dxy (9.28%) Mo-d_{x2-y2} (9.28%) F-p_z (21%) S-p_z (17.78%) S-p_x (6.1%) S-p_y (6.1%)
MoS_2-O	40.51%Mo-d_{xy} 40.51%Mo-d_{x2-y2} 8.95%S-p_x 8.95%S-p_y 1.00%O-p_x 1.00%O-p_y	86.02%Mo-d_{z2} 5.77%Mo-s 4.06%S-p_x 4.06%S-p_y	Mo-d_{z2} (36.65%) Mo-dxy (16.16%) Mo-d_{x2-y2} (16.16%) O-p_x (3.1%) O-p_y (3.1%) S-p_z (8.02%) S-p_x (10.20%) S-p_y (10.20%)
MoS_2-CH3	41.72%Mo-d_{xy} 41.72%Mo-d_{x2-y2} 8.35%S-p_x 8.35%S-p_y	86.01%Mo-d_{z2} 5.76%Mo-s 4.07%S-p_x 4.07%S-p_y	Mo-d_{z2} (22.38%) Mo-d_{x2-y2} (19.90%) Mo-d_{xy} (19.75%) S-p_x (9.3%) S-p_y (9.3%) S-p_z (5.1%) C-p_z (5.1%)
MoS_2-CF3	41.72%Mo-d_{xy} 41.72%Mo-d_{x2-y2} 8.35%S-p_x 8.35%S-p_y	86.01%Mo-d_{z2} 5.76%Mo-s 4.07%S-p_x 4.07%S-p_y	Mo-d_{x2-y2} (17.10%) Mo-d_{z2} (17.10%) Mo-d_{xy} (17.22%) S-p_x (8.2%) S-p_y (8.2%) C-p_z (7.3%) S-s (6.7%)

Table S6: Orbital characters of the VBM, CBM and trap states at the K-point for the four isolated functionalized monolayers.

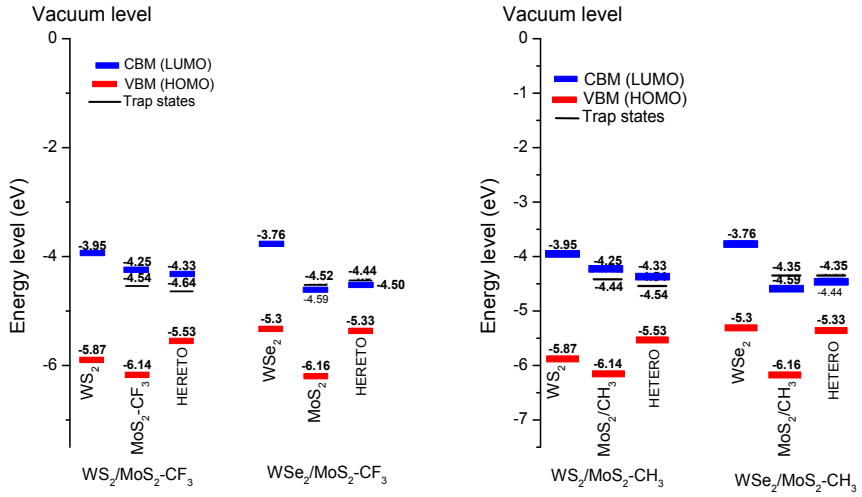
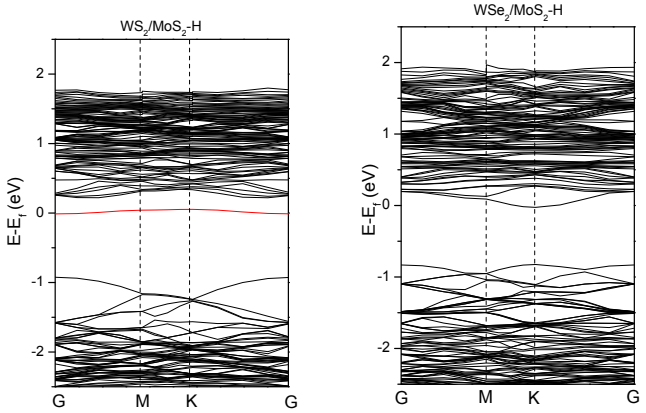
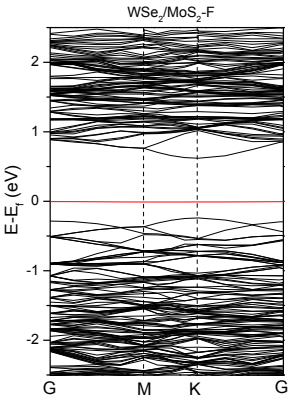
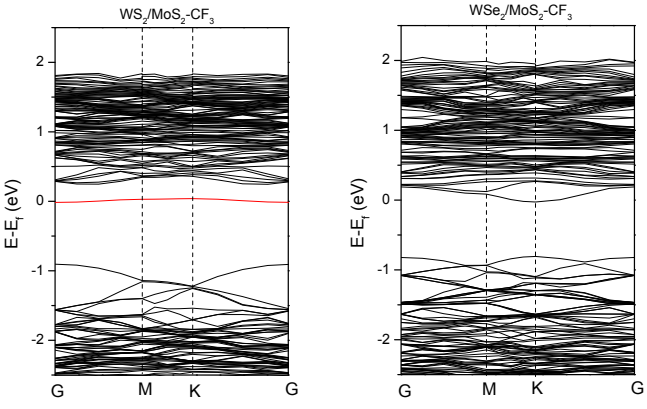


