Supporting Information

Electronic structure and interfacial features of triphenylamine- and phenothiazine-based hole transport materials for methylammonium lead iodide perovskite solar cells.

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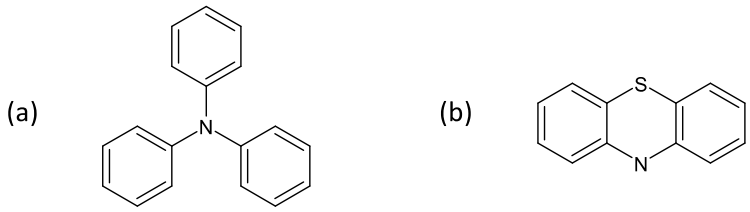

Scheme S1: Molecular structures of (a) triphenylamine TPA and (b) phenothiazine moieties PTZ.

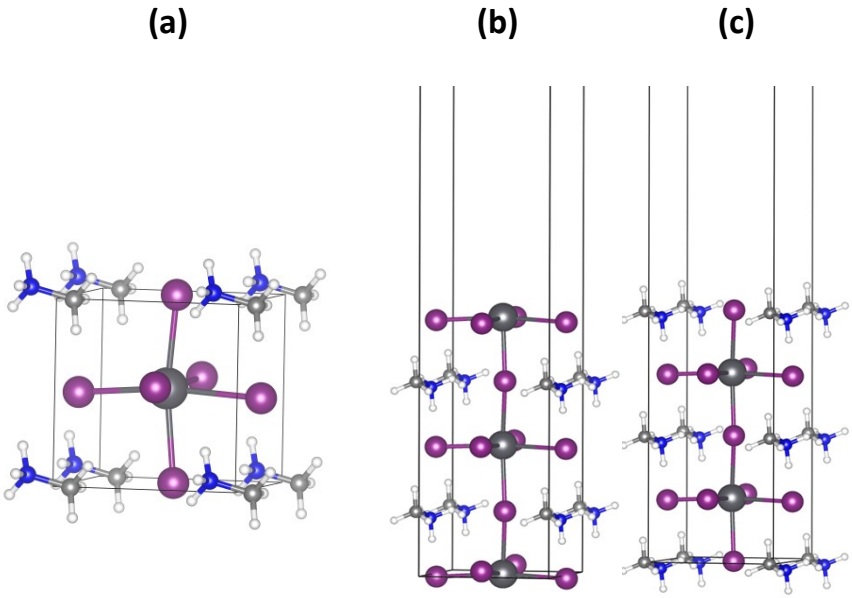

Figure S1: (a) unit cell of cubic MAPI; symmetric 5-layers slabs of (b) MAPI:PbI_2 and (c) MAPI:MAI. Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white.

Slab convergence tests

From the preoptimized cubic unit cell, 3 slabs of the MAPI (001) surface composed of 5, 7 and 9 crystal planes, respectively, have been built considering the two possible terminations, *i.e.* PbI_2- and the MAI-exposing facets. Their energies have been calculated at GGA-PBE, using DZP as basis set (including $5d^{10}$ semicore electrons for Pb atoms) and using Troullier-Martins norm-conserving pseudopotentials. A mesh cutoff of 400 Ry and a 8 x 8 x 1 Γ–centered Monkhorst-Pack *k*-point grid have been considered. The surface's energy ($E_{surface}$) have been calculated as follow:

$$E_{surface} = \frac{(E_{slab}^{MAI} + E_{slab}^{PbI_2}) - E_{bulk}}{2 * Area_{slab}}$$

where E_{slab}^{MAI} and $E_{slab}^{PbI_2}$ are the energy of the PbI_2- and the MAI-terminated slabs and E_{bulk} is the energy of the MAPI unit cell.

The energy of the three investigated systems has been then corrected including the dispersion forces calculated by D3BJ damping scheme.

Table S1: Surface's energy (eV/Å^2) of 5, 7 and 9-layers MAPI (001) slabs.

