Supporting Information (SI)

Modulating Electronic and Optical Properties of Monolayered MoS$_2$ by Covalent Mono- and Bisfunctionalization

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Fig. S1: (a) The QP band gaps of the functionalized 2H-MoS$_2$ with -CH$_3$ group as a function of vacuum thickness with 50 eV G$_0$W$_0$ self-energy and 12×12 k-point sampling (2×2 supercell). (b) The QP band gaps of the functionalized 2H-MoS$_2$ with -CH$_3$ group as a function of k-point sampling with 50 eV G$_0$W$_0$ self-energy and 8 Å vacuum thickness (2×2 supercell) . (c) Optical absorption spectra of the functionalized 2H-MoS$_2$ with -CH$_3$ group as a function of the number of valence and conduction bands with 50 eV self-energy and 8 Å vacuum thickness (2×2 supercell).

Fig. S2: Optimized structures of functionalized 2H-MoS$_2$ and 1T'-MoS$_2$ with various groups.

Fig. S3: Average energy difference ΔE between functionalized 2H- and 1T'-MoS$_2$ as a function of the group coverage. Here $\Delta E = (E_{1T'} - E_{2H})/m$, where m is the number of MoS$_2$ units, $E_{1T'}$ and E_{2H} are the total enegry of functionalized 2H- and 1T'-MoS$_2$ for a given coverage, respectively. The positive ΔE indicates that functionalized 2H-MoS$_2$ is more stable, while the negative ΔE indicates that functionalized 1T'-MoS$_2$ is more stable.

Fig. S4: Average Bader charge transfer ΔQ as a function of the group coverage with respect to the 2H- and 1T'-MoS$_2$ monolayers. Here $\Delta Q = \sum_i^N (Z_i - Q_i^{Bader})/n$, where N is the total number of atoms in the attached groups, Z_i is the number of electrons of atom i, Q_i^{Bader} is the Bader charge of atom i and n is the number of functional groups. A positive charge transfer value indicates electron flow from the substrate to the functional group.

Fig. S5: DFT band gaps as a function of the group coverage with respect to the functionalized 2H-MoS$_2$ and 1T'-MoS$_2$ monolayers.

Fig. S6: Total density of states and the projected density of states for the functionalized (a) 2H-MoS$_2$ and (b) 1T'-MoS$_2$ calculated by PBE functional.

Fig. S7: Optical absorption spectra of the functionalized 1T'-MoS$_2$ monolayer.

Table S1: The optical band gap (E_{opt}) for the functionalized 2H-MoS$_2$ at 6.25% coverage. Energies are in eV.

Fig. S1: (a) The QP band gaps of the functionalized 2H-MoS$_2$ with -CH$_3$ group as a function of vacuum thickness with 50 eV G$_0$W$_0$ self-energy and 12×12 k-point sampling (2×2 supercell). (b) The QP band gaps of the functionalized 2H-MoS$_2$ with -CH$_3$ group as a function of k-point sampling with 50 eV G$_0$W$_0$ self-energy and 8 Å vacuum thickness (2×2 supercell) . (c) Optical absorption spectra of the functionalized 2H-MoS$_2$ with -CH$_3$ group as a function of the number of valence and conduction bands with 50 eV self-energy and 8 Å vacuum thickness (2×2 supercell).