Figure S6: Alignment of the band edges in WS_2/MoS_2 and WSe_2/MoS_2 bilayers with covalently bounded CF_3 and CH_3 groups.


WS2/MoS2-H
WSe2/MoS2-H
E-Ef (eV)
2
1
0
-1
-2
G
M
K
G


WSe2/MoS2-F
E-Ef (eV)
2
1
0
-1
-2
G
M
K
G


WS2/MoS2-CF3
WSe2/MoS2-CF3
E-Ef (eV)
2
1
0
-1
-2
G
M
K
G

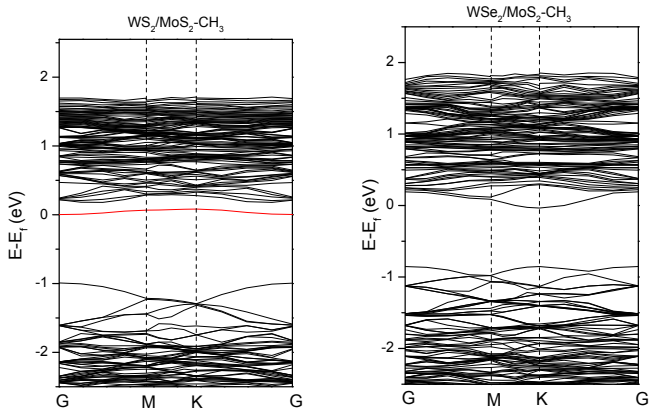


Figure S7: Band structures of bilayers with ad-atoms and groups attached to the MoS_2 layer. We highlight in red the trap levels appearing in the gap of the bilayer.

Systems	Q_{bader} (|e|)	μz (D)
MoS_2-H	**-0.09/+0.09**	**-0.79**
MoS_2-F	**+0.54/-0.54**	**1.13**
MoS_2-O	**+1.04/-1.04**	**1.16**
MoS_2/CH_3	**-0.11/+0.11**	**-1.80**
MoS_2/CF_3	**+0.08/-0.08**	**-0.40**
WS_2/MoS_2-H	**-0.07/+0.07 (130%↓)**	**-0.96**
WS_2/MoS_2-F	**+0.024/-0.24 (700%↑)**	**1.36**
WS_2/MoS_2-O	**+0.03/-0.03 (3%↑)**	**1.33**
WS_2/MoS_2-CH_3	**-0.04 /+0.04 (34%↑)**	**-2.08**
WS_2/MoS_2-CF_3	**-0.02/+0.02 (34%↓)**	**-0.513**
WSe_2/MoS_2-H	**+0.34/-0.34 (8.7%↓)**	**-0.53**
WSe_2/MoS_2-F	**+0.37/-0.37 (2%↑)**	**1.70**
WSe_2/MoS_2-O	**+0.37/-0.37 (1%↑)**	**1.86**
WSe_2/MoS_2-CH_3	**+0.35/-0.35 (6%↓)**	**-0.96**
WSe_2/MoS_2-CF_3	**+0.34/-0.34 (8.10%↓)**	**-0.37**

Table S7: Bader charge analysis and total dipole moment along the z axis perpendicular to the basal plane in the bilayer doped with ad-atoms or groups. We report between parentheses the relative changes with respect to the pristine systems.

