Supporting information

Wavelength-dependent optical transition mechanisms for light-harvesting of perovskite MAPbI₃ solar cells by first-principles calculations

A. Band structure and density of states of perovskite MAPbI₃
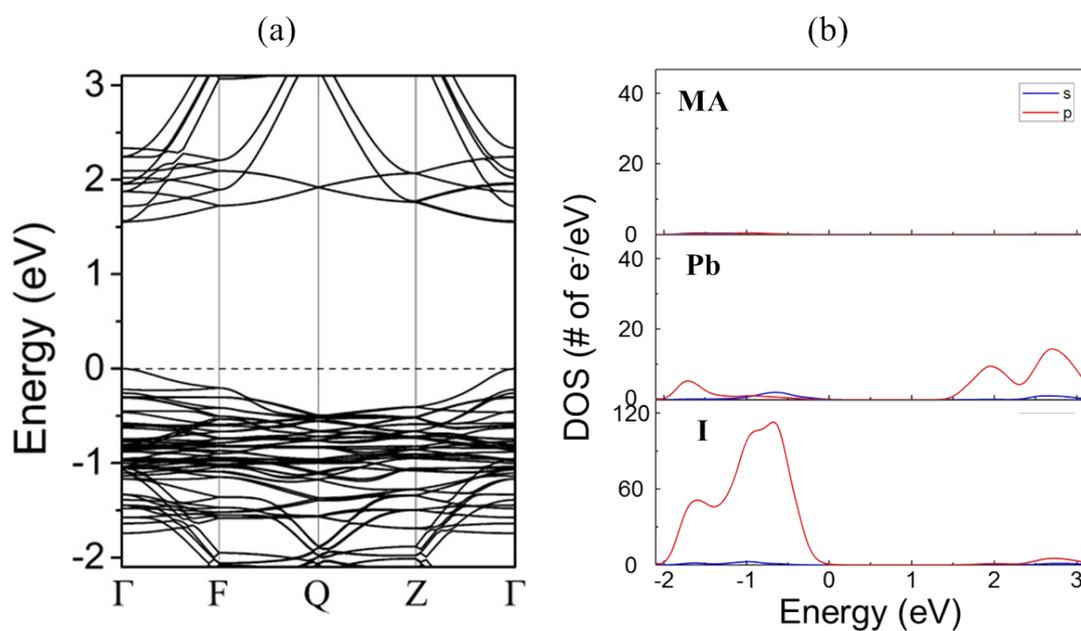
(a)   (b)

Figure S1 (a) The electronic band structure and (b) the density of states diagram projected by components and orbital types of the non-polar MAPbI₃, respectively

The electronic band structure and the density of states of perovskite MAPbI₃ were calculated as shown in Figure S1. These calculations were performed using the CASTEP code based on DFT. GGA-PBE and ultrasoft pseudopotential were used with

the cut-off energy of 400 eV, where no gap correction was used here.

The partial density of states (PDOS) of Pb, I and MA were projected and show that the states near Fermi energy mainly come from the lead triiodide framework. The occupied states are mainly consisting of I_p and Pb_s states and the unoccupied states are mainly consisting of Pb_p states, respectively. On the contrary, there is nearly no contribution of states of MA ions near Fermi energy.

B. Procedures of data using the ranking list analysis

E = 1.5 eV

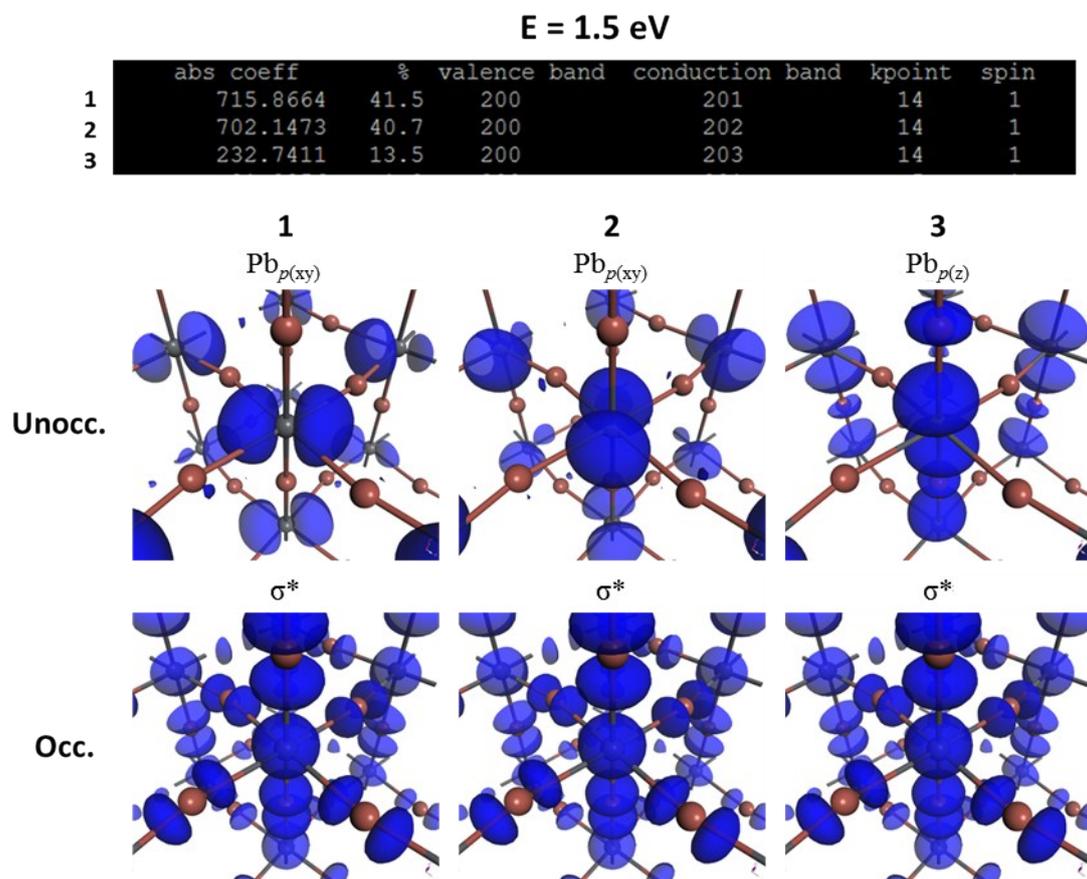|	abs coeff	%	valence band	conduction band	kpoint	spin
1	715.8664	41.5	200	201	14	1
2	702.1473	40.7	200	202	14	1
3	232.7411	13.5	200	203	14	1