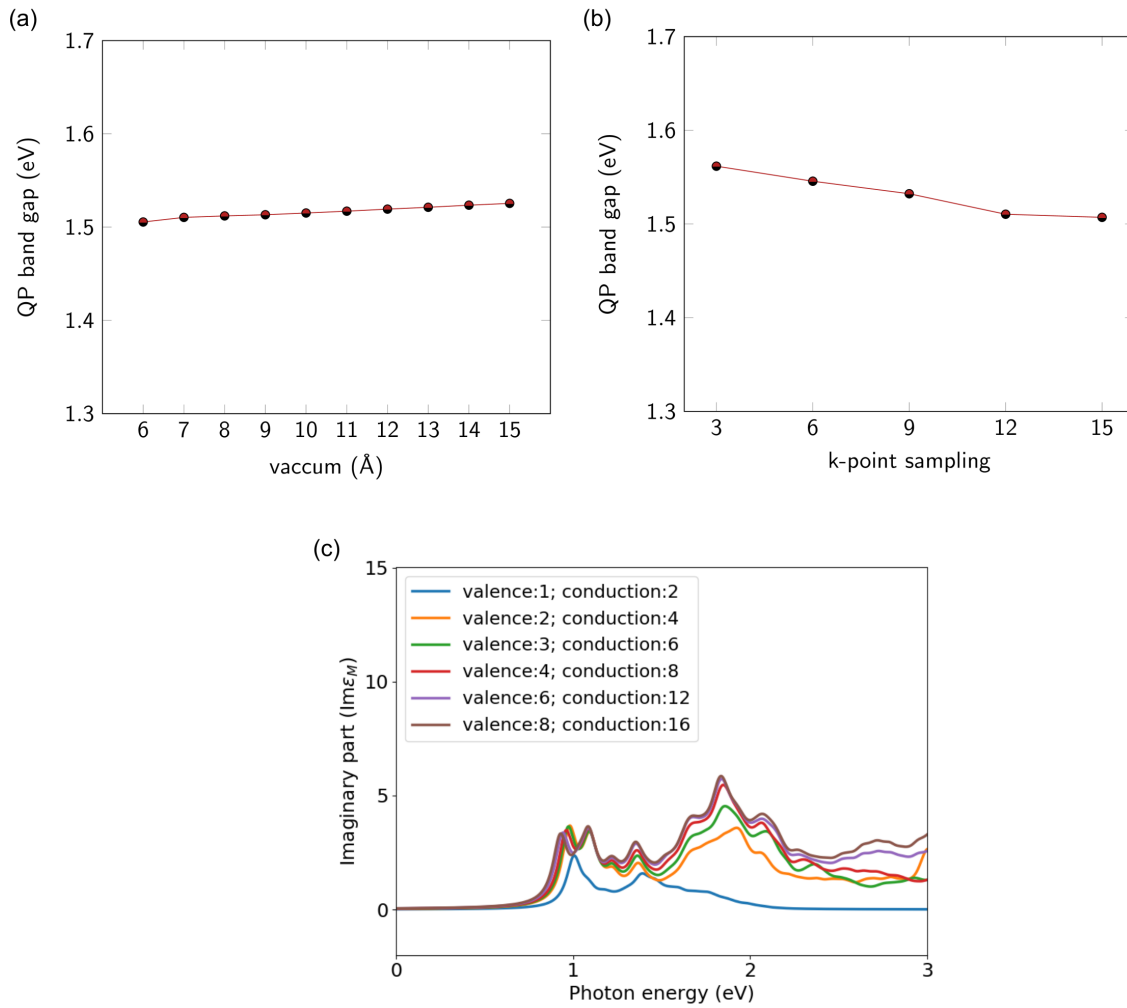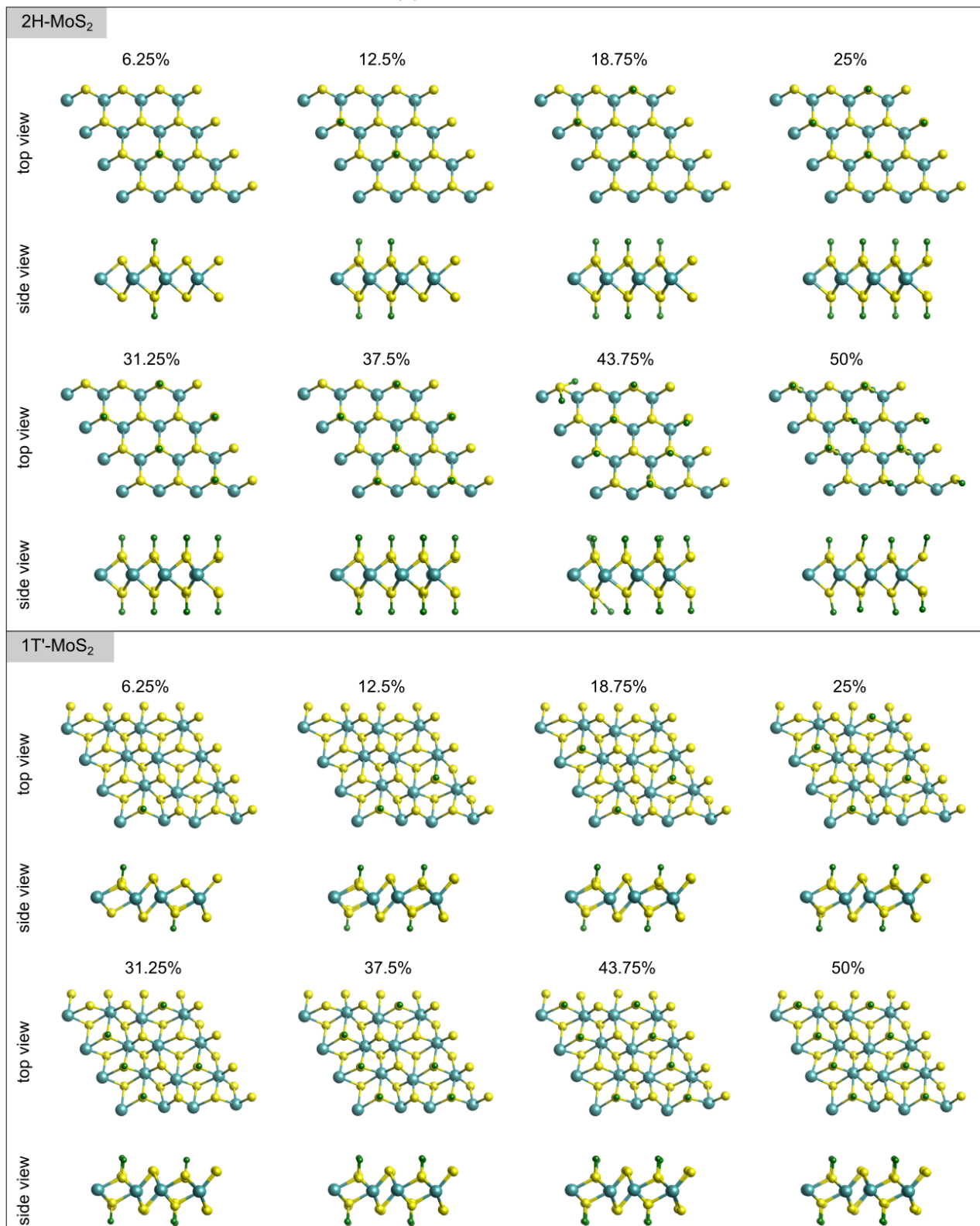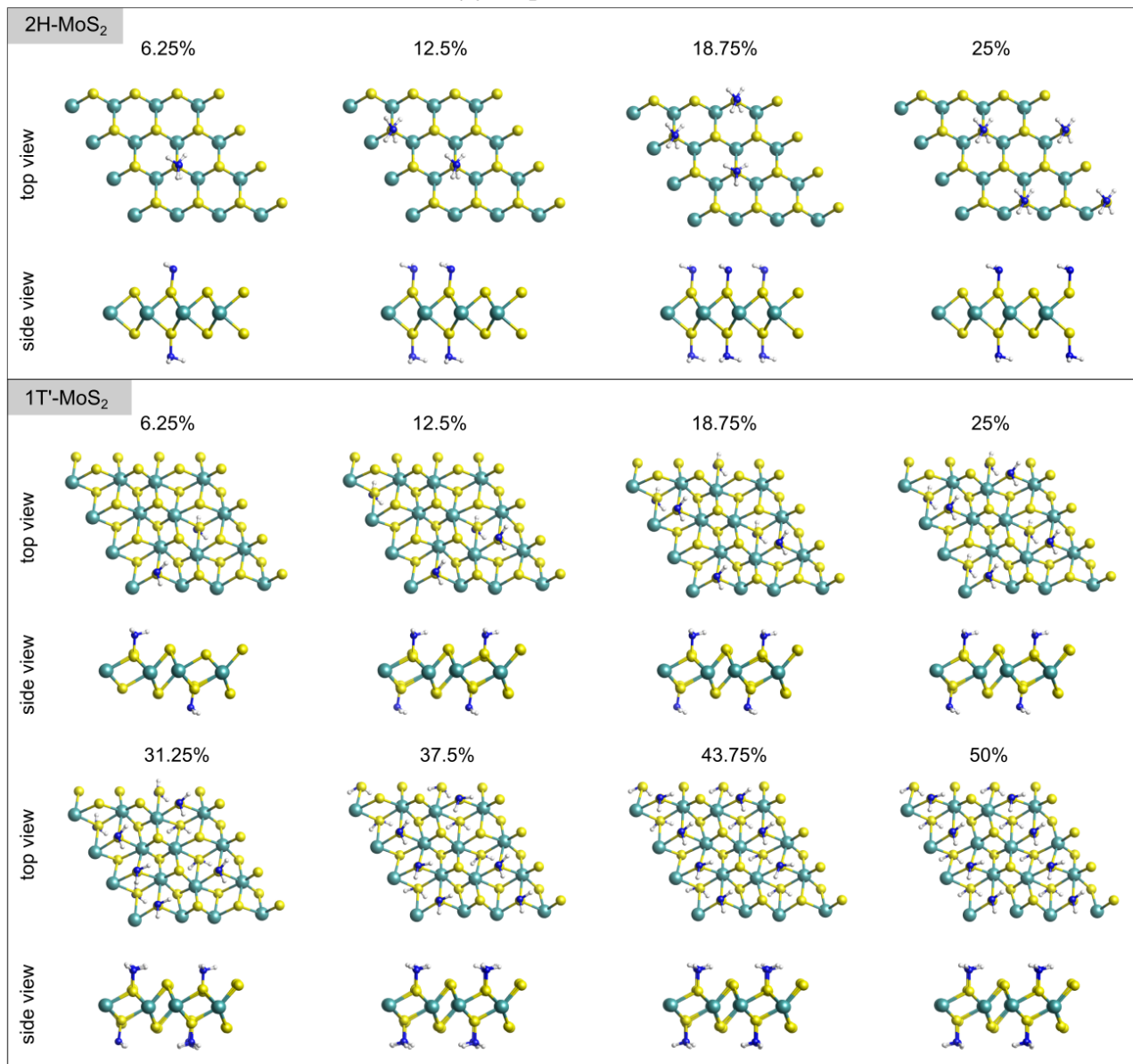Fig. S2: Optimized structures of functionalized 2H-MoS$_2$ and 1T'-MoS$_2$ with various groups.