Systems	a (A°)	d (A°)	D(A°)	E_b (eV)	Ea (eV)	$L_{(X-S)}$ bond length
MoS_2/TTF	15.60	-	2.71	-	-0.66	
MoS_2/F_4TCNQ	15.60	-	2.72	-	-0.78	
MoS_2/$C_{10}H_8$	16.60	-	2.83	-	-0.44	
WS_2/MoS_2/TTF	15.62 (↑0.02%)	2.81 (↓1.7%)	2.71 (↓0.1)	-2.79 (↓1.08%)	-0.68 (↑1.4%)	$L_{(W—S)}$ 2.402 $L_{(Mo—S)}$ 2.391
WS_2/MoS_2/F_4TCNQ	15.62 (↑0.02%)	2.77 (↓3.1%)	2.72 (↓0.1)	-2.87 (↑1.5%)	-0.86 (↑9.1%)	$L_{(W—S)}$ 2.401 $L_{(Mo—S)}$ 2.392
WS_2/MoS_2/$C_{10}H_8$	15.62 (↑0.02%)	2.80 (↓2.1%)	2.84 (↓0.4%)	-2.78 (↓1.1%	-0.42 (↓6.1%)	$L_{(W—S)}$ 2.402 $L_{(Mo—S)}$ 2.390
WSe_2/MoS_2/TTF	15.93 (↑0.13%)	2.87 (↓0.7%)	2.66 (↓1.8%)	-3.04 (↓0.33)	-0.82 (18%)	$L_{(W—Se)}$ 2.406 $L_{(Mo—S)}$ 2.504
WSe_2/MoS_2/F_4TCNQ	15.92 (↑0.12%)	2.82 (↓1.4%)	2.68 (↓1.49%)	-3.18 (↑4.2)	-0.87 (↑10.35%)	$L_{(W—Se)}$ 2.505 $L_{(Mo—S)}$ 2.407
WSe_2/MoS_2/$C_{10}H_8$	15.92 (↑0.12%)	2.87 (↓0.35%)	2.79 (↓1.4%)	-3.10 (↑1.64)	-0.53 (↑15.1%	$L_{(W—Se)}$ 2.506 $L_{(Mo—S)}$ 2.408

Table S8: Lattice constant a (A°), bond length $L_{(X-S) \text{ or } (X-Se)}$, interlayer distance d (A°) between top (MoS_2) and bottom layers (WS_2 or WSe_2), interlayer distance D (A°) between molecules and top layer (MoS_2) , binding energy E_b (eV), adsorption energy Ea (eV) of hetero-structures with physisorbed molecules.

System	K_{-VBM}	K_{-CBM}	K_{-Traps}
MoS_2-TTF	41.72%Mo-d_{xy} 41.72%Mo-d_{x2-y2} 8.35%S-p_x 8.35%S-p_y	86.01%Mo-d_{z2} 5.76%Mo-s 4.07%S-p_x 4.07%S-p_y	S-Pz (51.73 %) C-pz (34.30%)
MoS_2/F_4-TCNQ	40.51%Mo-d_{xy} 40.51%Mo-d_{x2-y2} 8.95%S-p_x 8.95%S-p_y 1.00%O-p_x 1.00%O-p_y	86.02%Mo-d_{z2} 5.77%Mo-s 4.06%S-p_x 4.06%S-p_y	C-pz (52.60%) N-pz (34.70%) F-pz (4.20%)
$MoS_2/C_{10}H_8$	41.72%Mo-d_{xy} 41.72%Mo-d_{x2-y2} 8.35%S-p_x 8.35%S-p_y	86.01%Mo-d_{z2} 5.76%Mo-s 4.07%S-p_x 4.07%S-p_y	C-p_z (51.30%) Mo-d_{xy} (16.62%) Mo-d_{x2-y2} (19.55%) S-pz (4.2%)

Table S9: Orbital characters of the VBM, CBM and trap states at the K-point for the three isolated functionalized monolayers.

