Supplementary Information for:

Modulating Luminescence through Anion Variation in Lead-free Cs_2NaInX_6 (X=Cl, Br, and I) Perovskites: A First-principles Study

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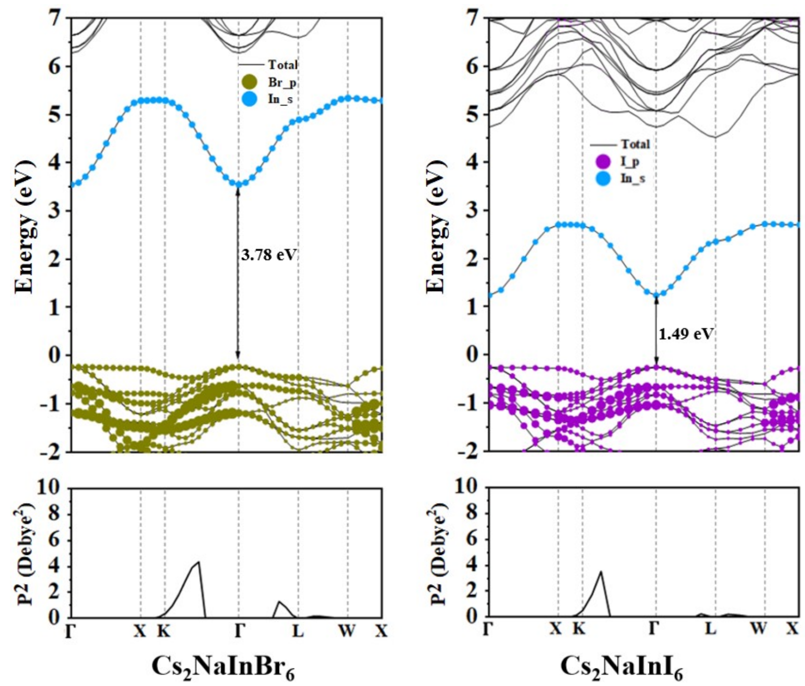

Figure S1. The projected band structures and transition dipole moments of Cs2NaInBr6 and Cs2NaInI6 calculated by HSE06 functional.

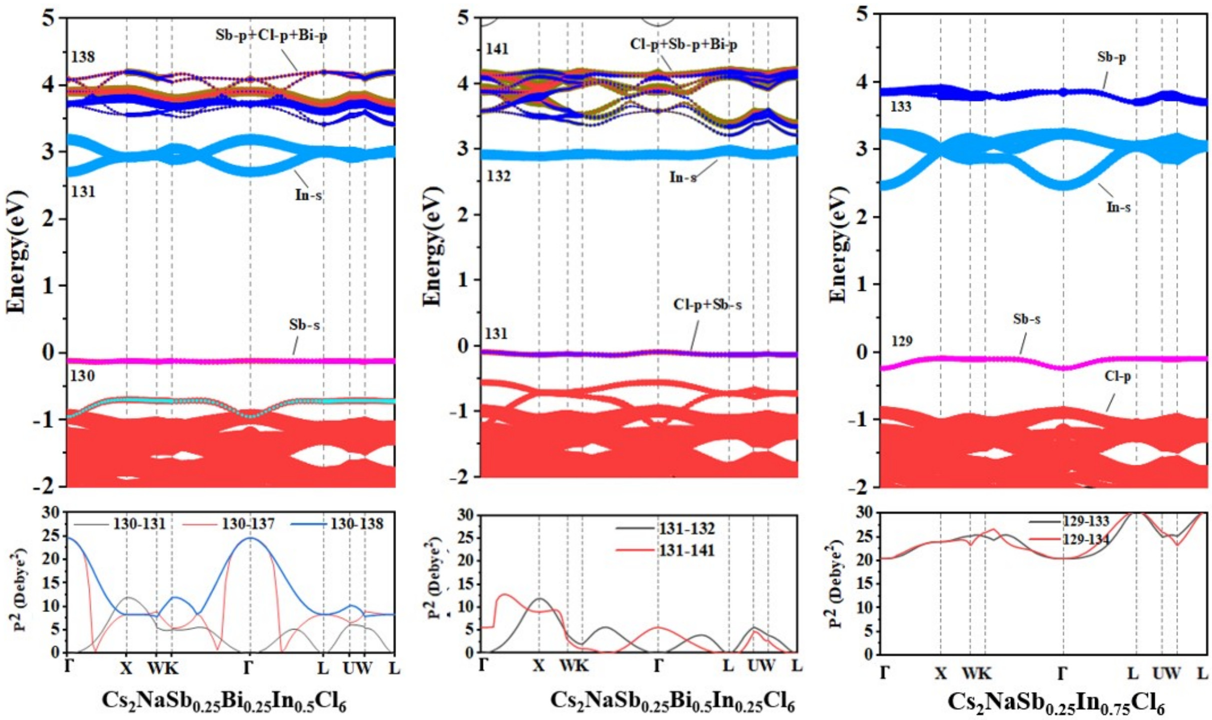

Figure S2. The projected band structures and transition dipole moments of $Cs_2NaSb_{0.25}In_{0.75}Cl_6$ and $Cs_2NaSb_{0.25}Bi_{0.5}In_{0.25}Cl_6$, $Cs_2NaSb_{0.25}Bi_{0.25}In_{0.5}Cl_6$.

