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# Electronic Structure of 2D Hybrid Perovskites: Rashba Spin-Orbit Coupling and Impact of Interlayer Spacing

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# Supporting Information

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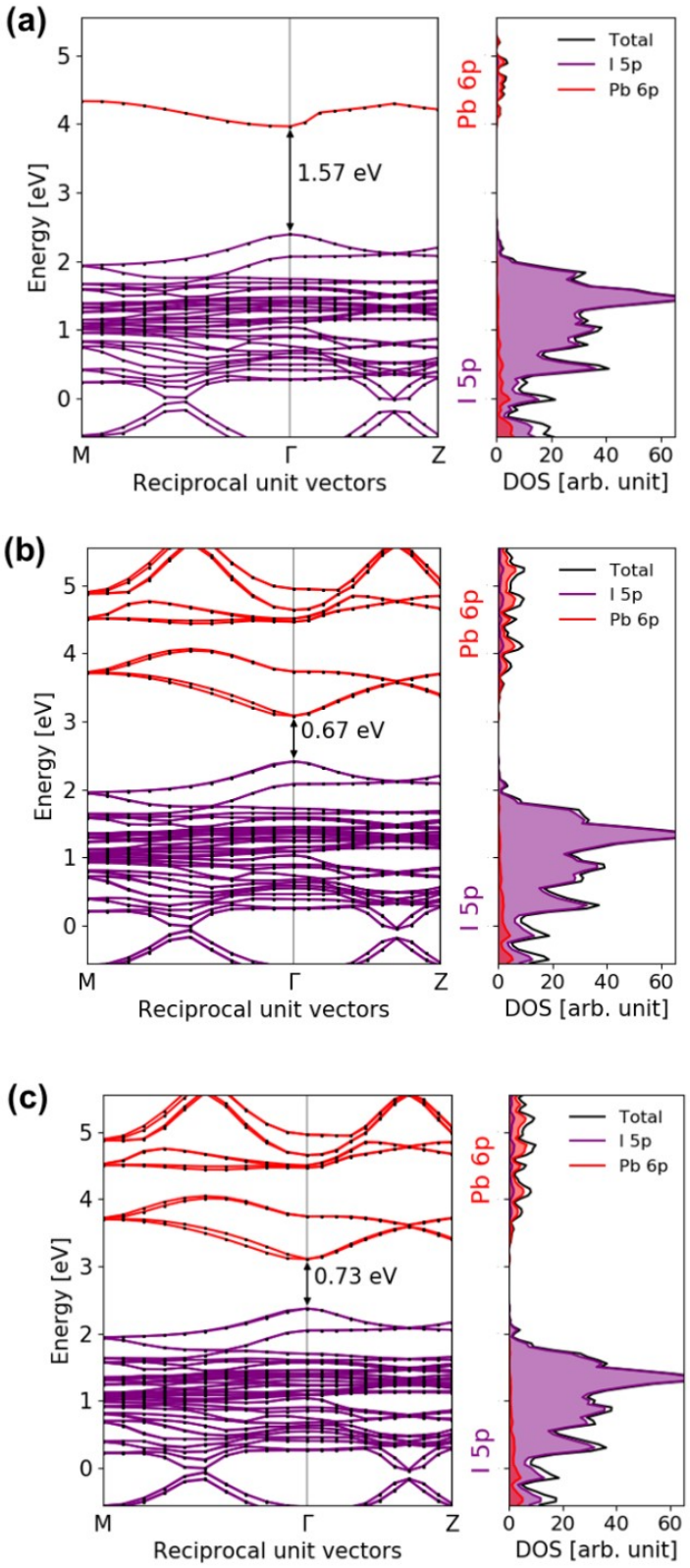


**Fig. S1** Calculated band structure and the corresponding partial density of states (PDOS) of $MAPbI_3$ within: (a) GGA approximation without SOC, core electrons represented by scalar-relativistic pseudopotentials, (b) GGA approximation with SOC, using projected augmented wave functions, (c) GGA approximation with SOC including the van der Waals effects, using projected augmented wave functions.