(a) -F

(b) -NH$_2$

2H-MoS$_2$

6.25%   12.5%   18.75%   25%

top view

side view

1T'-MoS$_2$

6.25%   12.5%   18.75%   25%

top view

side view

31.25%   37.5%   43.75%   50%

top view

side view

(c) -CH$_3$

2H-MoS$_2$

| 6.25% | 12.5% | 18.75% | 25% |

top view

side view

| 31.25% | 37.5% | 43.75% | 50% |

top view

side view

1T'-MoS$_2$

| 6.25% | 12.5% | 18.75% | 25% |

top view

side view

| 31.25% | 37.5% | 43.75% | 50% |

top view

side view

(d) -CH$_2$CH$_2$CN

2H-MoS$_2$

	6.25%	12.5%	18.75%	25%

top view

side view

31.25%	37.5%	43.75%	50%

top view

side view

1T'-MoS$_2$

6.25%	12.5%	18.75%	25%

top view

side view

31.25%	37.5%	43.75%	50%

top view

side view

(e) -CH$_2$CH$_2$OH

(f) -Ph

2H-MoS$_2$

	6.25%	12.5%	18.75%	25%
top view				
side view				

	31.25%	37.5%	43.75%	50%
top view				
side view				

1T'-MoS$_2$

	6.25%	12.5%	18.75%	25%
top view				
side view				

	31.25%	37.5%	43.75%	50%
top view				
side view				

(g) -PhNO$_2$

2H-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

1T'-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

(h) -PhOH

2H-MoS$_2$

6.25%   12.5%   18.75%   25%

top view

side view

31.25%   37.5%   43.75%   50%

top view

side view

1T'-MoS$_2$

6.25%   12.5%   18.75%   25%

top view

side view

31.25%   37.5%   43.75%   50%

top view

side view

(i) m-F-CH$_3$

2H-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

1T'-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

(j) m-NH$_2$-CH$_3$

2H-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

1T'-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

(k) m-CH$_3$-Ph

2H-MoS$_2$

| 6.25% | 12.5% | 18.75% | 25% |

top view

side view

| 31.25% | 37.5% | 43.75% | 50% |

top view

side view

1T'-MoS$_2$

| 6.25% | 12.5% | 18.75% | 25% |

top view

side view

| 31.25% | 37.5% | 43.75% | 50% |

top view

side view

S13

(l) s-F-CH$_3$

2H-MoS$_2$

| top view / side view | 6.25% | 12.5% | 18.75% | 25% |

| top view / side view | 31.25% | 37.5% | 43.75% | 50% |

1T'-MoS$_2$

| top view / side view | 6.25% | 12.5% | 18.75% | 25% |

| top view / side view | 31.25% | 37.5% | 43.75% | 50% |

(m) s-NH$_2$-CH$_3$

2H-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

1T'-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

(n) s-CH$_3$-Ph

2H-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

1T'-MoS$_2$

6.25% 12.5% 18.75% 25%

top view

side view

31.25% 37.5% 43.75% 50%

top view

side view

Fig. S3: Average energy difference ΔE between functionalized 2H- and 1T'-MoS$_2$ as a function of the group coverage. Here $\Delta E = (E_{1T'} - E_{2H})/m$, where m is the number of MoS$_2$ units, $E_{1T'}$ and E_{2H} are the total enegry of functionalized 2H- and 1T'-MoS$_2$ for a given coverage, respectively. The positive ΔE indicates that functionalized 2H-MoS$_2$ is more stable, while the negative ΔE indicates that functionalized 1T'-MoS$_2$ is more stable.
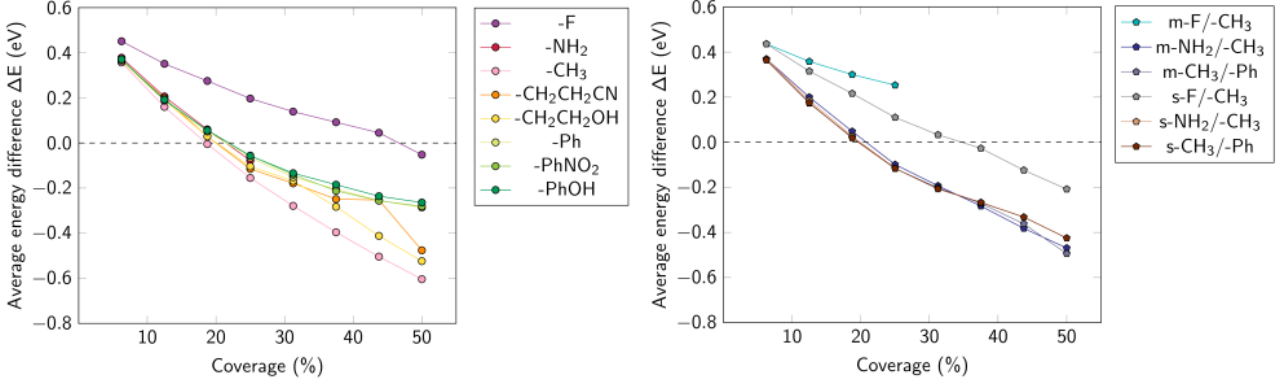