Slab	$E_{surface}$ (eV/Å^2)	$E_{surface}$ including D3BJ (eV/Å^2)
5-layers	1.97	0.03
7-layers	1.45	0.02
9-layers	2.24	0.03

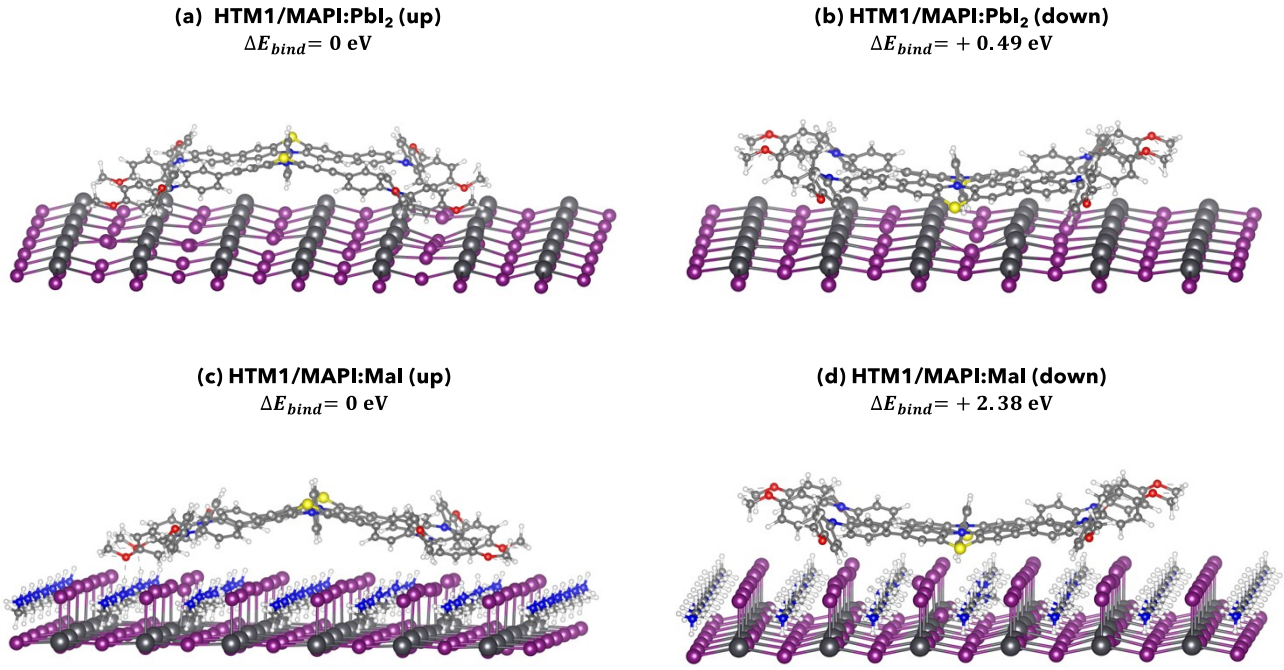

Figure S2: Minimum-energy interfaces of: (a) **HTM1**/MAPI:PbI_2 (*up*), (b) **HTM1**/MAPI:PbI_2 (*down*), (c) **HTM1**/MAPI:MAI (*up*) and (d) **HTM1**/MAPI:MAI (*down*).

Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white; O-red; S-yellow.