**Table. S1** Lattice parameters of the relaxed structures.

| Structure | Method | Lattice parameters | | |
|---|---|---|---|---|
| | | a | b | c |
| **$BDAPbI_4$** | **Scalar relativistic** | +1.016480934i<br>+0.001094221j<br>-0.011516648k | +0.010714555i<br>+1.055049708j<br>-0.009417520k | +0.453032042i<br>+0.302087656j<br>+1.235248221k |
| | **SOC** | +1.016480934i<br>+0.001094221j<br>-0.011516648k | +0.010714555i<br>+1.055049708j<br>-0.009417520k | +0.453032042i<br>+0.302087656j<br>+1.235248221k |
| | **SOC+London** | +1.016480934i<br>+0.001094221j<br>-0.011516648k | +0.010714555i<br>+1.055049708j<br>-0.009417520k | +0.453032042i<br>+0.302087656j<br>+1.235248221k |
| **$HDAPbI_4$** | **Scalar relativistic** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+0.7158443164j<br>+0.000000000k | -0.2244716445i<br>+0.000000000j<br>+0.7308821332k |
| | **SOC** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+0.715844316j<br>+0.000000000k | -0.224471644i<br>+0.0000000000j<br>+0.730882133k |
| | **SOC+London** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+0.715844316j<br>+0.000000000k | -0.224471644i<br>+0.000000000j<br>+0.730882133k |
| **$ODAPbI_4$** | **Scalar relativistic** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+0.60749364j<br>+0.000000000k | -0.18701i<br>+0.0000j<br>+0.6282k |
| | **SOC** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+0.607493640j<br>+0.000000000k | -0.187010000i<br>+0.000000000j<br>+0.628200000k |
| | **SOC+London** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+0.607493640j<br>+0.000000000k | -0.187010000i<br>+0.000000000j<br>+0.628200000k |
| **$DDAPbI_4$** | **Scalar relativistic** | +1.126691658i<br>+0.006270929j<br>+0.100747423k | +0.004816344i<br>+0.599415307j<br>+0.002201466k | -0.150646731i<br>-0.000679544j<br>+0.612748237k |
| | **SOC** | +1.126691658i<br>+0.006270929j<br>+0.100747423k | +0.004816344i<br>+0.599415307j<br>+0.002201466k | -0.150646731i<br>-0.000679544j<br>+0.612748237k |

| | | | | |
|---|---|---|---|---|
| | **SOC+London** | +1.126691658i<br>+0.006270929j<br>+0.100747423k | +0.004816344i<br>+0.599415307j<br>+0.002201466k | -0.150646731i<br>-0.000679544j<br>+0.612748237k |
| **$MAPbI_3$** | **Scalar relativistic** | +0.988930439i<br>-0.000060348j<br>+0.000218033k | -0.000060722i<br>+0.986392170j<br>-0.000695749k | +0.000307984i<br>-0.000982271j<br>+1.442764694k |
| | **SOC** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+1.000000000j<br>+0.000000000k | +0.000000000i<br>+0.000000000j<br>+1.429581282k |
| | **SOC+London** | +1.000000000i<br>+0.000000000j<br>+0.000000000k | +0.000000000i<br>+1.000000000j<br>+0.000000000k | +0.000000000i<br>+0.000000000j<br>+1.429581282k |

