Supplementary Information

Figure S1. The cell structure of CsPbX3

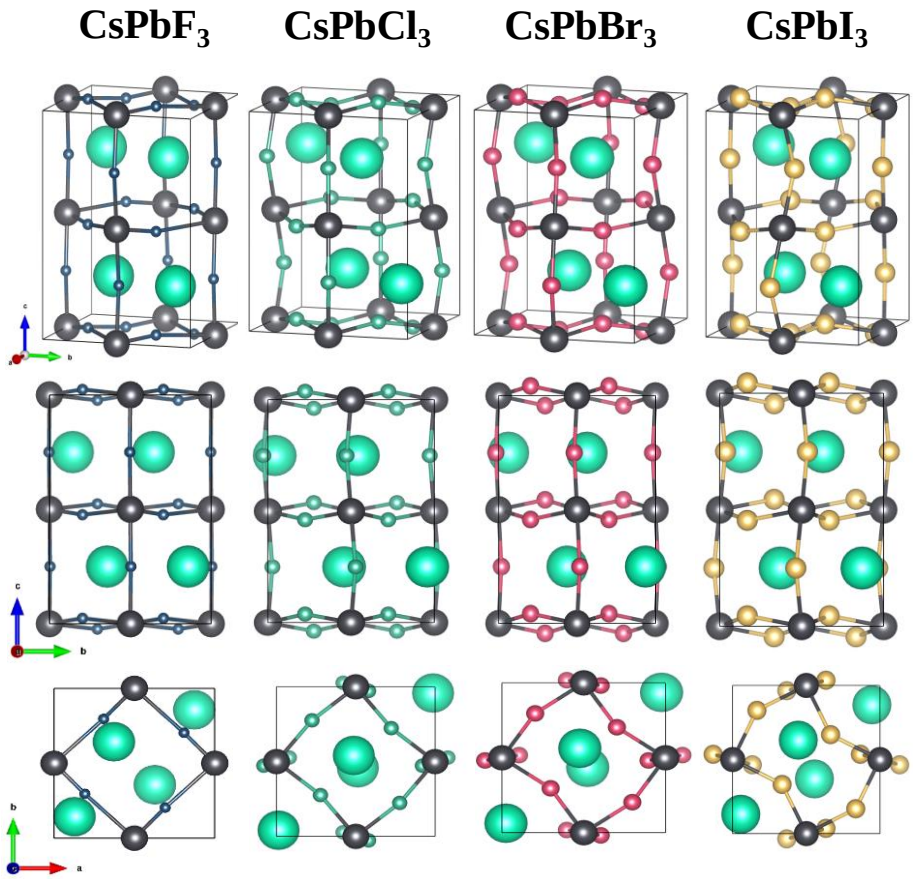


Figure S2. Details of the four structures optimized (CIF)

```
CsPbF3
1.0
       8.2069997787        0.0000000000        0.0000000000
       0.0000000000        8.2550001144        0.0000000000
       0.0000000000        0.0000000000       11.7589998245
   F   Cs   Pb
  12    4    4
Direct
     0.691559970         0.203950003         0.023830000
     0.308440030         0.796050012         0.976170003
     0.191559970         0.296050012         0.976170003
     0.808440030         0.703949988         0.023830000
     0.308440030         0.796050012         0.523829997
     0.691559970         0.203950003         0.476170003
     0.808440030         0.703949988         0.476170003
     0.191559970         0.296050012         0.523829997
     0.963020027         0.503239989         0.250000000
     0.036979999         0.496760011         0.750000000
     0.463019997         0.996760011         0.750000000
     0.536979973         0.003239989         0.250000000
     0.872690022         0.856729984         0.250000000
     0.127309978         0.143270016         0.750000000
     0.372690022         0.643270016         0.750000000
     0.627309978         0.356729984         0.250000000
     0.500000000         0.000000000         0.000000000
     0.000000000         0.500000000         0.000000000
     0.500000000         0.000000000         0.500000000
     0.000000000         0.500000000         0.500000000
```

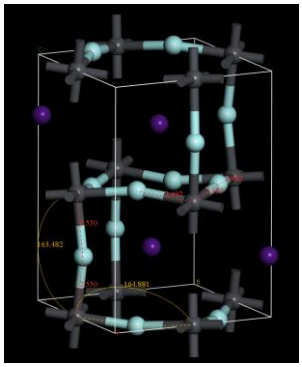
```
CsPbCl3
1.0
       8.2069997787        0.0000000000        0.0000000000
       0.0000000000        8.2550001144        0.0000000000
       0.0000000000        0.0000000000       11.7589998245
  Cl   Cs   Pb
  12    4    4
Direct
     0.776690006         0.223830000         0.038400002
     0.223309994         0.776170015         0.961600006
     0.276690006         0.276170015         0.961600006
     0.723309994         0.723829985         0.038400002
     0.223309994         0.776170015         0.538399994
     0.776690006         0.223830000         0.461600006
     0.723309994         0.723829985         0.461600006
     0.276690006         0.276170015         0.538399994
     0.080380000         0.527079999         0.250000000
     0.919619977         0.472920001         0.750000000
     0.580380023         0.972920001         0.750000000
     0.419620007         0.027079999         0.250000000
     0.987259984         0.958670020         0.250000000
     0.012740016         0.041329980         0.750000000
     0.487259984         0.541329980         0.750000000
     0.512740016         0.458670020         0.250000000
     0.500000000         0.000000000         0.000000000
     0.000000000         0.500000000         0.000000000
     0.500000000         0.000000000         0.500000000
     0.000000000         0.500000000         0.500000000
```