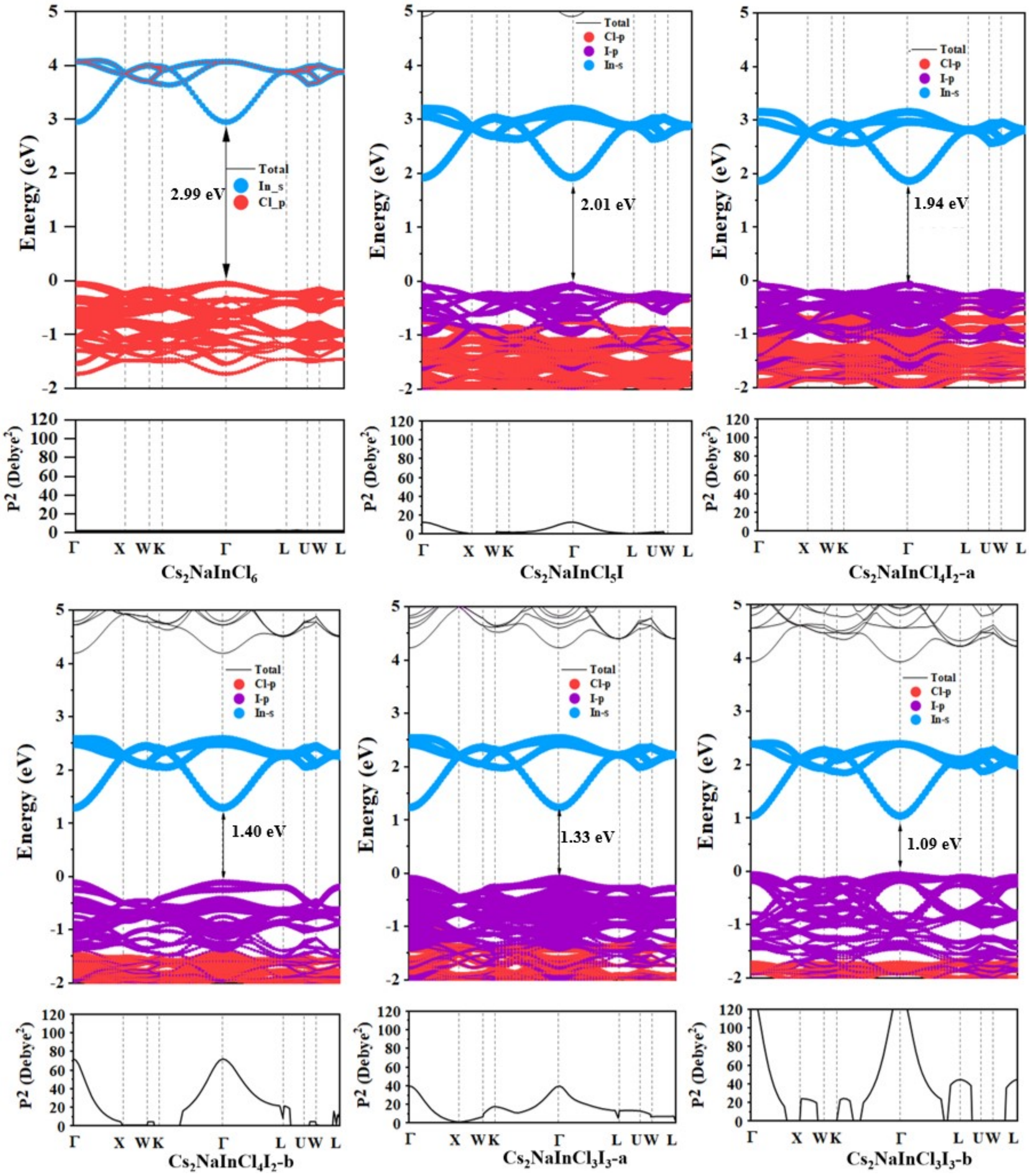

Figure S3. The detailed projected band structures and transition dipole moments of $Cs_2NaInCl_6$ and corresponding substituted structures (I substitution) calculated by PBE functional.

