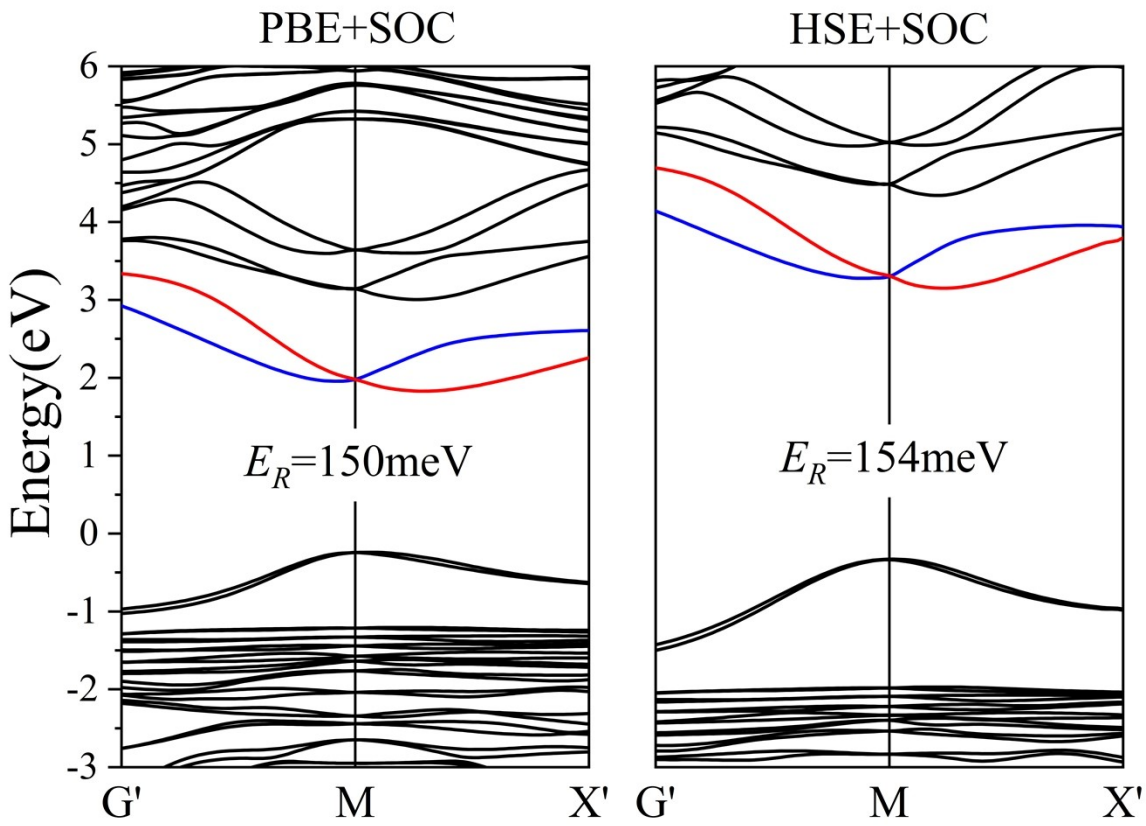
STable.1 The $\Delta\theta_{Cl}$ (°) parameters representing the distortion degrees of 2D $MAPbCl_3$.