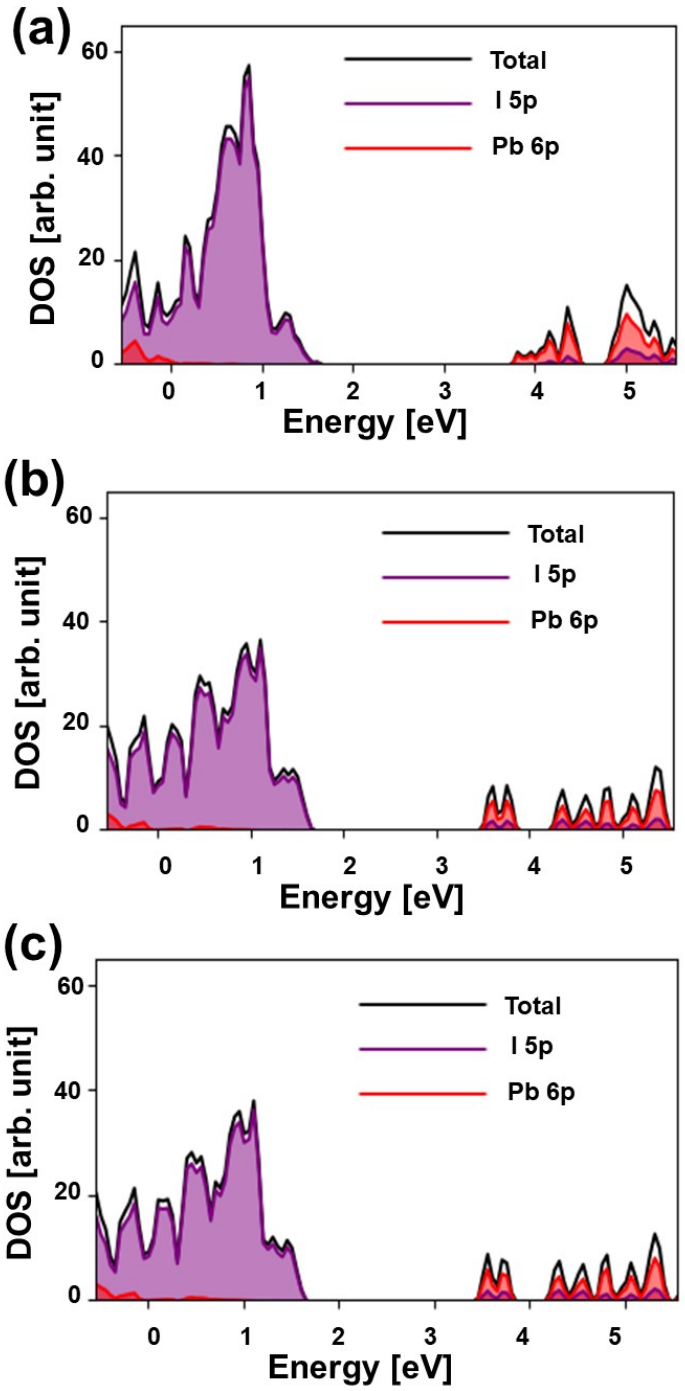


**Fig. S2** Calculated total and partial density of states (PDOS) of $BDAPbI_4$ within: (a) GGA approximation without SOC, core electrons represented by scalar-relativistic pseudopotentials, (b) GGA approximation with SOC, using projected augmented wave functions, (c) GGA approximation with SOC including London dispersion, using projected augmented wave functions.

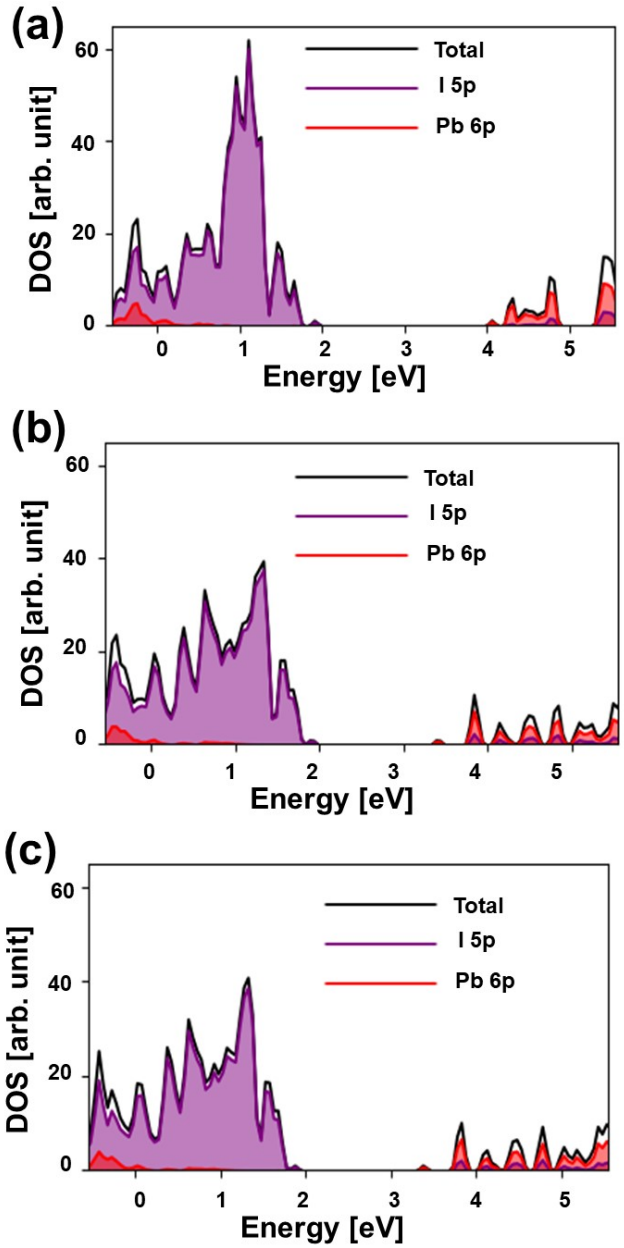


**Fig. S3** Calculated total and partial density of states (PDOS) of $HDAPbI_4$ within: (a) GGA approximation without SOC, core electrons represented by scalar-relativistic pseudopotentials, (b) GGA approximation with SOC, using projected augmented wave functions, (c) GGA approximation with SOC including London dispersion, using projected augmented wave functions.

