Supporting Information

Crystallographic Orientation	001	110	111-Pb
Pb (82)	0.81	0.80	0.59
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Se(Pb for 111) (34)(82)	-0.78	-0.75	0.59
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Table 1 Bader charges of atoms at top layer of the slab represents pristine PbSe surfaces. Positive number indicates loss of charges while negative means gaining charges.

Crystallographic Orientation	001	110	111-Pb
Pb (82)	0.81	0.77	0.68
Pb (82)	0.90	0.85	0.73
Se(Pb for 111) (34)(82)	-0.73	-0.69	0.73
Se(Pb for 111) (34)(82)	-0.73	-0.62	0.73

Table 2 Bader charges of atoms at top layer of the with 25% coverage of Iodine ligand attached on PbSe surfaces. Positive number indicates loss of charges while negative means gaining charges.

Ligand DOS contribution near Fermi level over total DOS	
I	18.1%
Br	15.6%
Cl	13.4%

Table 3 Ligand DOS contribution near Fermi level over total DOS within energy bandwidth of 1.5kT from the valence band maxima

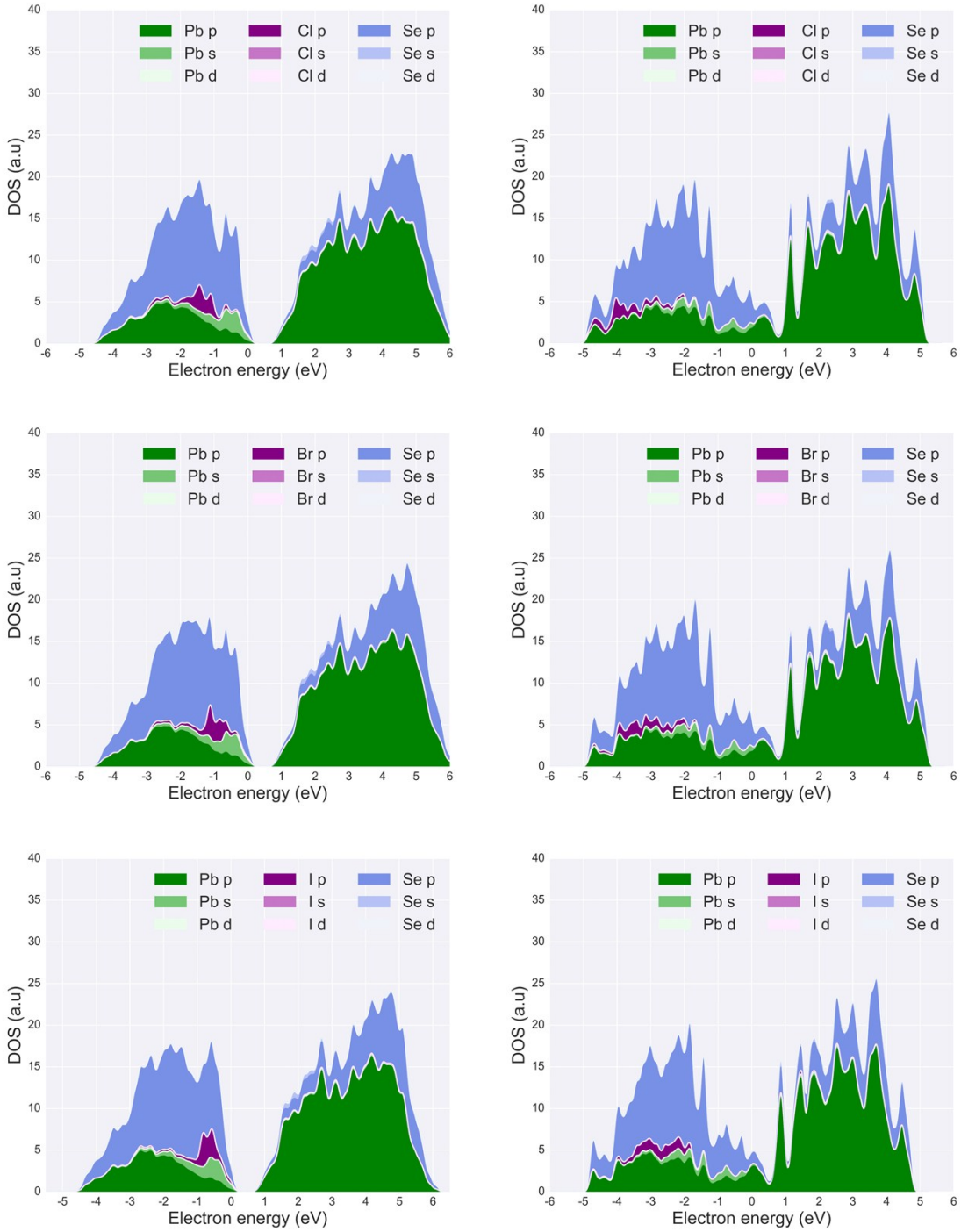

Figure 1 Projected DOS of PbSe (110) and (111) surfaces with three different halide ligands. (top-left: Chlorine on (110) plane, top-right: Chlorine on (111) plane, middle-left: Bromine on (110) plane; middle-right: Bromine on (111) plane, bottom-left: Iodine on (110) plane, bottom-right: Iodine (110) plane.)

