Supplementary Information for “Promising photovoltaic and solid-state-lighting materials: two-dimensional Ruddlesden-Popper type lead-free halide double perovskites

$Cs_{n+1}In_{n/2}Sb_{n/2}I_{3n+1}$ (n=3) and

$Cs_{n+1}In_{n/2}Sb_{n/2}Cl_{3n+1}/Cs_{m+1}Cu_{m/2}Bi_{m/2}Cl_{3m+1}$ (n=3, m=1)

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Table S1 Values of the parameter CUT (in atomic units) and l together with the detailed half-ionized orbitals for M^+, M^{3+} and X^- in our GGA-1/2 calculations are listed. Our CUT values for X^- are slightly smaller than those of ref. a-c (3.12, 3.34 and 3.76 for Cl^-, Br^- and I^-). This is because the anion CUT value usually has a small dependence on the chemical environment, as pointed out by Ferreira et al.\textsuperscript{d}

<table>
<thead>
<tr>
<th>Atom</th>
<th>CUT</th>
<th>l</th>
<th>Half-ionized orbital</th>
<th>Atom</th>
<th>CUT</th>
<th>l</th>
<th>Half-ionized orbital</th>
</tr>
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<tr>
<td>In^+</td>
<td>2.6</td>
<td>100</td>
<td>d</td>
<td>Sb^{3+}</td>
<td>2.8</td>
<td>90</td>
<td>d</td>
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<tr>
<td>Cu^+</td>
<td>2.8</td>
<td>100</td>
<td>d</td>
<td>Cl^-</td>
<td>2.9</td>
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<td>p</td>
</tr>
<tr>
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<td>100</td>
<td>d</td>
<td>Br^-</td>
<td>3.1</td>
<td>100</td>
<td>p</td>
</tr>
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<td>Au^+</td>
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<td>d</td>
<td>I^-</td>
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<td>90</td>
<td>d</td>
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Table S2 The dependence of the GGA-1/2 bandgap on the half-ionized orbitals of metal atoms in Cs$_2$In$_{1/2}$Sb$_{1/2}$I$_4$ and Cs$_2$Cu$_{1/2}$Bi$_{1/2}$Cl$_4$, in which the half ionization of the $p$-orbital in I and Cl atoms is included. Compared with the accurate GW bandgap, we can easily find that the correction of $d$ orbital for both M$^+$ and M$^{3+}$ is necessary.

<table>
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<tr>
<th>Material</th>
<th>Half-ionized orbital</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
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<tr>
<td>Cs$<em>2$In$</em>{1/2}$Sb$_{1/2}$I$_4$</td>
<td>In: $\times$ Sb: $\times$</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>In: $p$ Sb: $\times$</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>In: $d$ Sb: $\times$</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>In: $d$ Sb: $p$</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>In: $d$ Sb: $d$</td>
<td>1.55, 1.55(GW)</td>
</tr>
<tr>
<td>Cs$<em>2$Cu$</em>{1/2}$Bi$_{1/2}$Cl$_4$</td>
<td>Cu: $\times$ Bi: $\times$</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>Cu: $p$ Bi: $\times$</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>Cu: $d$ Bi: $\times$</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>Cu: $d$ Bi: $p$</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
<td>Cu: $d$ Bi: $d$</td>
<td>3.82, 3.82(GW)</td>
</tr>
</tbody>
</table>
Table S3: Fully optimized lattice parameter $a$ (in unit of Å) in lead-free $n=1$ halide Cs$_2$M$^{+1/2}$M$^{3+1/2}$X$_4$ double perovskites. Some previous experimental results in bulk phase are also given.

