(SI) Transition Metal Inverse-Hybrid Perovskites

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For the promising d^8 fluorides $(MA)_3FNi$ and $(MA)_3FPd$, we observe band hybridization of the transition metal (TM) valence band (VB, TM d and s) and conduction band (CB, TM p) states with the MA sp^3 states (note that we disregard small hybridization between TM $d(s)$ and p states for simplicity, see Fig. S1 (a) and Fig. 4). MA forms sets of bonding and antibonding sp^3 states from C–H, N–H, and C–N bonds. These MA states show large energetic splitting, with bands below ($\approx -5\,\mathrm{eV}$ and below) and above ($\approx 3\,\mathrm{eV}$ onward) the Fermi level. However, they also contribute to both VB and CB edge states. From these findings, a schematic picture is deduced in Fig. S1 (b), with antibonding states at the VBE and bonding states at the CBE. Such a band ordering is analogous to other semiconductors such as Cu_3N[1] or $MAPbI_3$[2]. As a result, the VBE (CBE) is energetically shifted above (below) the level of the constituting atomic (or molecular in case of MA) energy levels. Since defects usually introduce acceptor or donor levels that are located close in energy to their atomic (molecular) states, such a band ordering leads to shallow defect states inside or close to the respective band edges instead of deep trap states. Such shallow defect levels do not act as trap states, i.e., are no major factor for charge carrier recombination. This has been shown, e.g., for $MAPI_3$ and is in line with *ab initio* investigations of possible defect levels and defect formation energies.[2, 3] This property is, of course, highly desirable for photovoltaics.

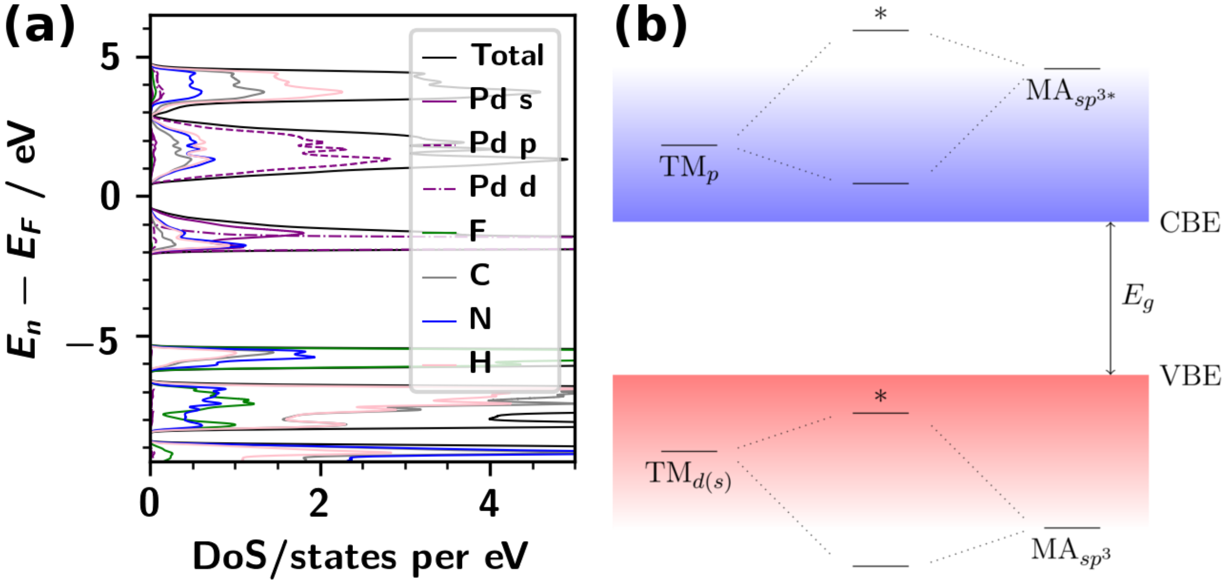

FIG. S1. (a) Density of states of $(MA)_3FPd$ and (b) simplified schematic model of the hybridization between TM and MA states in $(MA)_3FNi$ and $(MA)_3FPd$.

In order to confirm the character of the hybridization at the band edges, we investigated the maximally localized Wannier functions that result from a projection of the computed HSE densities onto a Wannier basis (focusing on the TM valence bands).