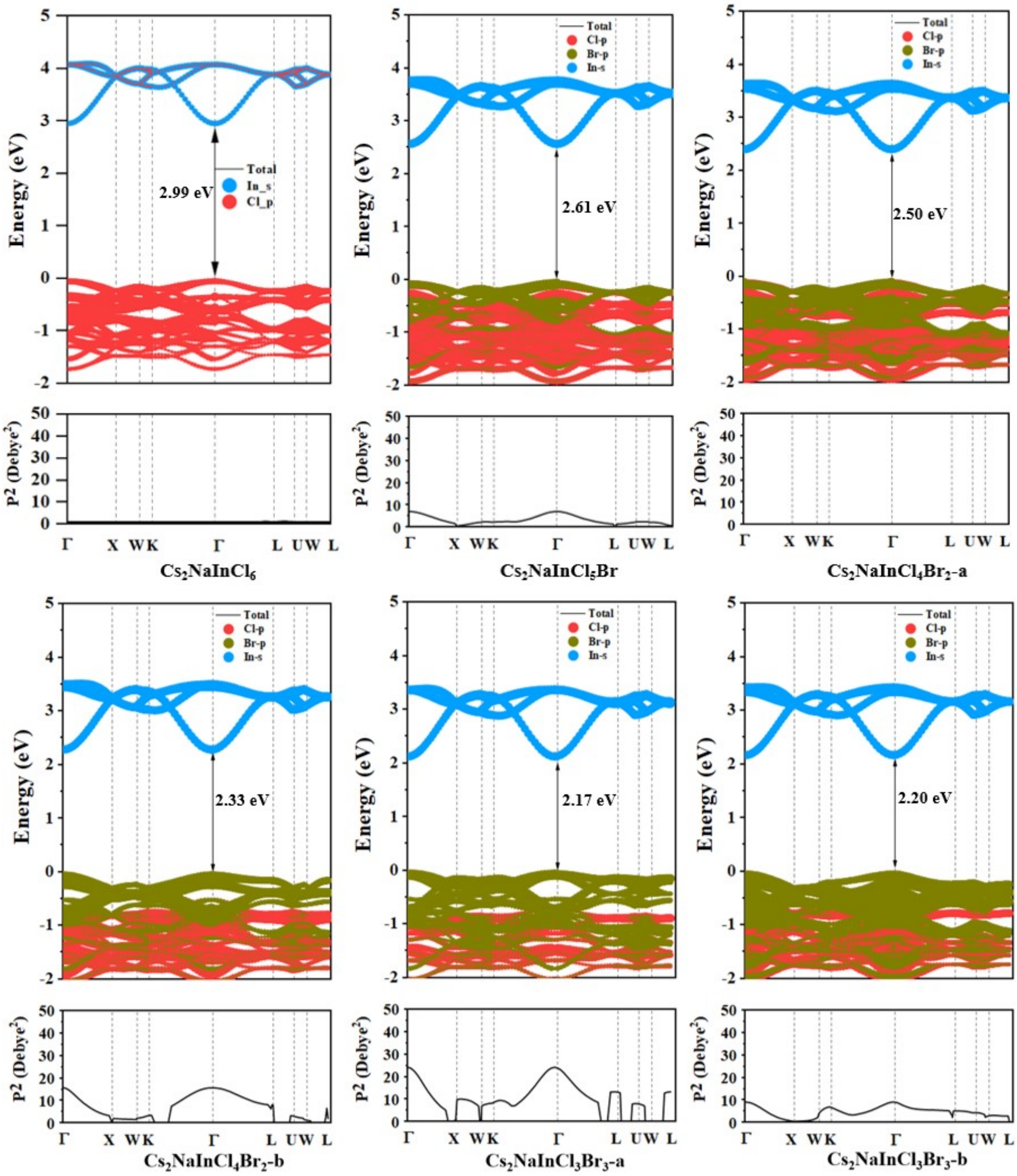

Figure S4. The detailed projected band structures and transition dipole moments of $Cs_2NaInCl_6$ and corresponding substituted structures (Br substitution) calculated by PBE functional.