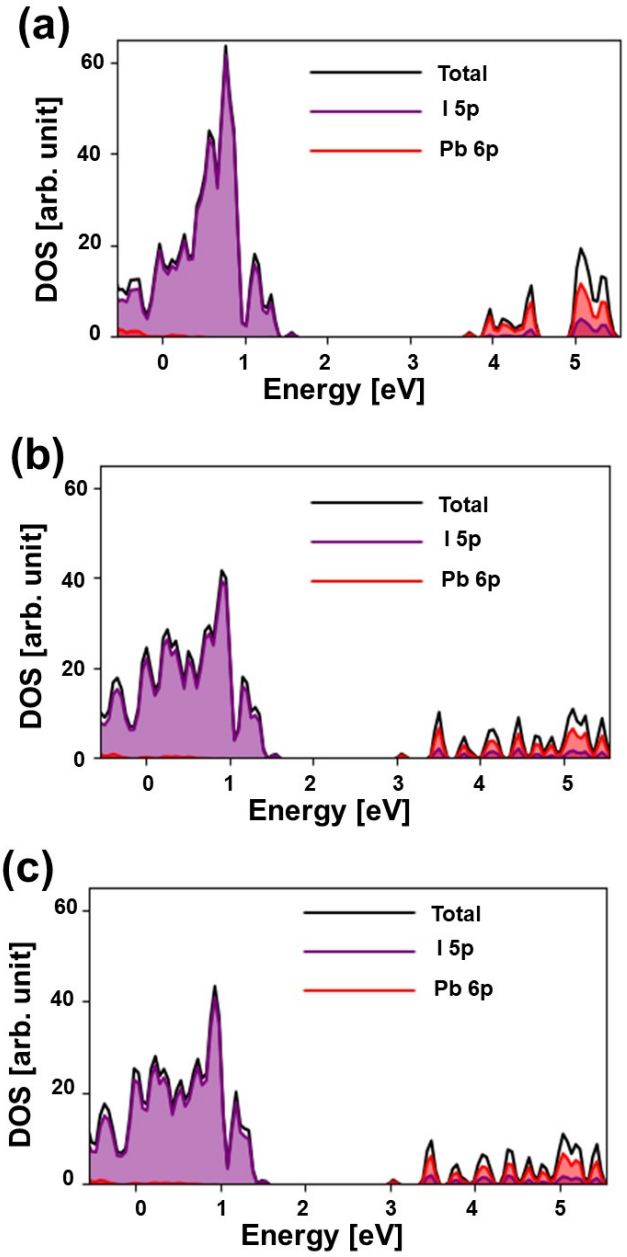


**Fig. S4** Calculated total and partial density of states (PDOS) of $ODAPbI_4$ within: (a) GGA approximation without SOC, core electrons represented by scalar-relativistic pseudopotentials, (b) GGA approximation with SOC, using projected augmented wave functions, (c) GGA approximation with SOC including London dispersion, using projected augmented wave functions.