Fig. S4: Average Bader charge transfer ΔQ as a function of the group coverage with respect to the 2H- and 1T'-MoS$_2$ monolayers. Here $\Delta Q = \sum_i^N (Z_i - Q_i^{Bader})/n$, where N is the total number of atoms in the attached groups, Z_i is the number of electrons of atom i, Q_i^{Bader} is the Bader charge of atom i and n is the number of functional groups. A positive charge transfer value indicates electron flow from the substrate to the functional group.
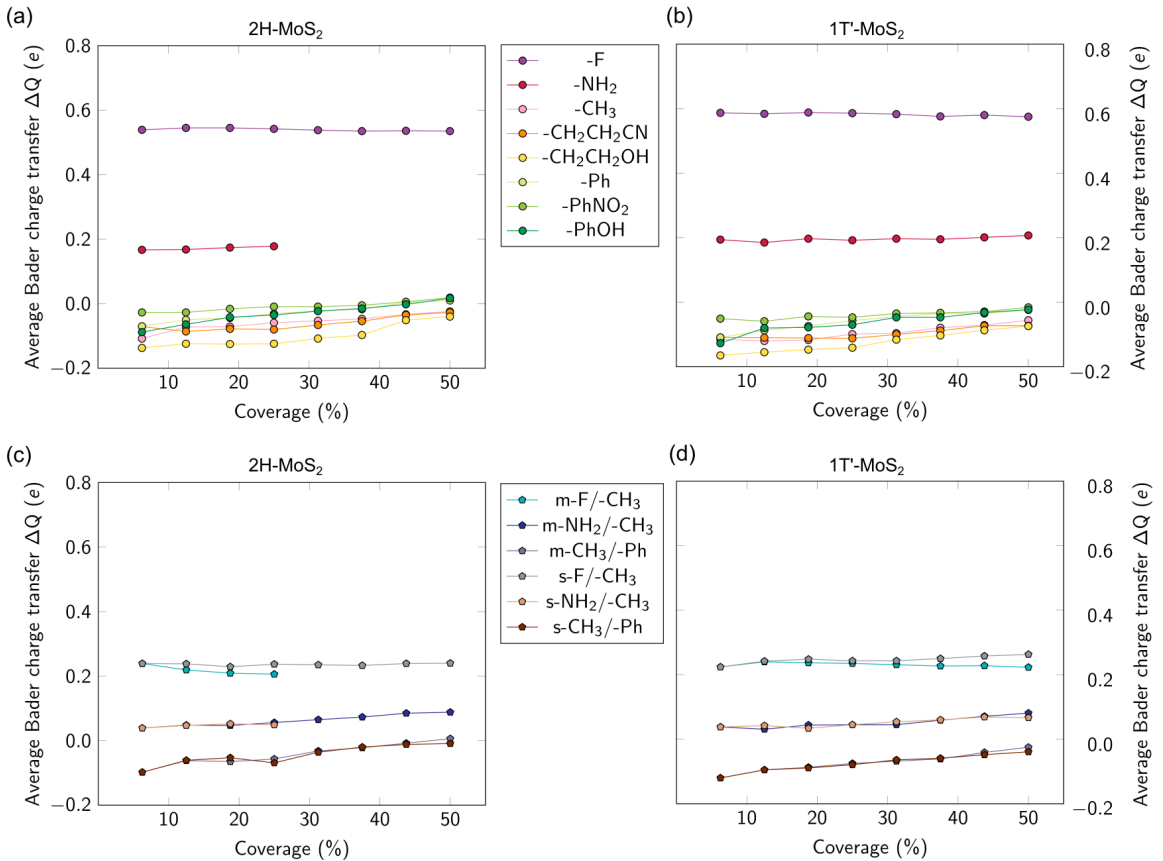
Fig. S5: DFT band gaps as a function of the group coverage with respect to the functionalized 2H-MoS_2 and 1T'-MoS_2 monolayers.
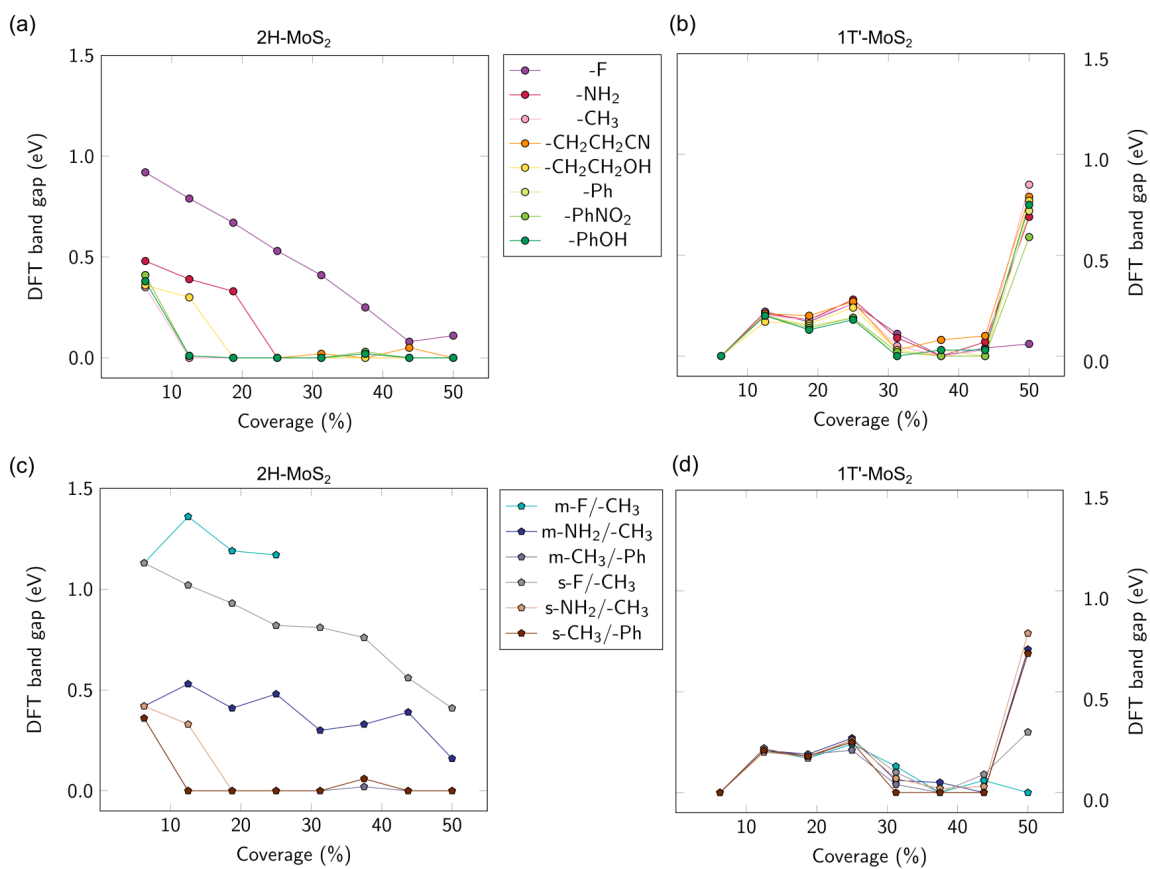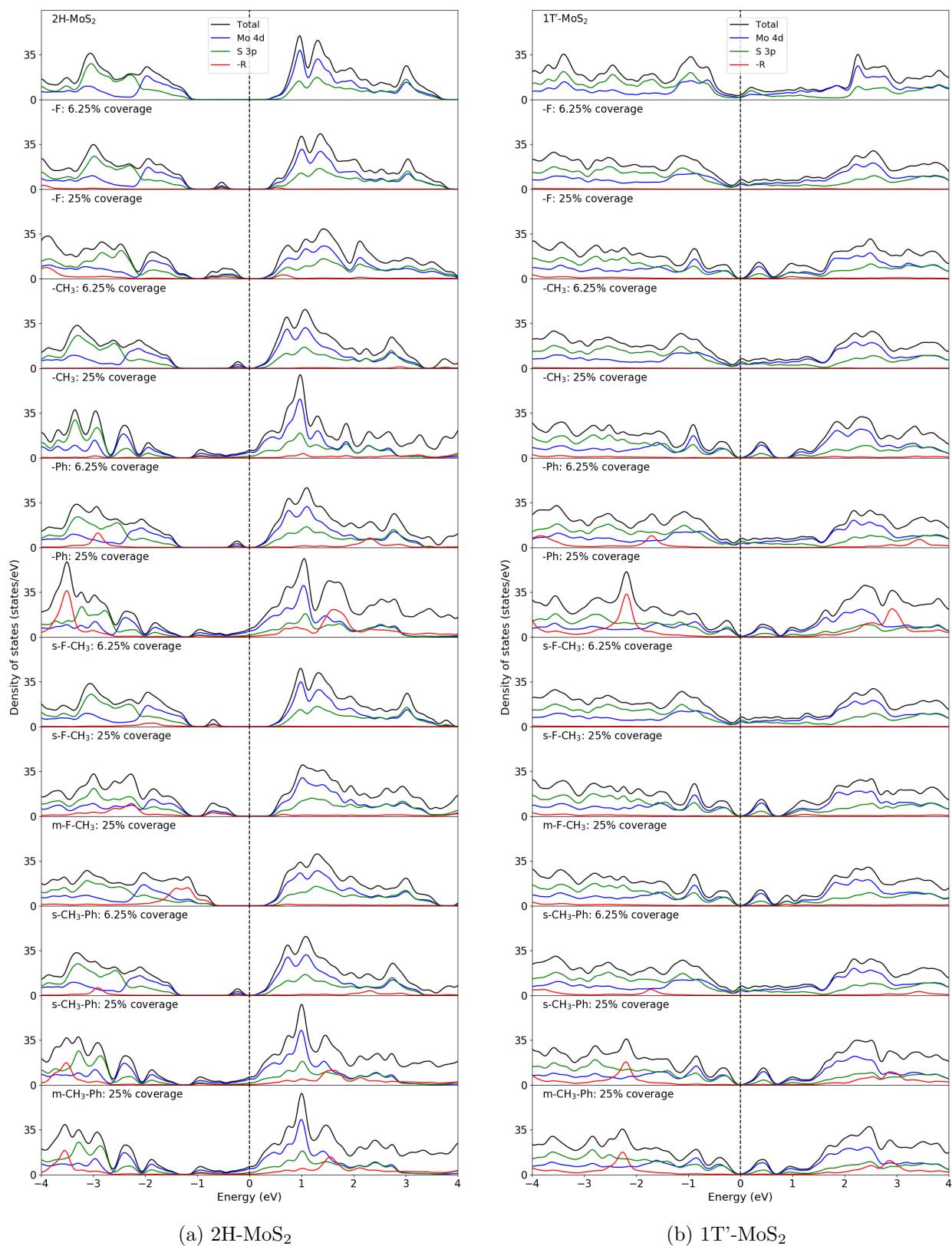