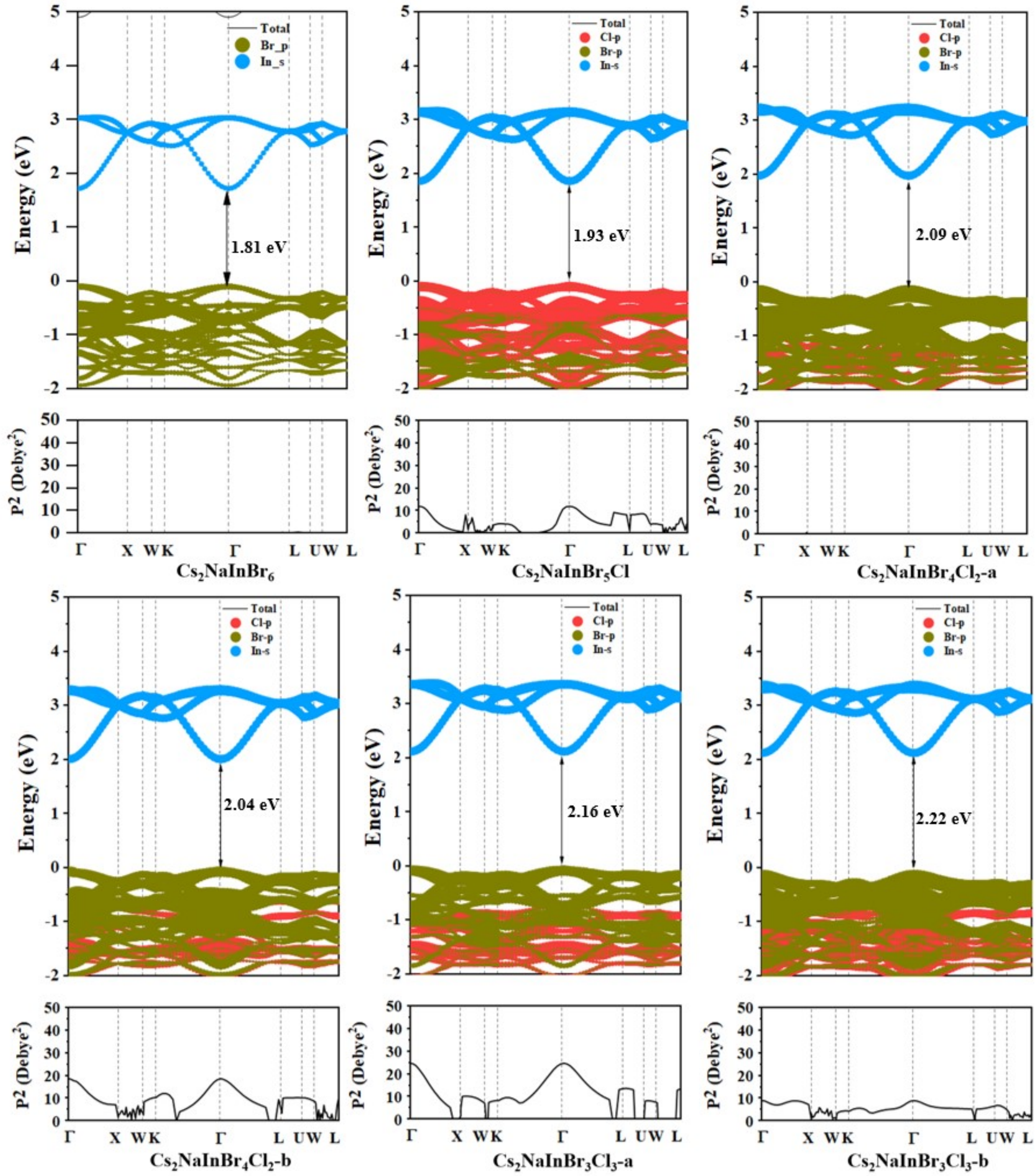

Figure S5. The detailed projected band structures and transition dipole moments of $Cs_2NaInBr_6$ and corresponding substituted structures (Cl substitution) calculated by PBE functional.

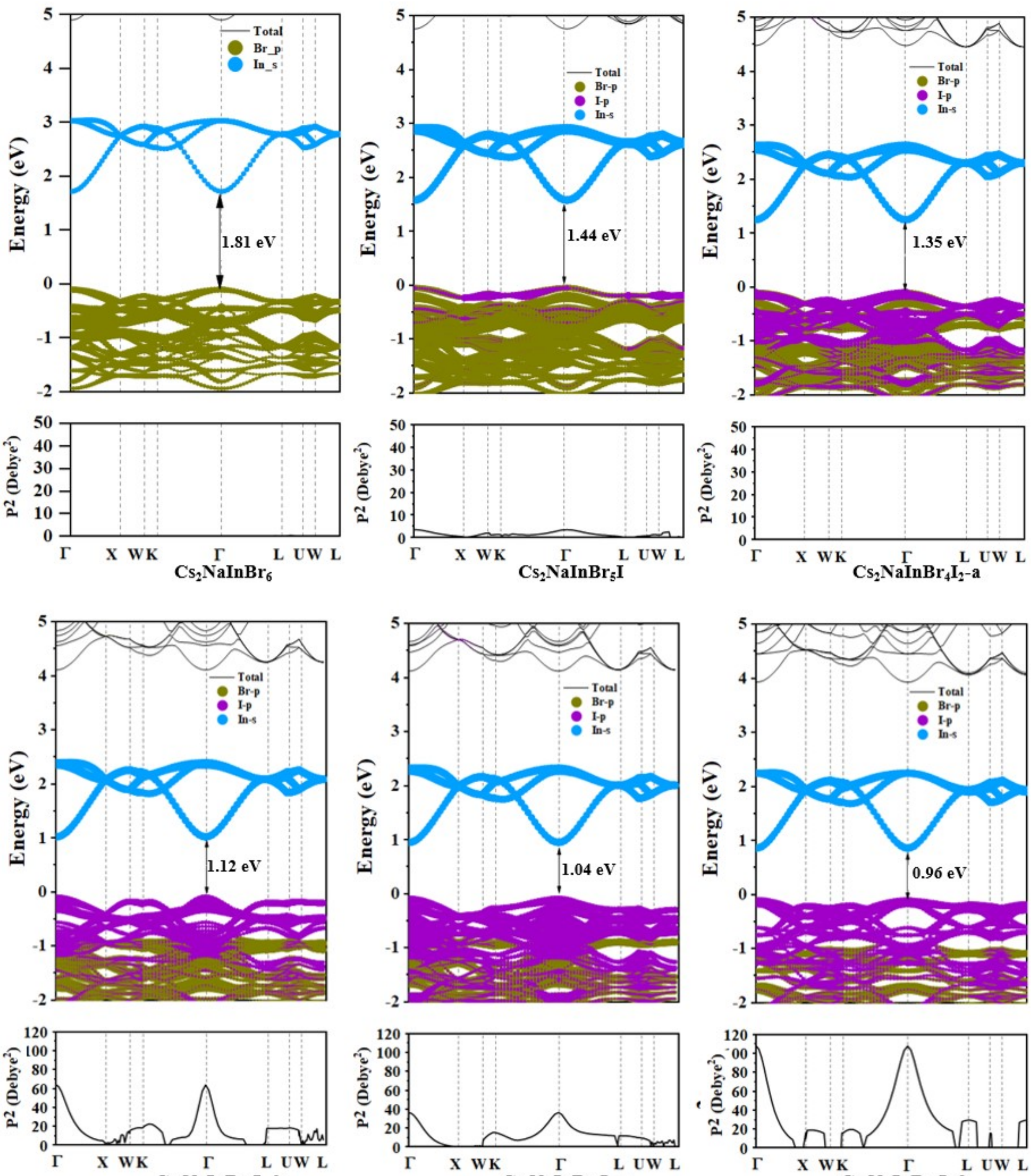

Figure S6. The detailed projected band structures and transition dipole moments of $Cs_2NaInBr_6$ and corresponding substituted structures (I substitution) calculated by PBE functional.