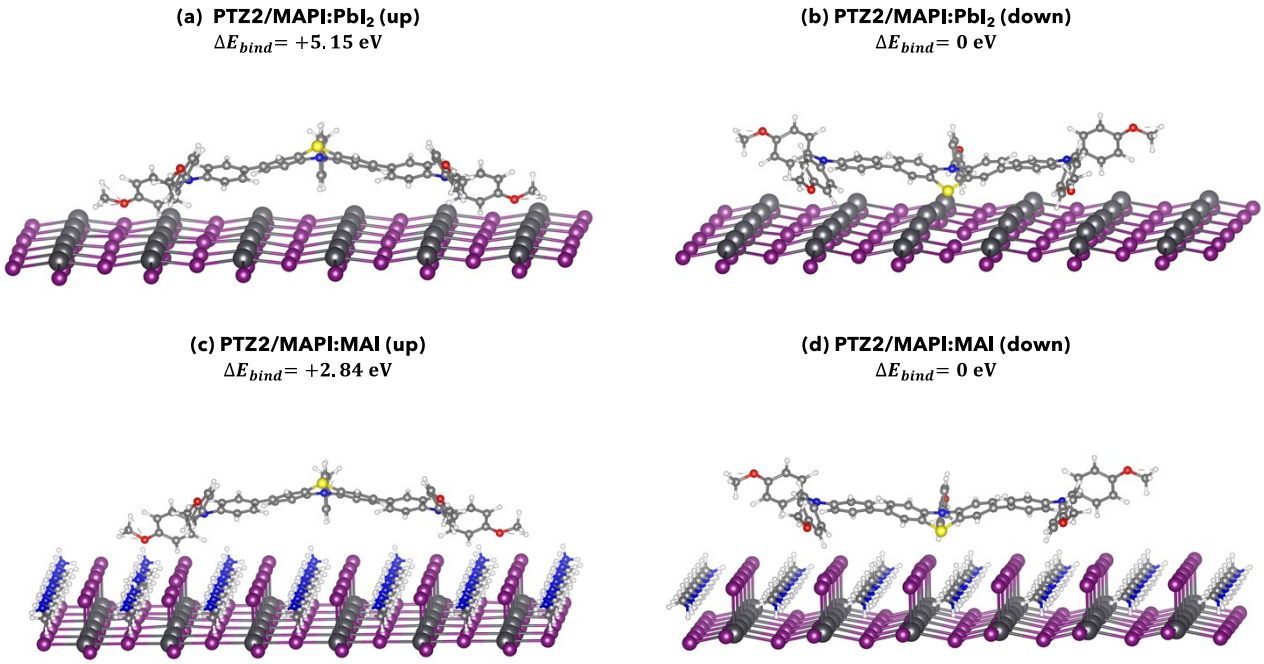

Figure S3: Minimum-energy interfaces of: (a) **PTZ2**/MAPI:PbI_2 (*up*), (b) **PTZ2**/MAPI:PbI_2 (*down*), (c) **PTZ2**/MAPI:MAI (*up*), and (d) **PTZ2**/MAPI:MAI (*down*).

Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white; O-red; S-yellow.