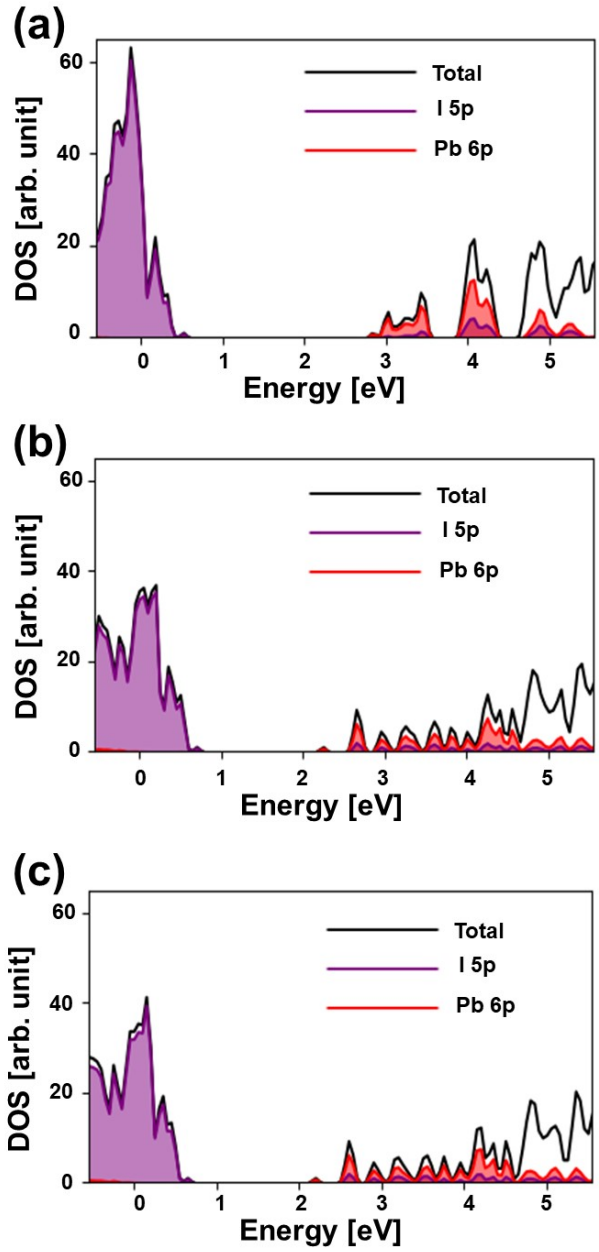


**Fig. S5** Calculated total and partial density of states (PDOS) of $DDAPbI_4$ within: (a) GGA approximation without SOC, core electrons represented by scalar-relativistic pseudopotentials, (b) GGA approximation with SOC, using projected augmented wave functions, (c) GGA approximation with SOC including London dispersion, using projected augmented wave functions.

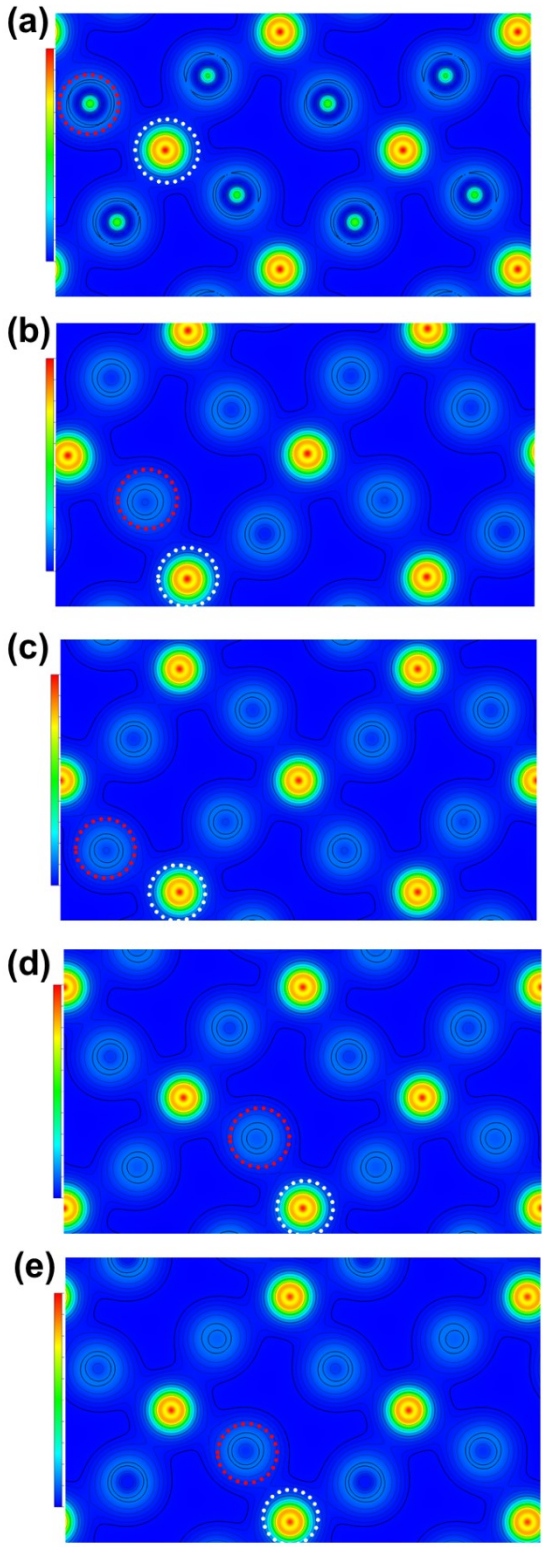


**Fig. S6** Charge density plots within the inorganic plane for (a) $MAPbI_3$, (b) $BDAPbI_4$, (c) $HDAPbI_4$, (d) $ODAPbI_4$, and (e) $DDAPbI_4$. The circles with white represent the lead atom and the circles with red represent the iodine atoms. A more covalent bond in between Pb and I for $MAPbI_3$ can be observed compared to layered perovskite.