<table>
<thead>
<tr>
<th>Cs$_2$M$^{+1/2}$M$^{3+1/2}$X$_4$</th>
<th>X</th>
<th>$a$</th>
<th>Cs$_2$M$^{+1/2}$M$^{3+1/2}$X$_4$</th>
<th>X</th>
<th>$a$</th>
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<tbody>
<tr>
<td>Cs$<em>2$In$</em>{1/2}$Bi$_{1/2}$</td>
<td>Cl</td>
<td>11.22</td>
<td>Cs$<em>2$Cu$</em>{1/2}$Bi$_{1/2}$</td>
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<td>Br</td>
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<td>Br</td>
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</tr>
<tr>
<td></td>
<td>I</td>
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<td></td>
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<td>12.36</td>
</tr>
<tr>
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<td>11.10</td>
<td>Cs$<em>2$Cu$</em>{1/2}$Sb$_{1/2}$</td>
<td>Cl</td>
<td>10.89</td>
</tr>
<tr>
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<td>Br</td>
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<td>Br</td>
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</tr>
<tr>
<td></td>
<td>I</td>
<td>12.28</td>
<td></td>
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<td>12.34</td>
</tr>
<tr>
<td>Cs$<em>2$Ag$</em>{1/2}$Bi$_{1/2}$</td>
<td>Cl</td>
<td></td>
<td>Cs$<em>2$Au$</em>{1/2}$Bi$_{1/2}$</td>
<td>Cl</td>
<td>11.51</td>
</tr>
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<td>Br</td>
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<td></td>
<td>Br</td>
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</tr>
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<td>I</td>
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<td>12.64</td>
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<td>10.87</td>
<td>Cs$<em>2$Au$</em>{1/2}$Sb$_{1/2}$</td>
<td>Cl</td>
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<td>Br</td>
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</tr>
<tr>
<td></td>
<td>I</td>
<td>12.24</td>
<td></td>
<td>I</td>
<td>12.42</td>
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Figure S1 Energy band structures of $n=1$ lead-free halide double perovskites with direct bandgap (a) Cs$_2$In$_{1/2}$Bi$_{1/2}$I$_4$, (b) Cs$_2$Cu$_{1/2}$Sb$_{1/2}$I$_4$ and (c) Cs$_2$Cu$_{1/2}$Bi$_{1/2}$I$_4$, and indirect bandgap (d) Cs$_2$Ag$_{1/2}$Bi$_{1/2}$I$_4$, (e) Cs$_2$Au$_{1/2}$Sb$_{1/2}$I$_4$ and (f) Cs$_2$Au$_{1/2}$Bi$_{1/2}$I$_4$. Here, the band structures are derived from the GGA-PBE calculations, in which the underestimated bandgaps are modified according to GGA-1/2 calculations.
Figure S2 PDOSs of $n=1$ lead-free halide double perovskites with direct bandgap (a) Cs$_2$In$_{1/2}$Bi$_{1/2}$I$_4$, (b) Cs$_2$Cu$_{1/2}$Sb$_{1/2}$I$_4$ and (c) Cs$_2$Cu$_{1/2}$Bi$_{1/2}$I$_4$, and indirect bandgap (d) Cs$_2$Ag$_{1/2}$Bi$_{1/2}$I$_4$, (e) Cs$_2$Au$_{1/2}$Sb$_{1/2}$I$_4$ and (f) Cs$_2$Au$_{1/2}$Bi$_{1/2}$I$_4$. 
**Figure S3** The 2D double perovskite crystal structures of (a) $n=2$ Cs$_3$InSbI$_7$ and (b) $n=3$ Cs$_4$In$_{12}$Sb$_{32}$I$_{10}$ with the vertical distance of $h=6.92$ and $13.24$ Å, respectively. Here, the stacking order of layered double perovskites, composed by the alternative $M^+X$ (pink) and $M^{3+}X$ (blue) octahedrons, is similar to their bulk counterparts.

**Figure S4** Schematic illustration of the crystal structure of 2D lead-free halide double perovskite heterostructure. The different perovskite layers in the heterostructure are directly stacked together with a shift of $b/2$ along the $b$-axis just as the bulk RP-type perovskite. A suitable strain exists to match the lattice constants of different layers. The $d$ represents the interlayer distance between two different layers in the heterostructure.
Table S4 The interlayer distance $d$ (Å) and lattice mismatch of all considered 2D RP-type lead-free halide double perovskite heterostructures

<table>
<thead>
<tr>
<th>Material</th>
<th>Layer thickness</th>
<th>$d$</th>
<th>Lattice mismatch</th>
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<tr>
<td>CsInSbCl/CsCuBiCl</td>
<td>$n=1/m=1$</td>
<td>5.51</td>
<td>0.45%</td>
</tr>
<tr>
<td></td>
<td>$n=2/m=1$</td>
<td>5.54</td>
<td>0.67%</td>
</tr>
<tr>
<td></td>
<td>$n=1/m=2$</td>
<td>5.56</td>
<td>0.51%</td>
</tr>
<tr>
<td></td>
<td>$n=2/m=2$</td>
<td>5.65</td>
<td>0.53%</td>
</tr>
<tr>
<td></td>
<td>$n=3/m=1$</td>
<td>5.62</td>
<td>0.72%</td>
</tr>
<tr>
<td>CsInBiCl/CsCuBiCl</td>
<td>$n=1/m=1$</td>
<td>5.58</td>
<td>0.98%</td>
</tr>
<tr>
<td>CsInSbCl/CsAgBiCl</td>
<td>$n=1/m=1$</td>
<td>5.59</td>
<td>0.54%</td>
</tr>
<tr>
<td>CsInBiCl/CsCuSbCl</td>
<td>$n=1/m=1$</td>
<td>5.57</td>
<td>1.47%</td>
</tr>
<tr>
<td>CsAgSbBr/CsCuSbCl</td>
<td>$n=1/m=1$</td>
<td>5.64</td>
<td>2.27%</td>
</tr>
<tr>
<td>CsAgSbBr/CsCuSbBr</td>
<td>$n=1/m=1$</td>
<td>5.78</td>
<td>0.17%</td>
</tr>
<tr>
<td>CsAgSbI/CsCuSbI</td>
<td>$n=1/m=1$</td>
<td>5.69</td>
<td>0.41%</td>
</tr>
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</table>
Figure S5 The weighted energy band structures of $n=1/m=1$ lead-free halide double perovskite heterostructures with type-II band alignment can be classified into two types, *i.e.*, direct bandgap (a) $\text{Cs}_2\text{In}_{1/2}\text{Bi}_{1/2}\text{Cl}_4/\text{Cs}_2\text{Cu}_{1/2}\text{Bi}_{1/2}\text{Cl}_4$, (b) $\text{Cs}_2\text{In}_{1/2}\text{Sb}_{1/2}\text{Cl}_4/\text{Cs}_2\text{Ag}_{1/2}\text{Bi}_{1/2}\text{Cl}_4$, and (c) $\text{Cs}_2\text{In}_{1/2}\text{Bi}_{1/2}\text{Cl}_4/\text{Cs}_2\text{Cu}_{1/2}\text{Sb}_{1/2}\text{Cl}_4$ and indirect bandgap (d) $\text{Cs}_2\text{Ag}_{1/2}\text{Sb}_{1/2}\text{Br}_4/\text{Cs}_2\text{Cu}_{1/2}\text{Sb}_{1/2}\text{Cl}_4$, (e) $\text{Cs}_2\text{Ag}_{1/2}\text{Sb}_{1/2}\text{Br}_4/\text{Cs}_2\text{Cu}_{1/2}\text{Sb}_{1/2}\text{Br}_4$, and (f) $\text{Cs}_2\text{Ag}_{1/2}\text{Sb}_{1/2}\text{I}_4/\text{Cs}_2\text{Cu}_{1/2}\text{Sb}_{1/2}\text{I}_4$. Here, the band structures are derived from the GGA-PBE calculations, in which the underestimated bandgaps are modified according to GGA-1/2 calculations.