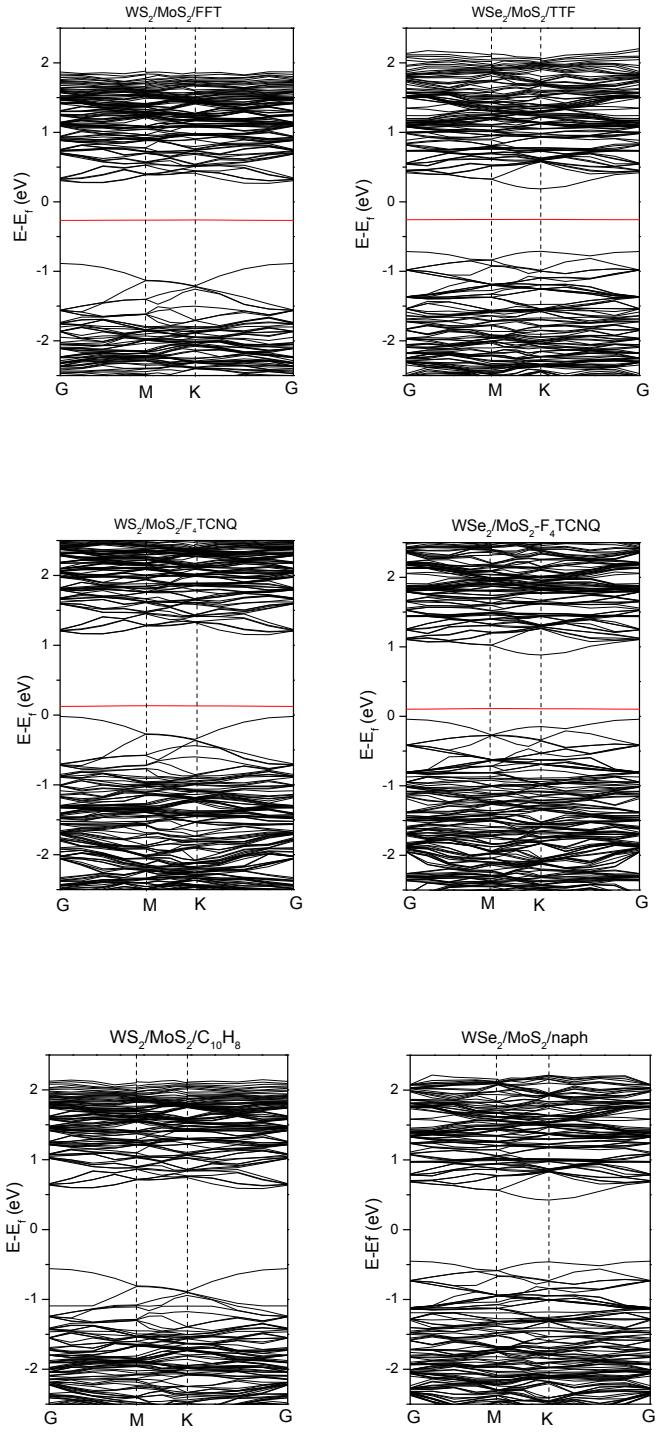


Figure S8: Band structures of bilayers with adsorbed molecules, with the trap states within the gap highlighted in red

Systems	Q_{bader} (|e|)	ΔV (eV)	μ_z (D)
MoS_2/TTF	**-0.22 /+0.22**	**+0.3**	**-1.66**
MoS_2/F_4TCNQ	**+0.24/-0.24**	**-0.08**	**+0.45**
MoS_2/$C_{10}H_8$	**-0.07/0.07**	**+0.15**	**-0.87**
WS_2/MoS_2/TTF	**+0.02 /-0.02 (34%↓)** **(+0.02 /-0.22 /+0.20)**	**0.28**	**-1.58**
WS_2/MoS_2/F_4-TCNQ	**+0.12 /-0.12 (300↑)** **(+0.12 /+0.27/-0.38)**	**-0.46**	**+2.55**
WS_2/MoS_2/$C_{10}H_8$	**+0.03/-0.03 (2%↑)** **(+0.03/-0.107/+0.07)**	**0.07**	**-0.37**
WSe_2/MoS_2/TTF	**+0.37 /-0.37 (1%↑)** **(+0.37/ -0.62 / +0.25)**	**0.21**	**-1.20**
WSe_2/MoS_2/F_4-TCNQ	**+0.51 /-0.51 (37.84%↑)** **(+0.51/-0.052 /-0.46)**	**-0.68**	**+3.96**
WSe_2/MoS_2/$C_{10}H_8$	**+0.37/-0.37 (1%↑)** **(+0.37/-0.46/+0.09)**	**-0.05**	**+0.40**

Table S10: Bader charge and total dipole moment along the direction perpendicular to the 2D sheets for the systems with physisorbed molecules. We report between parentheses the relative changes with respect to the pristine systems.