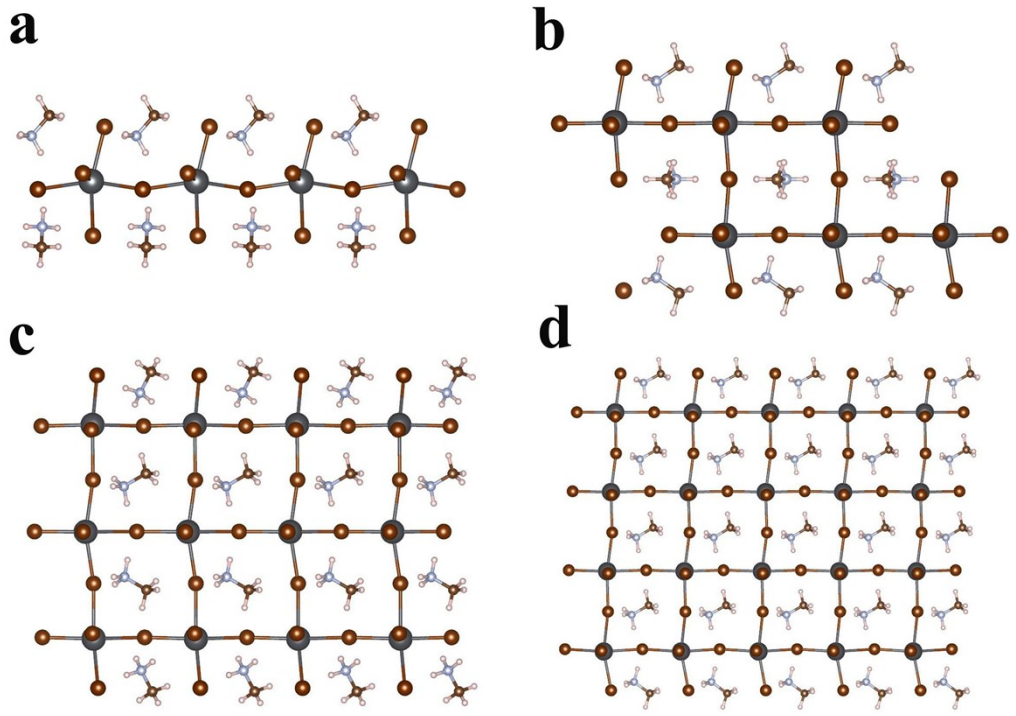
Layers	**1L**	**2L**	**3L**	**4L**
S1	27.1	12.7	9.6	8.0
S2		12.8	13.8	8.7
S3			9.7	8.7
S4				13.5

STable.2 The effective masses (m_0) of electrons at CBM and holes at VBM of 2D HOIPs, denoted by m_e and m_h respectively. Note that m_0 is the rest mass of a free electron.

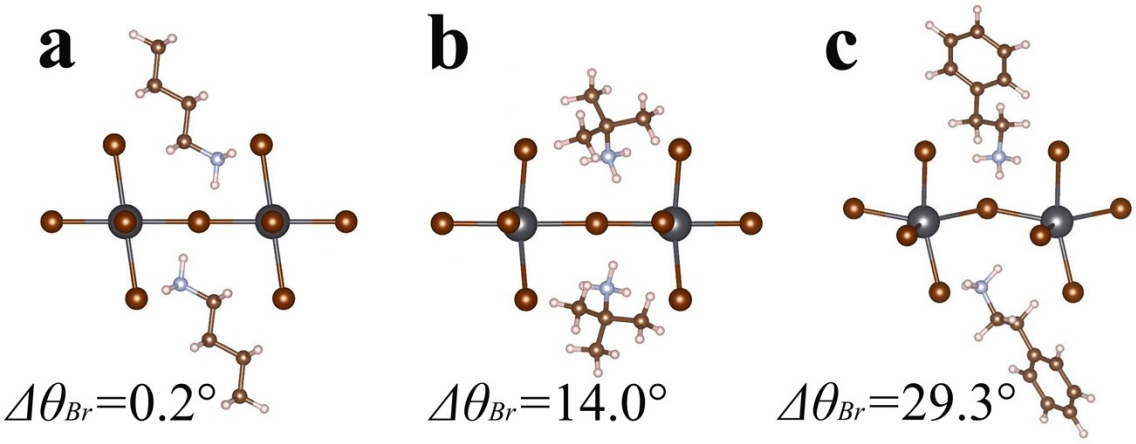
	$MAPbCl_3$		$MAPbBr_3$		$MAPbI_3$	
m (m_0)	m_e	m_h	m_e	m_h	m_e	m_h
1L	0.278	0.359	0.192	0.319	0.109	0.208
2L	0.207	0.338	0.113	0.269	0.069	0.136
3L	0.163	0.280	0.101	0.144	0.072	0.120
4L	0.158	0.264	0.094	0.127	0.066	0.076