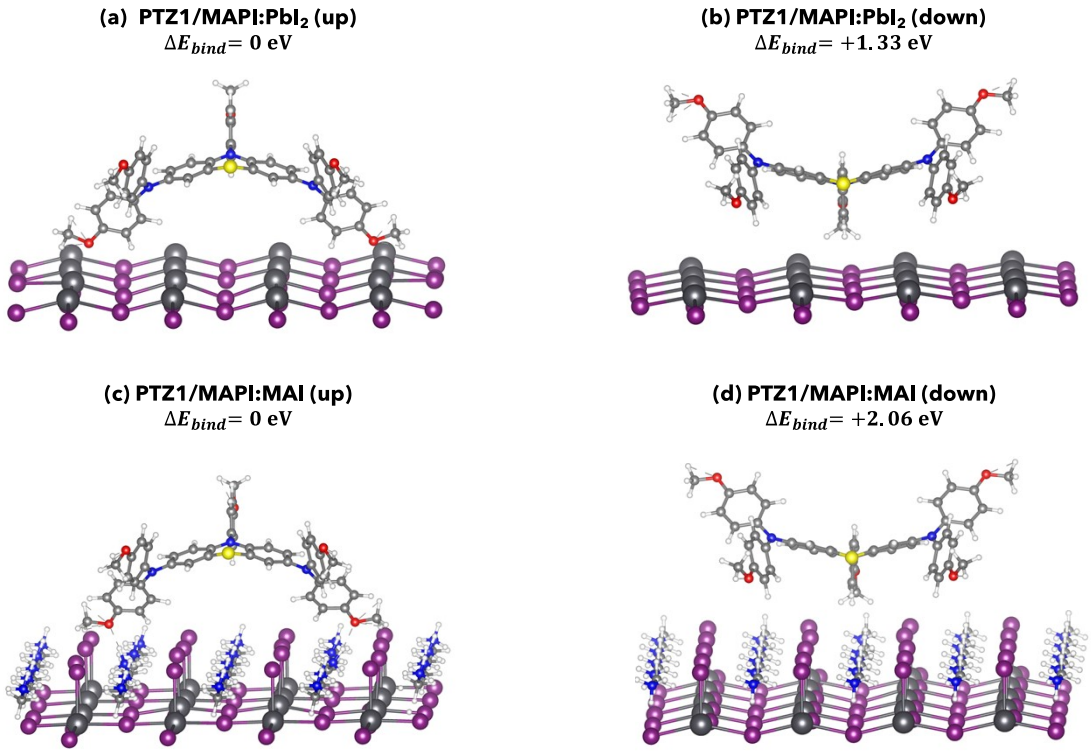

Figure S4: Minimum-energy interfaces of: (a) **PTZ1**/MAPI:PbI_2 (*up*), (b) **PTZ1**/MAPI:PbI_2 (*down*), (c) **PTZ1**/MAPI:MAI (*up*), and (d) **PTZ1**/MAPI:MAI (*down*).

Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white; O-red, S-yellow.

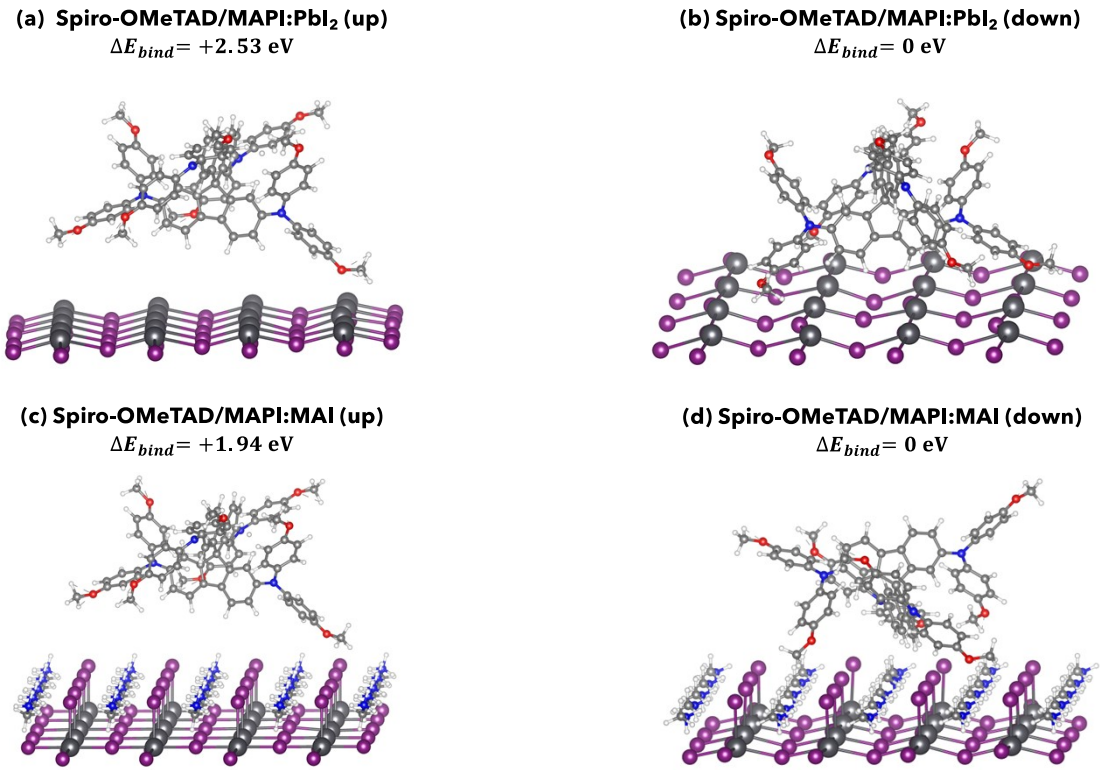

Figure S5: Minimum-energy interfaces of: (a) **Spiro-OMeTAD**/MAPI:PbI_2 (*up*), (b) **Spiro-OMeTAD**/MAPI:PbI_2 (*down*), (c) **Spiro-OMeTAD**/MAPI:MAI (*up*), and (d) **Spiro-OMeTAD**/MAPI:MAI (*down*).

Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white; O-red.

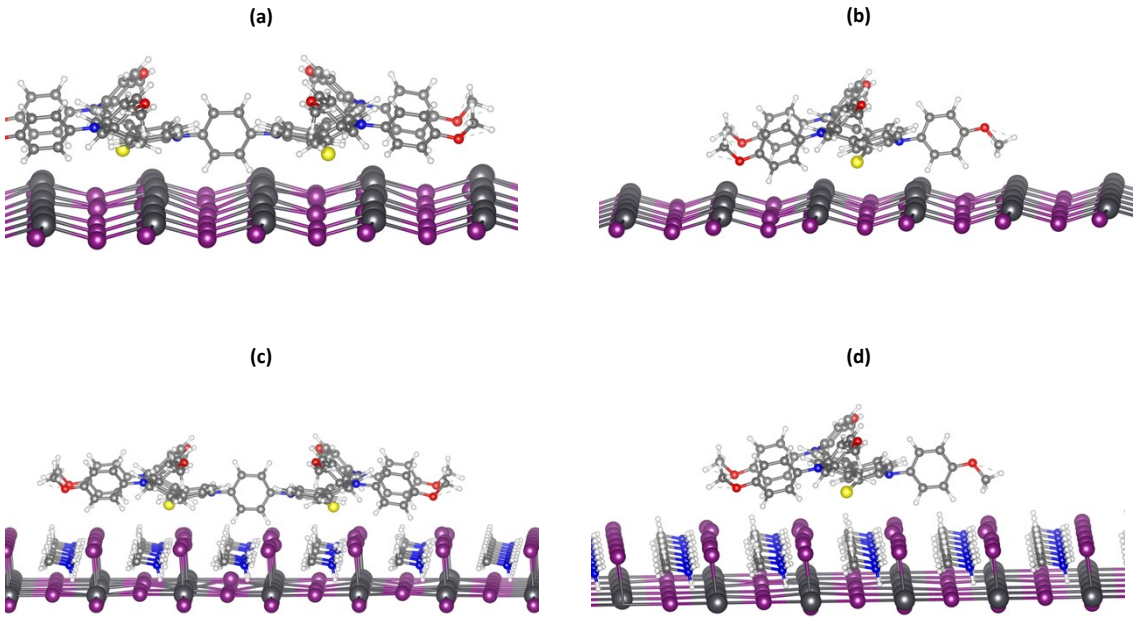

Figure S6: (a) **HTM1** *down* orientation on MAPI:PbI_2 surface, (b) **PTZ2** *down* orientation on MAPI:PbI_2 surface, (c) **HTM1** *down* orientation on MAPI:MAI surface, (d) **PTZ2** *down* orientation on MAPI:MAI surface.

Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white; O-red; S-yellow.