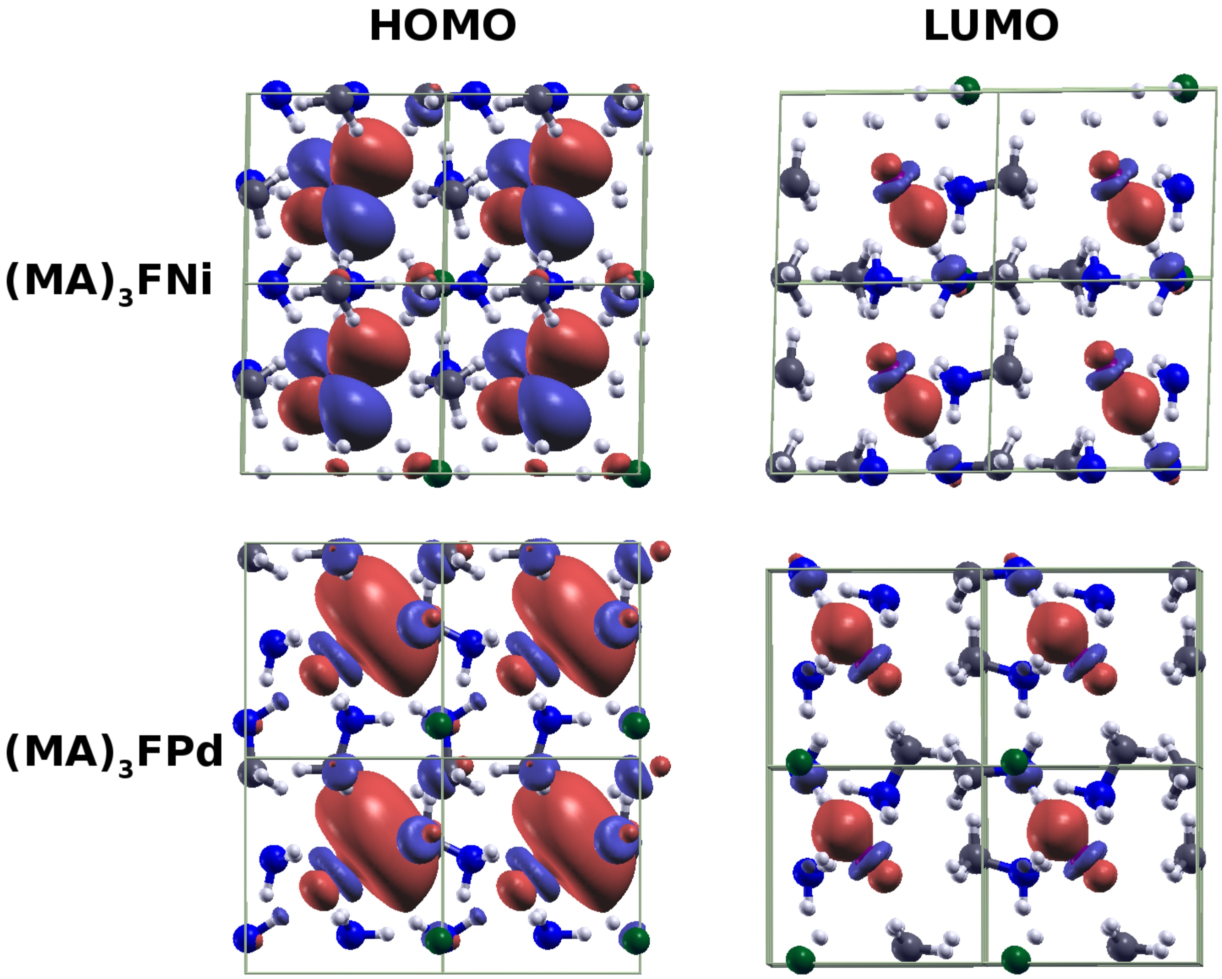

FIG. S2. Wannier representation of HOMO and LUMO states of (MA)$_3$FNi and (MA)$_3$FPd. Atoms are colored according to the main text. Negative and positive values of the Wannier orbitals are displayed as blue and red isosurfaces, respectively. Isovalues are 3.0 (LUMOs), 0.7 (HOMO, Ni), and 1.0 (HOMO, Pd). In both cases, the HOMO shows antibonding hybridization between TM *d* and CH$_3$, whereas the LUMO is a bonding combination between TM and one NH$_3$ group.

[1] A. Zakutayev, C. M. Caskey, A. N. Fioretti, D. S. Ginley, J. Vidal, V. Stevanovic, E. Tea, and S. Lany, J. Phys. Chem. Lett. **5**, 1117 (2014), arXiv:arXiv:1011.1669v3.

[2] R. E. Brandt, V. Stevanovic, D. S. Ginley, and T. Buonassisi, MRS Commun. **5**, 265 (2015), arXiv:1504.02144.

[3] W.-J. Yin, T. Shi, and Y. Yan, Appl. Phys. Lett. **104**, 063903 (2014).