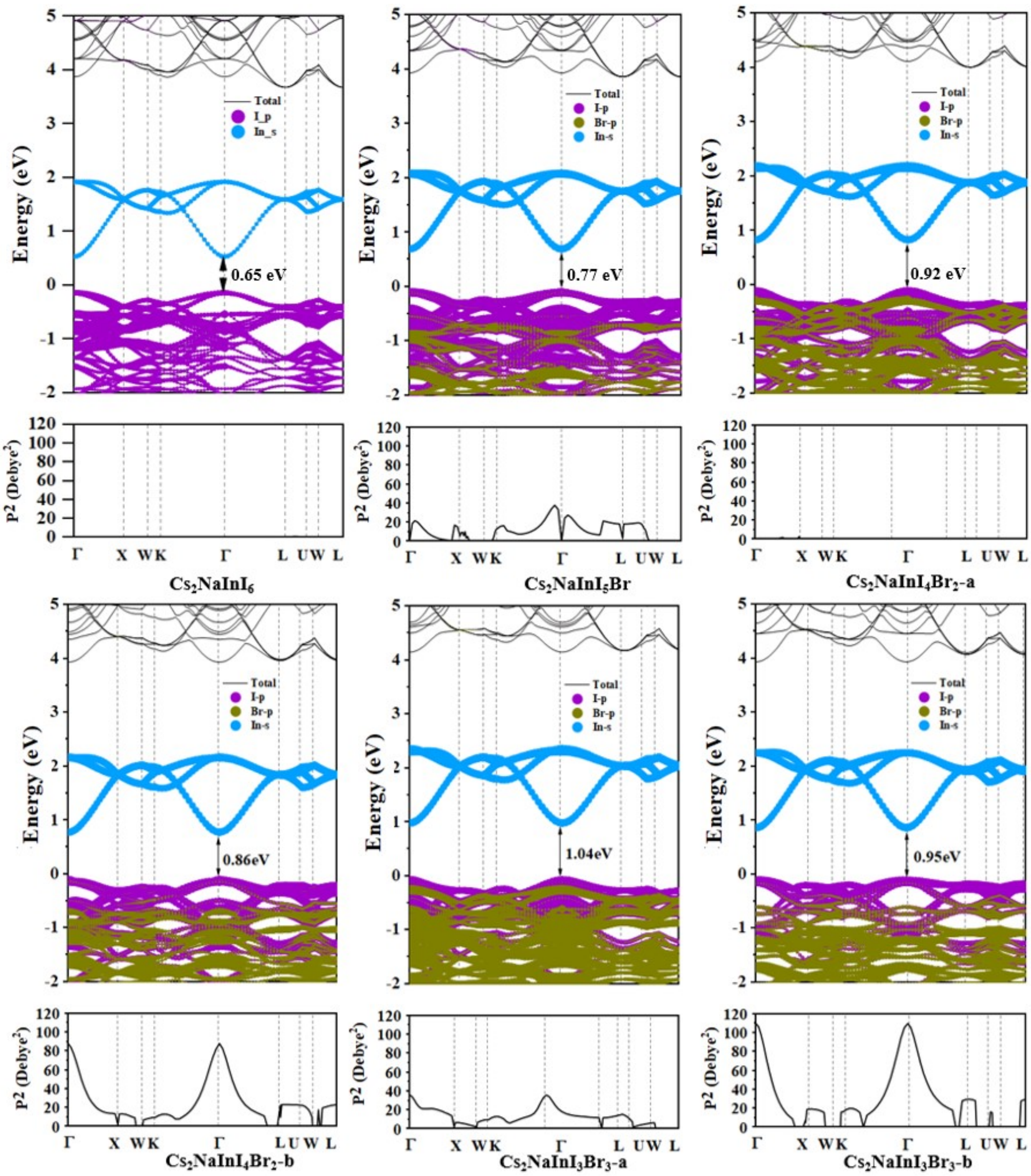

Figure S7. The detailed projected band structures and transition dipole moments of Cs_2NaInI_6 and corresponding substituted structures (Br substitution) calculated by PBE functional.