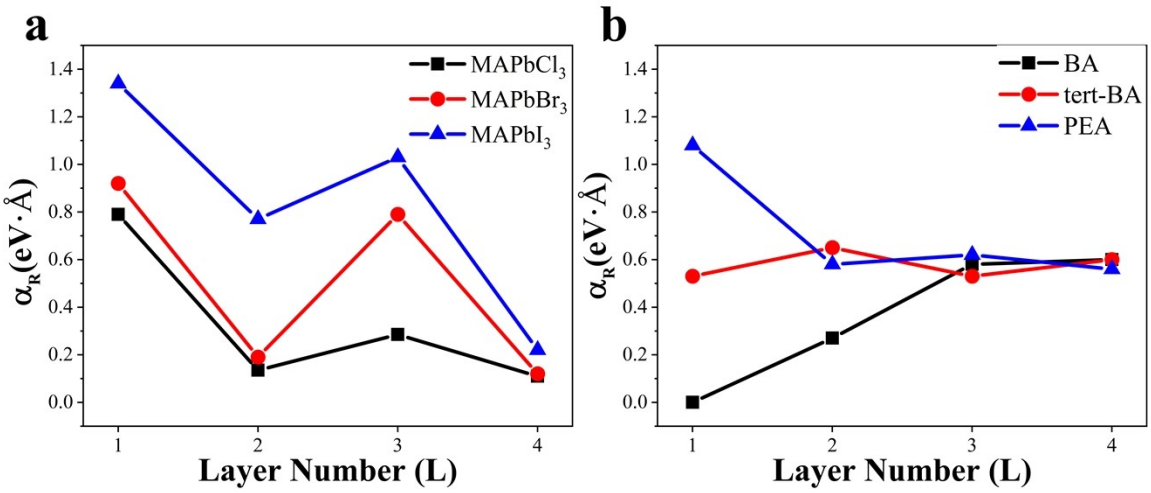
SFig.1 The comparison calculation between adopting PBE+SOC or HSE+SOC method on the energy bands near M point of 1L $MAPbBr_3$.



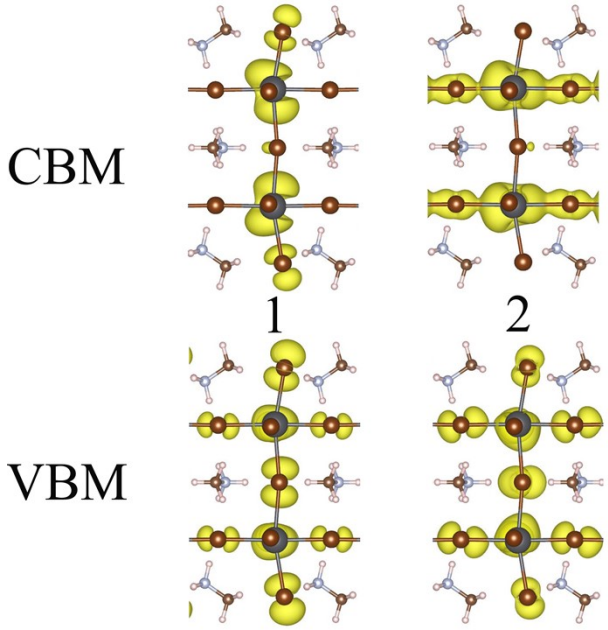
SFig.2 The structures for 2D $MAPbBr_3$: (a) 1L, (b) 2L, (c) 3L, (d) 4L.