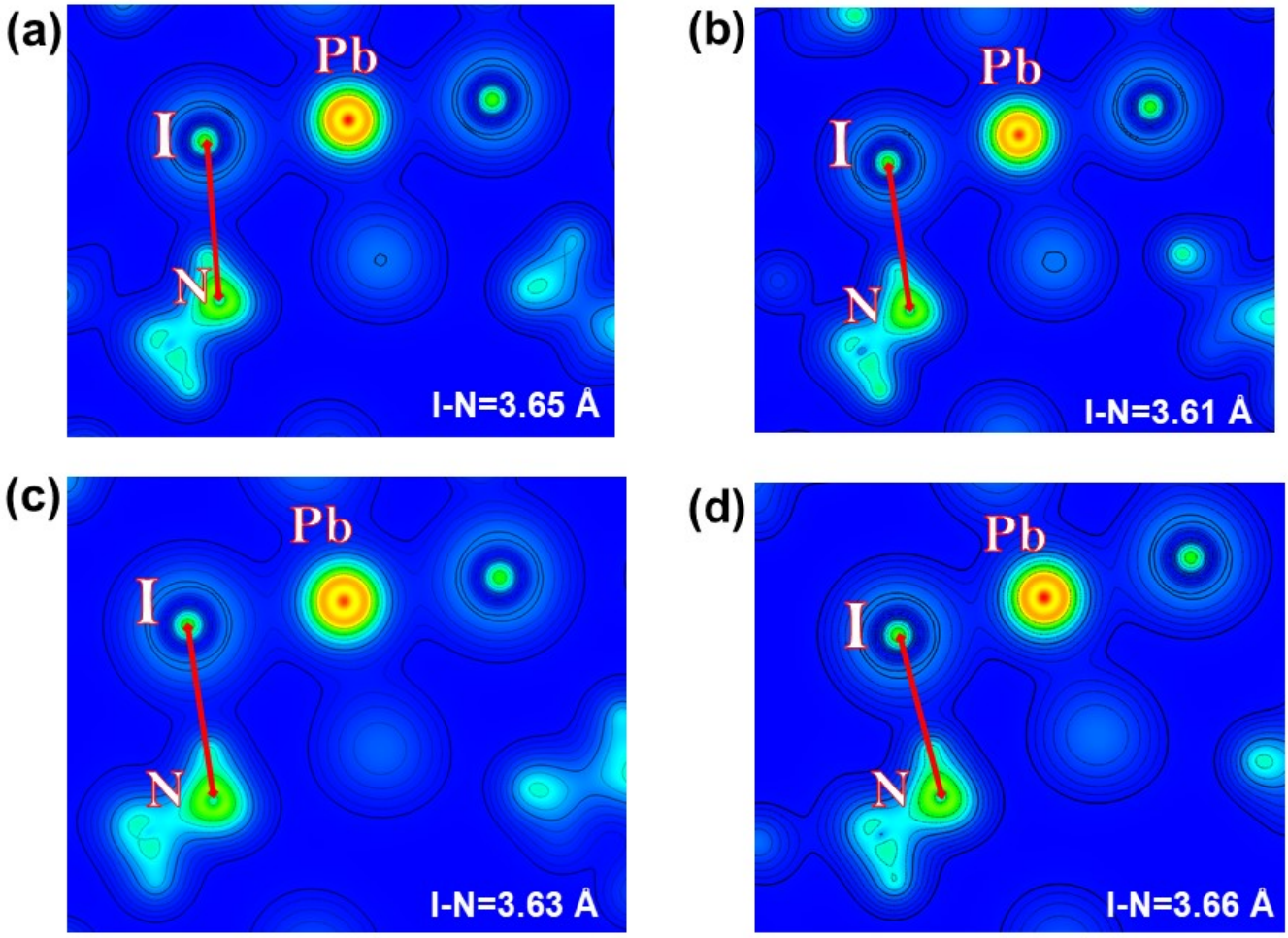


**Fig. S7** Charge density plots in between the inorganic plane and organic cation for (a) $BDAPbI_4$, (b) $HDAPbI_4$, (c) $ODAPbI_4$, and (d) $DDAPbI_4$.