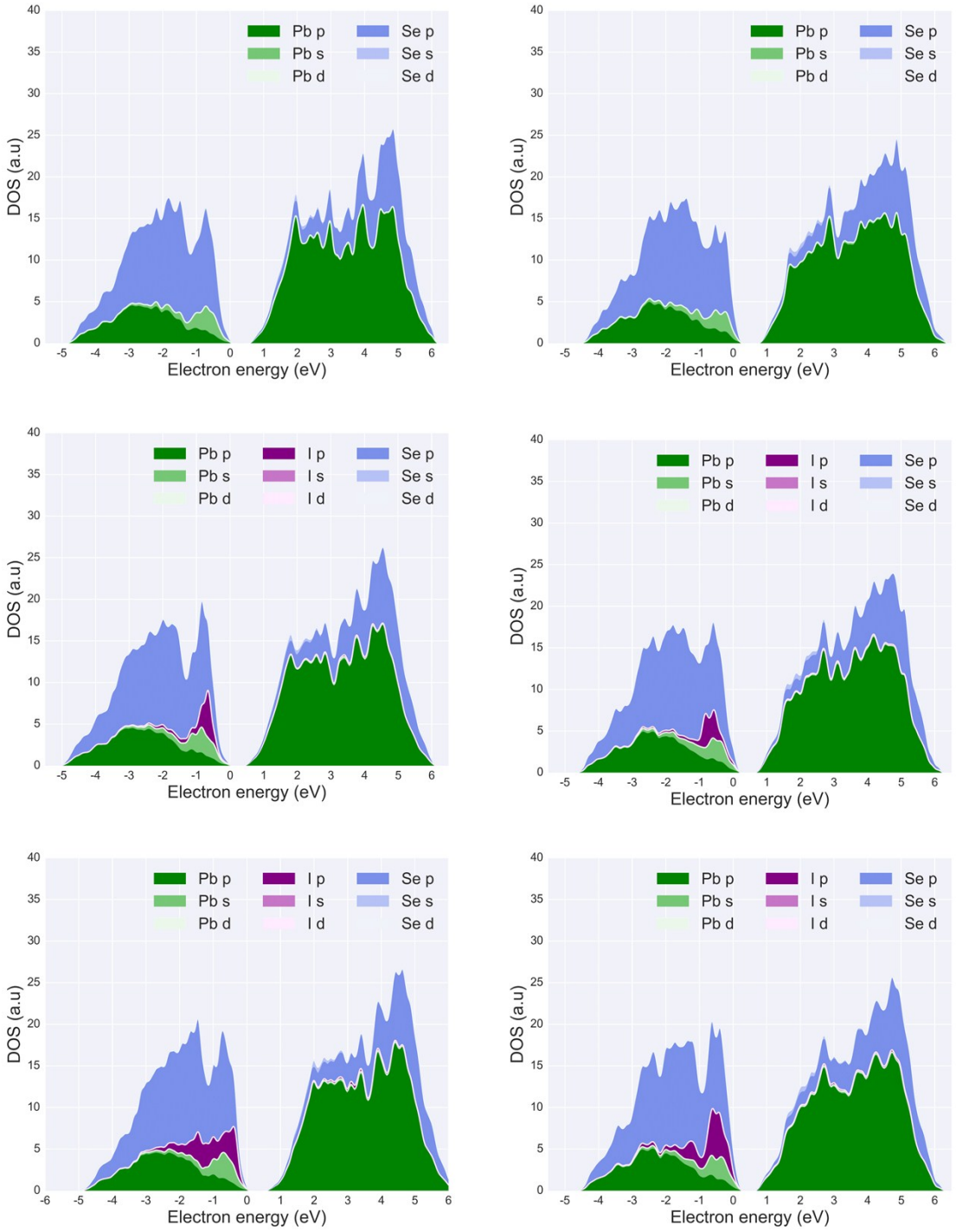

Figure 2 Projected DOS of PbSe (001) and (110) surfaces with three different coverages of iodine ligands. (top-left: 0% for (001) plane, middle-left: 25% for (001) plane, bottom-left: 50% for (001) plane; top-right: 0% for (110) plane, middle-right: 25% for (110) plane, bottom-right: 50% for (110) plane.)

Rough estimation of Dipole with ligand coverage changes:
Assumptions:

1. Adding more ligands to surfaces the relative distances of each effective charges do not change much.
2. The surface charge is condensed to a point charge as in 1D consideration.

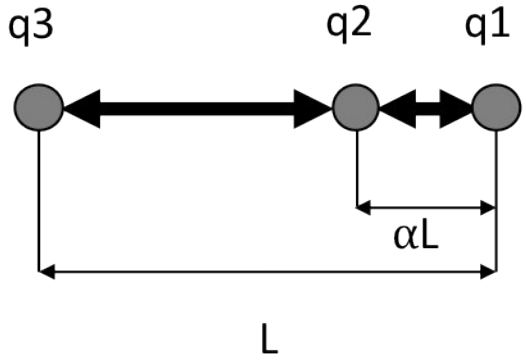