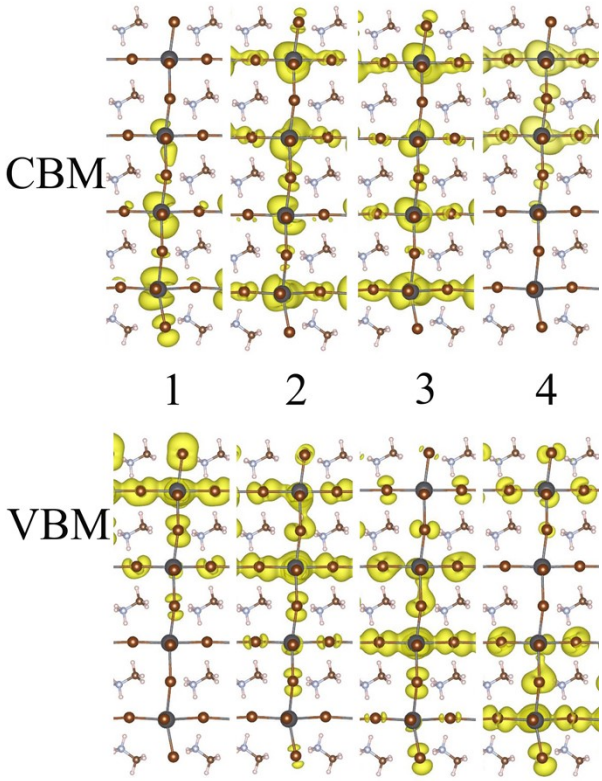
SFig.3 The structures of (a) 1L BA-$MAPbBr_3$, (b) 1L tert-BA-$MAPbBr_3$ and (c) 1L PEA-$MAPbBr_3$. The structural distortion parameters are denoted as $\Delta\theta_{Br}$.



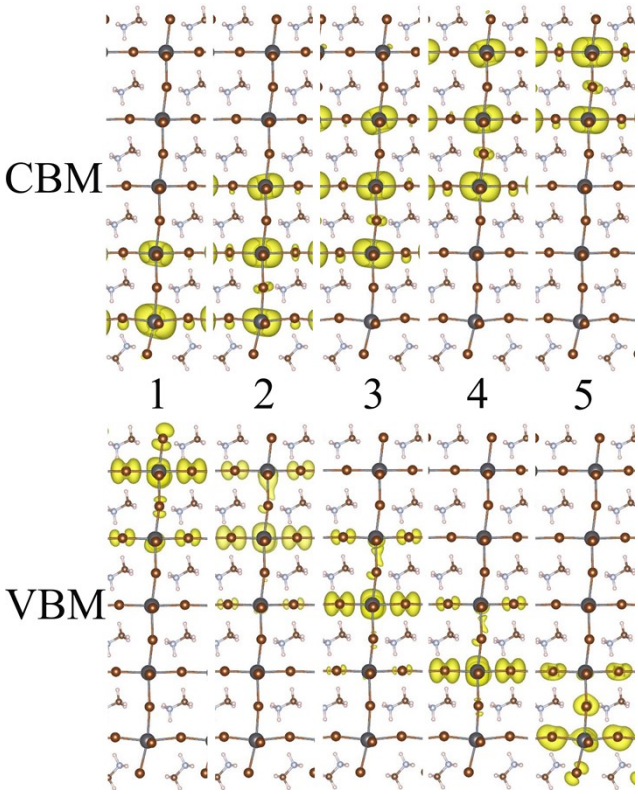
SFig.4 α_R parameters for (a) $MAPbX_3$ (X=Cl, Br, I) without ligands and (b) $MAPbBr_3$ with BA, tert-BA and PEA ligands.



SFig.5 The partial charge density of different CBMs and VBMs for 2L $MAPbBr_3$.



SFig.6 The partial charge density of different CBMs and VBMs for 4L $MAPbBr_3$.



SFig.7 The partial charge density of different CBMs and VBMs for 5L $MAPbBr_3$.