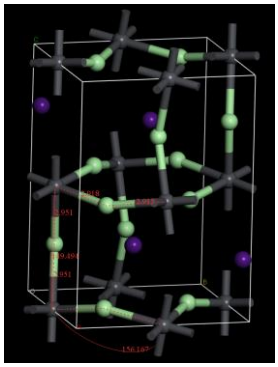
```
CsPbBr3
1.0
       8.2069997787        0.0000000000        0.0000000000
       0.0000000000        8.2550001144        0.0000000000
       0.0000000000        0.0000000000       11.7589998245
   Br   Cs   Pb
   12    4    4
Direct
     0.797219992         0.203759998         0.043269999
     0.202780008         0.796239972         0.956730008
     0.297219992         0.296240002         0.956730008
     0.702780008         0.703760028         0.043269999
     0.202780008         0.796239972         0.543269992
     0.797219992         0.203759998         0.456730008
     0.702780008         0.703760028         0.456730008
     0.297219992         0.296240002         0.543269992
     0.103720002         0.517840028         0.250000000
     0.896279991         0.482159972         0.750000000
     0.603720009         0.982159972         0.750000000
     0.396279991         0.017840028         0.250000000
     0.975910008         0.936670005         0.250000000
     0.024089992         0.063329995         0.750000000
     0.475910008         0.563329995         0.750000000
     0.524089992         0.436670005         0.250000000
     0.500000000         0.000000000         0.000000000
     0.000000000         0.500000000         0.000000000
     0.500000000         0.000000000         0.500000000
     0.000000000         0.500000000         0.500000000
```

```
CsPbI3
1.0
       8.2069997787        0.0000000000        0.0000000000
       0.0000000000        8.2550001144        0.0000000000
       0.0000000000        0.0000000000       11.7589998245
   I   Cs   Pb
   12    4    4
Direct
     0.835449994         0.168099999         0.045189999
     0.164550006         0.831900001         0.954810023
     0.335449994         0.331900001         0.954810023
     0.664550006         0.668099999         0.045189999
     0.164550006         0.831900001         0.545189977
     0.835449994         0.168099999         0.454809994
     0.664550006         0.668099999         0.454809994
     0.335449994         0.331900001         0.545189977
     0.133039996         0.464540005         0.250000000
     0.866959989         0.535459995         0.750000000
     0.633040011         0.035459995         0.750000000
     0.366959989         0.964540005         0.250000000
     0.945100009         0.869149983         0.250000000
     0.054899991         0.130850017         0.750000000
     0.445100009         0.630850017         0.750000000
     0.554899991         0.369149983         0.250000000
     0.500000000         0.000000000         0.000000000
     0.000000000         0.500000000         0.000000000
     0.500000000         0.000000000         0.500000000
     0.000000000         0.500000000         0.500000000
```

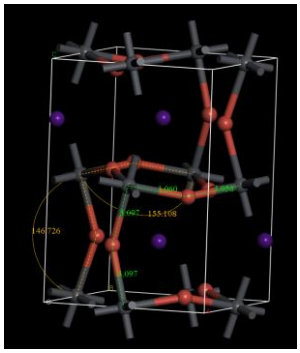
Figure S3. The figure illustrates the different bond lengths and bond angles in the four structures

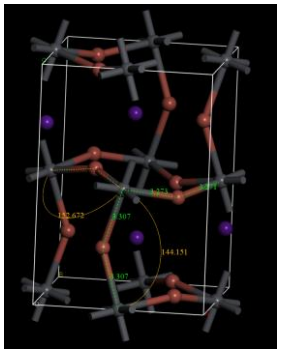
$CsPbF_3$ **$CsPbCl_3$**





$CsPbBr_3$ **$CsPbI_3$**





System	Pb-X bond length/ Å		Pb-X-Pb bond angle/ °	
	I	II	I	II
$CsPbF_3$	2.494/ 2.493	2.550	164.758	163.341
$CsPbCl_3$	2.918/ 2.915	2.951	156.167	149.494
$CsPbBr_3$	3.060/ 3.056	3.097	155.108	146.726
$CsPbI_3$	3.273/ 3.271	3.307	152.672	144.151

Figure S4. CASTEP Geometry Optimization and Optimization Convergence