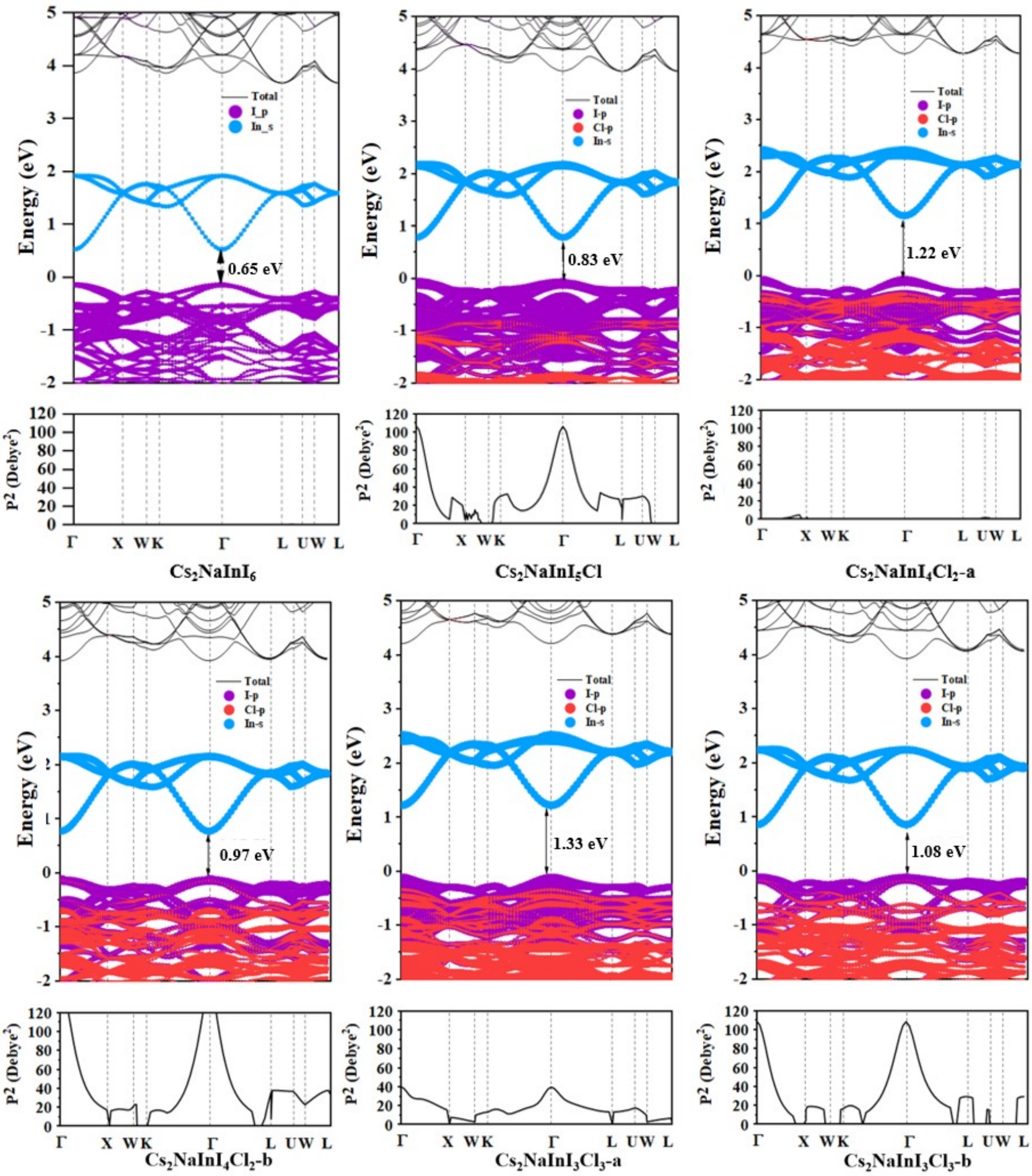

Figure S8. The detailed projected band structures and transition dipole moments of Cs_2NaInI_6 and corresponding substituted structures (Cl substitution) calculated by PBE functional.

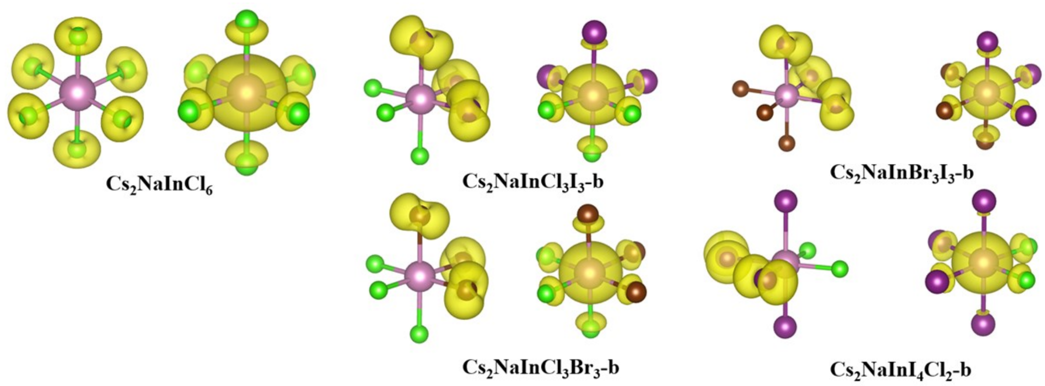

Figure S9. The VBM (left) and CBM (right) associated partial charge density of $Cs_2NaInCl_6$, $Cs_2NaInCl_3Br_3$-b, $Cs_2NaInBr_3I_3$-b, $Cs_2NaInCl_3I_3$-b, $Cs_2NaInI_4Cl_2$-b.

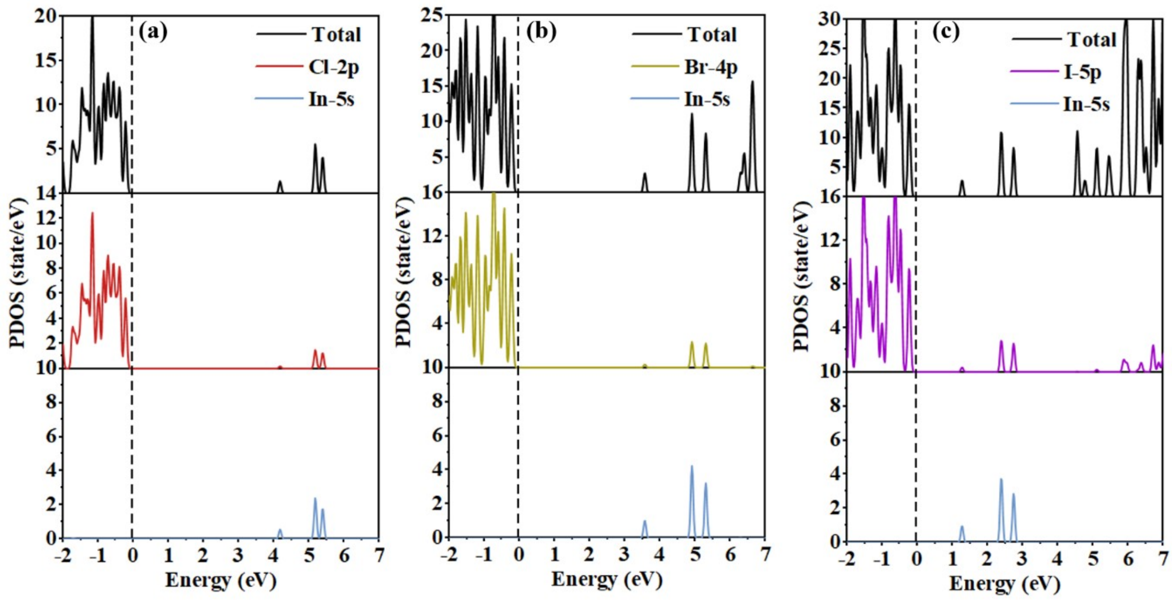

Figure S10. Density of state of intrinsic structures. a) $Cs_2NaInCl_6$. b) $Cs_2NaInBr_6$. c) Cs_2NaInI_6