Figure S6 The calculated imaginary parts $\varepsilon_2$ of dielectric function for freestanding $n=1$ (a) $\text{Cs}_2\text{In}_{1/2}\text{Sb}_{1/2}\text{Cl}_4$ and (b) $\text{Cs}_2\text{Cu}_{1/2}\text{Bi}_{1/2}\text{Cl}_4$. 
Table S5 The carrier effective mass $m^*$ ($m_0$) and the predicted carrier mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) in 2D lead-free $n=1$ halide double perovskite Cs$_2$M+ 1/2M3+ 1/2X 4 and their $n=1/m=1$ heterostructures

<table>
<thead>
<tr>
<th>Material</th>
<th>X</th>
<th>$m^*_h$</th>
<th>$m^*_e$</th>
<th>$\mu_h$</th>
<th>$\mu_e$</th>
<th>Material</th>
<th>X</th>
<th>$m^*_h$</th>
<th>$m^*_e$</th>
<th>$\mu_h$</th>
<th>$\mu_e$</th>
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<tbody>
<tr>
<td>MAPbI$_3$</td>
<td>I</td>
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<td>1.14</td>
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<td>1.10</td>
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<tr>
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<td>1.09</td>
<td>0.40</td>
<td>0.25</td>
<td>Cs$<em>2$Cu$</em>{1/2}$Bi$_{1/2}$</td>
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<td>0.90</td>
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<td>1.02</td>
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<td>Br</td>
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<td>101</td>
<td>50</td>
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<td>0.85</td>
<td>0.94</td>
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<tr>
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<td>I</td>
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<td>I</td>
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<td>0.80</td>
<td>0.87</td>
<td>70</td>
<td>165</td>
<td>Cs$<em>2$Ag$</em>{1/2}$Sb$_{1/2}$Br$<em>4$/Cs$<em>2$Cu$</em>{1/2}$Sb$</em>{1/2}$Cl$_4$</td>
<td>0.76</td>
<td>0.72</td>
<td>330</td>
<td>90</td>
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<tr>
<td>Cs$<em>2$In$</em>{1/2}$Bi$_{1/2}$Cl$<em>4$/Cs$<em>2$Cu$</em>{1/2}$Bi$</em>{1/2}$Cl$_4$</td>
<td>0.81</td>
<td>0.90</td>
<td>50</td>
<td>65</td>
<td>Cs$<em>2$Ag$</em>{1/2}$Sb$_{1/2}$Br$<em>4$/Cs$<em>2$Cu$</em>{1/2}$Sb$</em>{1/2}$Br$_4$</td>
<td>0.74</td>
<td>0.81</td>
<td>395</td>
<td>110</td>
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<tr>
<td>Cs$<em>2$In$</em>{1/2}$Sb$_{1/2}$Cl$<em>4$/Cs$<em>2$Ag$</em>{1/2}$Bi$</em>{1/2}$Cl$_4$</td>
<td>0.85</td>
<td>0.42</td>
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<td>122</td>
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<td>0.89</td>
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<tr>
<td>Cs$<em>2$In$</em>{1/2}$Bi$_{1/2}$Cl$<em>4$/Cs$<em>2$Cu$</em>{1/2}$Sb$</em>{1/2}$Cl$_4$</td>
<td>0.80</td>
<td>0.42</td>
<td>74</td>
<td>70</td>
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