Figure S2 The ranking list of the band-resolved result for the absorption energy of 1.5 eV, where the corresponding orbital contour plots of occupied and unoccupied states of the perovskite $MAPbI_3$ are also shown.

Figure S2 is the table of the band-resolved analysis of the optical absorption spectrum for each k point, where the decomposed absorption coefficient (abs coeff) with its ratio of the contribution (%, defined by the ratio of each decomposed absorption coefficient to the overall absorption coefficient), the band number of the occupied state

(valence band) and the unoccupied state (conduction band) of each transition set with the k-point dependency (kpoint) and the spin dependency (spin). The result is ranked by the ratio of the contribution of each transition set. As mentioned above, two occupied states, σ^* and $I_{p(\text{nb})}$, and two unoccupied states, $Pb_{p(\text{xy})}$ and $Pb_{p(\text{z})}$, participated optical transitions in NIR-VIS-UV region, constructing four predominant transitions. For a selected absorption energy, the characteristics of the occupied state and the unoccupied state of each set can be identified and further be classified to the four predominant transitions by projecting and the observing the orbital contour plot of each state of each set as shown in the main manuscript. The ratios of these four transitions at a certain absorption energy can be obtained by calculating the weighting ratios of the contributions in the whole optical transitions. By summing above weighted results at different k points with increased absorption energies in NIR-VIS-UV region, the relative ratios of the four predominant transitions can be plotted as shown in Figure 4(a) of the main manuscript.

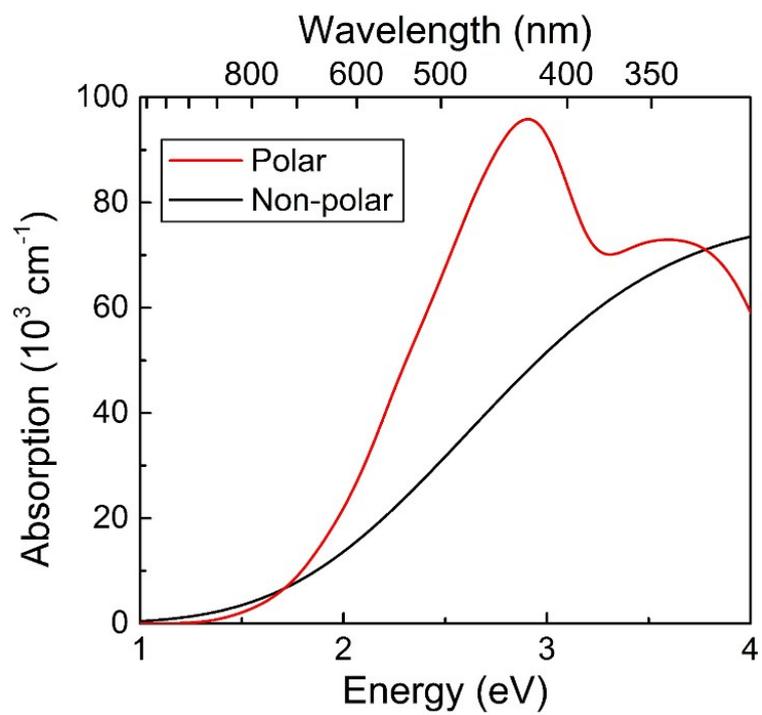**C. The calculated absorption spectrum of non-polar MAPbI₃ (np-MAPbI₃)**

Figure S3 The calculated absorption spectrum of non-polar MAPbI$_3$ (in comparing to polar-MAPbI$_3$)