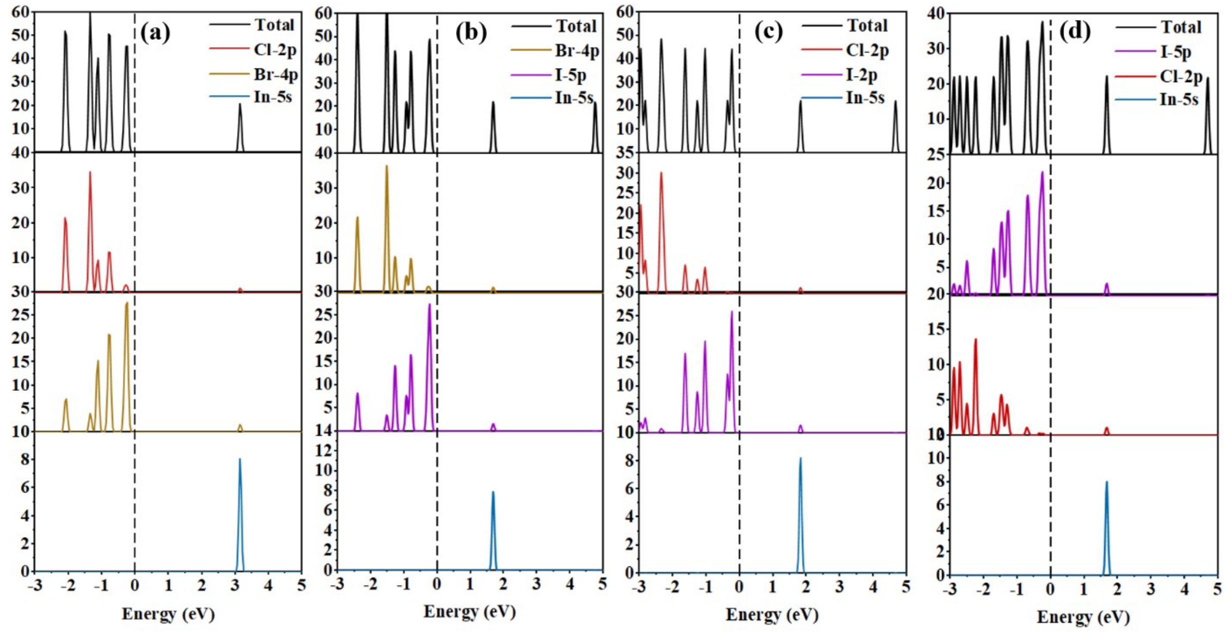

Figure S11. Density of state of substituted structures. a) $Cs_2NaInCl_3Br_3$-b. b) $Cs_2NaInBr_3I_3$-b. c) $Cs_2NaInCl_3I_3$-b. d) $Cs_2NaInI_4Cl_2$-b.