Figure 3 schematic diagram of dipole moment of PbSe (111) surface with iodine ligand passivated. q1 represents effective charges of ligands, q2 represents the effective charges of first lead atom layer and q3 represents the rest of charges in the slab.

Then we can have a rough calculation of dipole moment of the system as following:

$Dipole\ Moment = L * D = L * |q1 - (1 - \alpha) * q2|$

After substitute alpha with different numbers, we generated

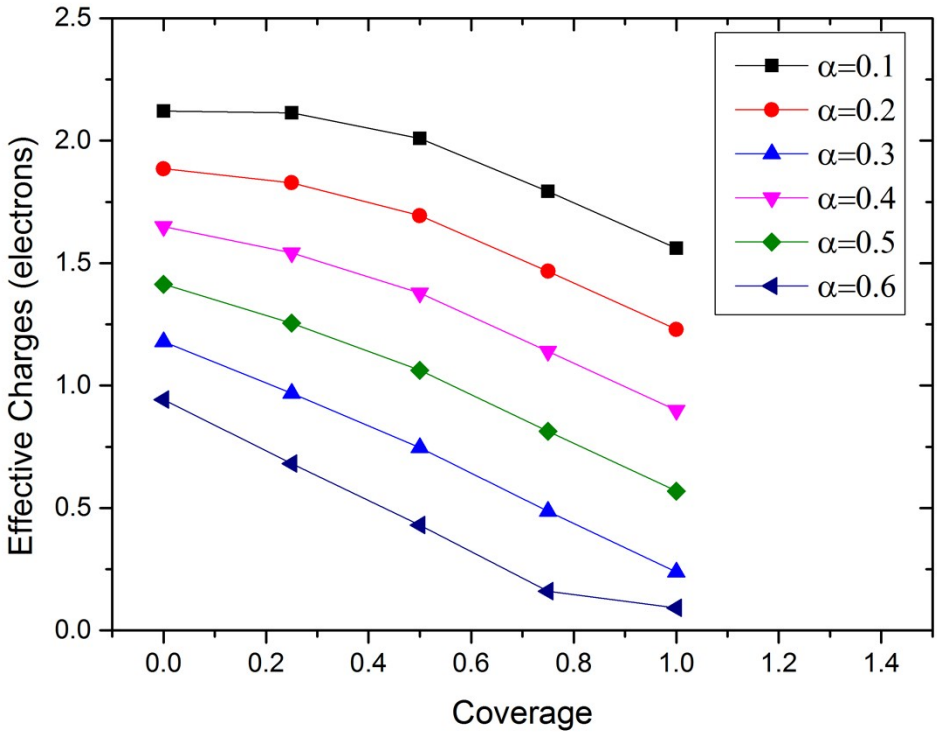

Figure 4 Change of dipole moment of PbSe (111) surface with iodine ligand passivated at different level of coverage. In this work alpha should be around 0.2.