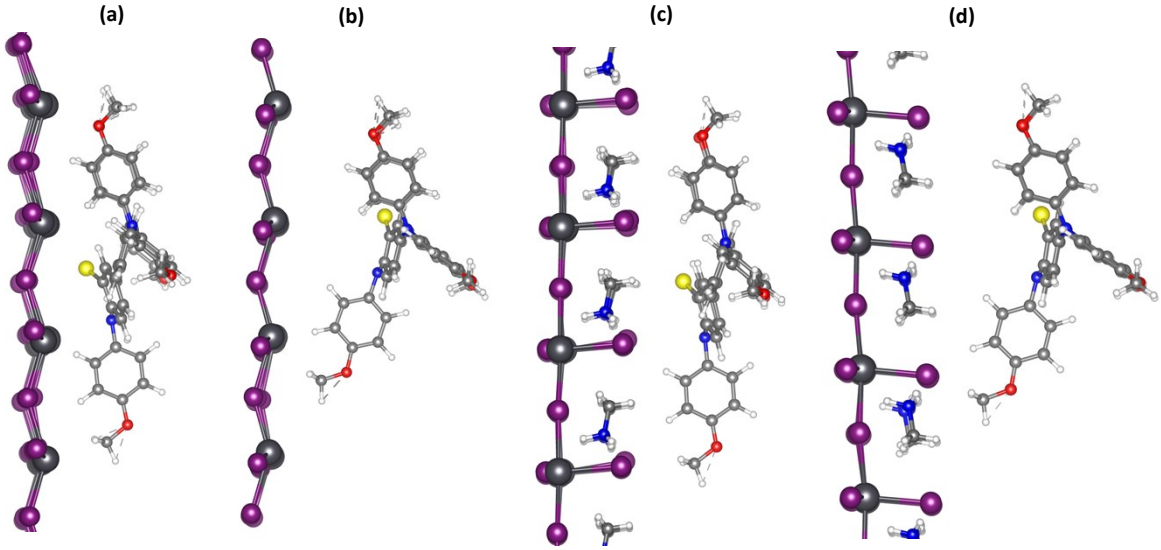

Figure S7: (a) **PTZ2** *down* orientation on MAPI:PbI_2 surface, (b) **PTZ1** *down* orientation on MAPI:PbI_2 surface, (c) **PTZ2** *down* orientation on MAPI:MAI surface, (d) **PTZ1** *down* orientation on MAPI:MAI surface.

Color code: Pb-dark gray; I-violet; C-light grey; N-blue; H-white; O-red; S-yellow.