Fig. S6: Total density of states and the projected density of states for the functionalized (a) 2H-MoS$_2$ and (b) 1T'-MoS$_2$ calculated by PBE functional.
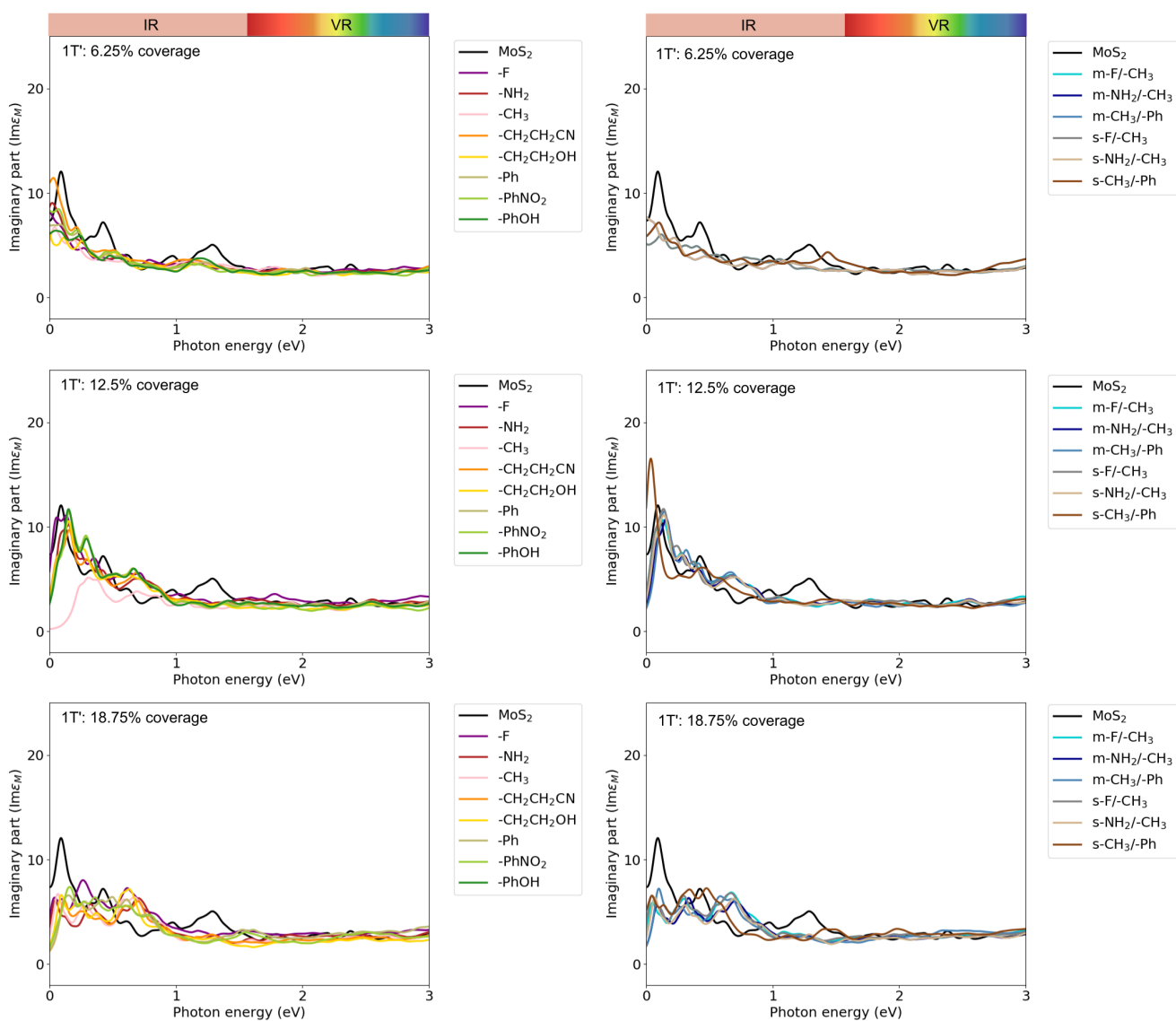

(a) 2H-MoS$_2$

(b) 1T'-MoS$_2$

Fig. S7: Optical absorption spectra of the functionalized 1T'-MoS$_2$ monolayer.

Table S1: The optical band gap (E_{opt}) for the functionalized 2H-MoS$_2$ at 6.25% coverage. Energies are in eV.

	2H-MoS$_2$	-F	-NH$_2$	-CH$_3$	-CH$_2$CH$_2$CN	-CH$_2$CH$_2$OH
E_{opt}	1.84	1.14	0.55	0.37	0.49	0.37
E_{ext}	0.67	0.67	0.65	0.63	0.60	0.64
	-Ph	-PhNO$_2$	PhOH	m-F/-NH$_2$	m-NH$_2$/-CH$_3$	m-CH$_3$/-Ph
E_{opt}	0.37	0.43	0.37	1.49	0.48	0.17
E_{ext}	0.63	0.59	0.62	0.73	0.63	0.82
	s-F/-NH$_2$	s-NH$_2$/-CH$_3$	s-CH$_3$/-Ph			
E_{opt}	1.49	0.48	0.17			
E_{ext}	0.73	0.63	0.82			