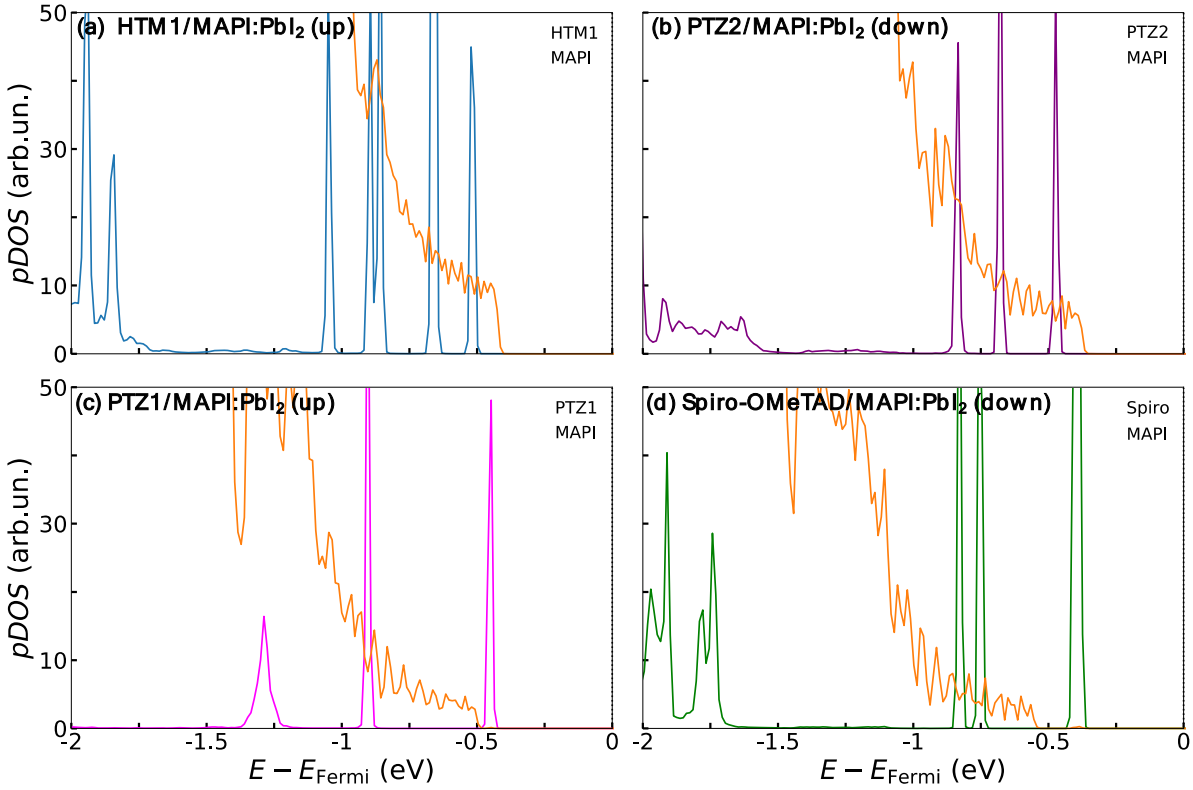

Figure S8: pDOS zoom of (a) **HTM1**/MAPI:PbI_2 (*up*), (b) **PTZ2**/MAPI:PbI_2 (*down*), (c) **PTZ1**/MAPI:PbI_2 (*up*) and (d) **Spiro-OMeTAD**/MAPI:PbI_2 (*down*).

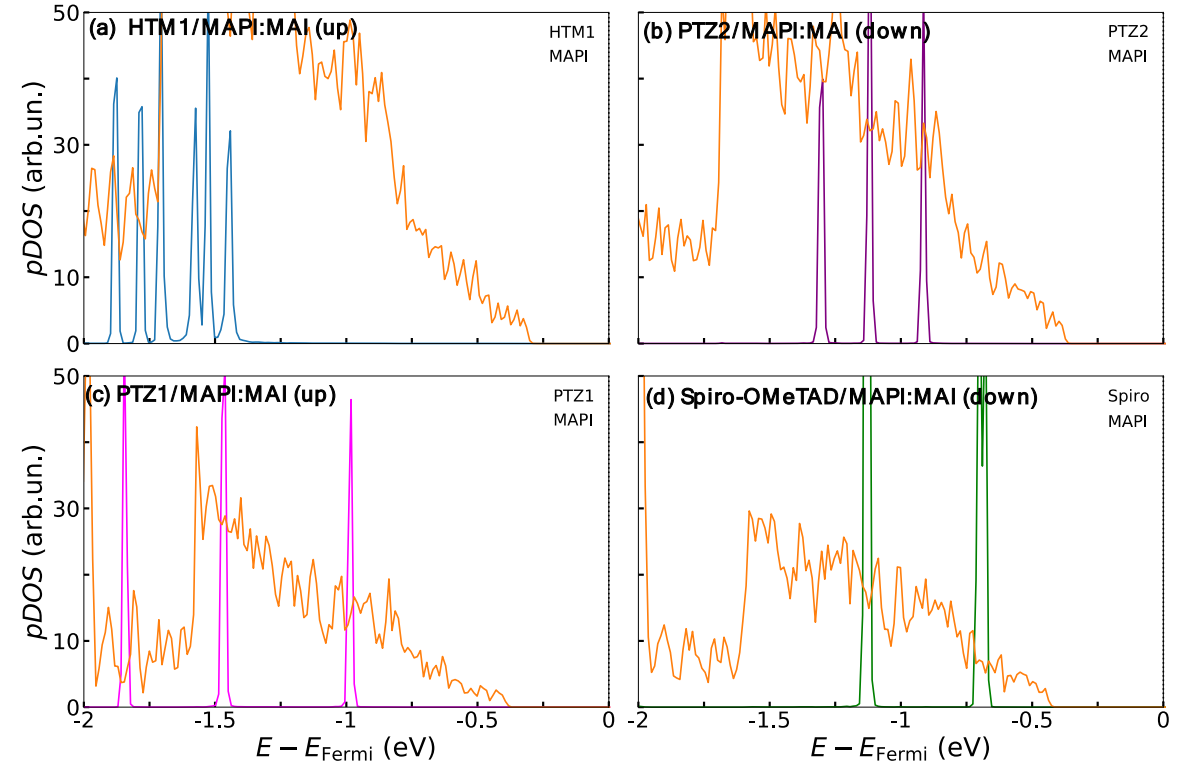

Figure S9: pDOS zoom of (a) **HTM1**/MAPI:MAI (*up*), (b) **PTZ2**/MAPI:MAI (*down*), (c) **PTZ1**/MAPI:MAI (*up*) and (d) **Spiro-OMeTAD**/MAPI:MAI (*down*).