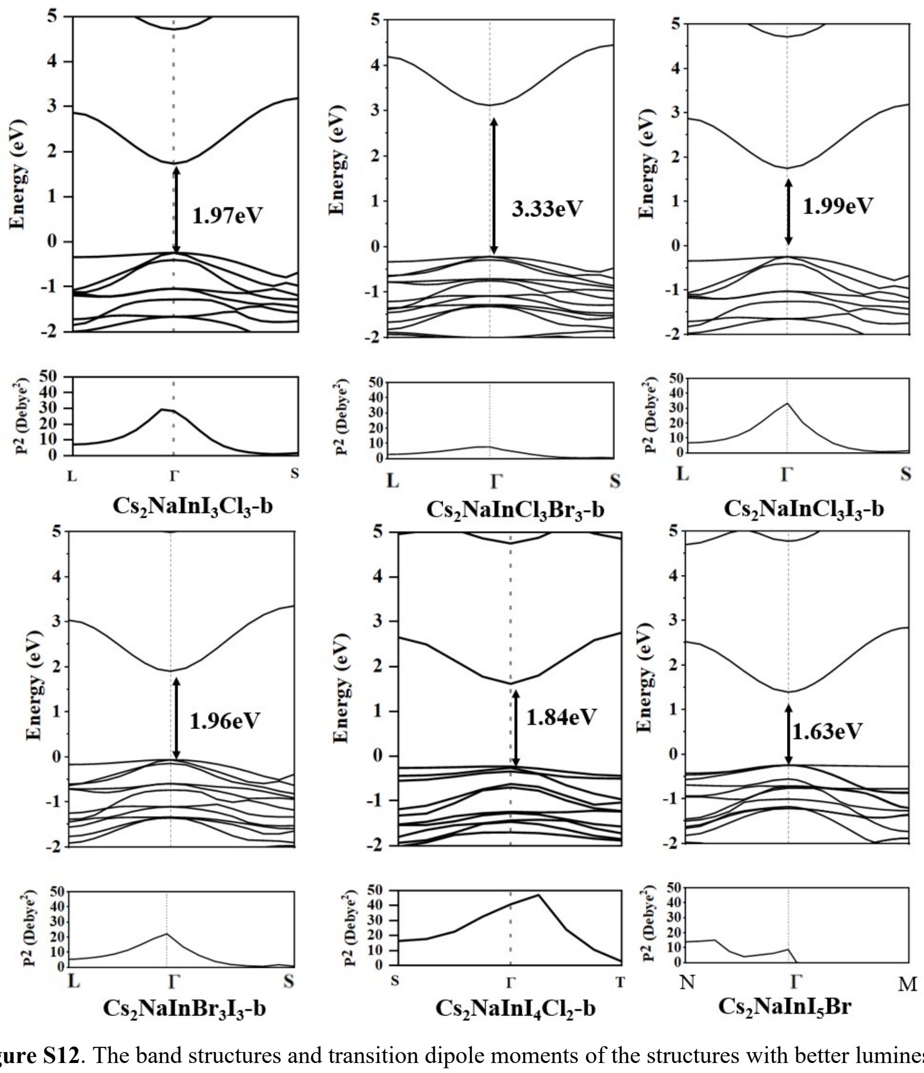

Figure S12. The band structures and transition dipole moments of the structures with better luminescent performance calculated by HSE06 functional

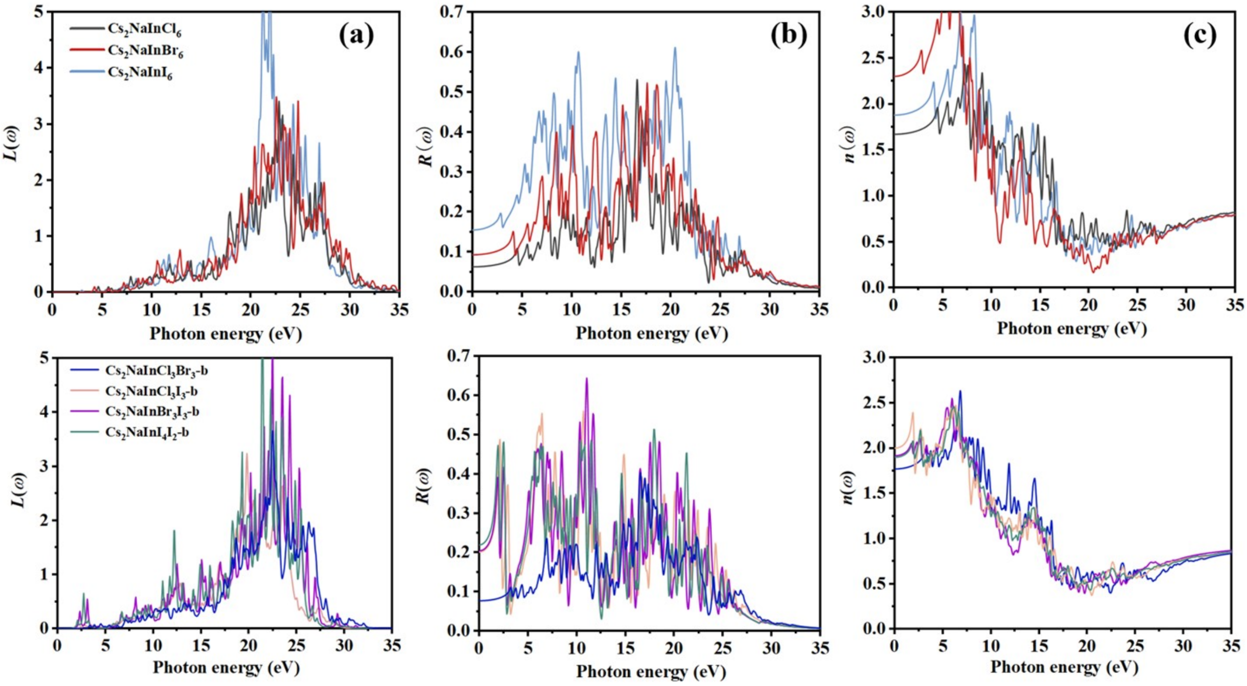

Figure S13. Other optical properties of intrinsic structures (upper panel) and selected substituted structures (lower panel). a) Energy loss spectrum $L(\omega)$. b) Reflectivity spectrum $R(\omega)$. c) Refractivity index $n(\omega)$.

Table S1 The comparation between experiment and theoretical calculations.

Materials	**Bandgap$_{exp}$(eV)**	**Bandgap$_{pbe}$(eV)**	**Bandgap$_{HSE06}$(eV)**
$Cs_2NaInCl_6$	4.13	2.99	4.35
$Cs_2NaInBr_6$		1.81	3.78
Cs_2NaInI_6		0.65	1.49

Table S2 The bond length in $Cs_2NaInCl_6$ and corresponding substituted structures (I substitution) supercell containing 40 atoms *di* (*i* = 1, 2, 3, 4, 5, 6; Å) and corresponding distortion Δ*d*

Materials	d_1	d_2	d_3	d_4	d_5	d_6	Δ*d*
$Cs_2NaInCl_6$	2.54	2.54	2.54	2.54	2.54	2.54	0.00
$Cs_2NaInCl_5I$	2.56	2.86	2.56	2.57	2.56	2.56	8.81E-04
$Cs_2NaInCl_4I_2$-a	2.89	2.56	2.89	2.56	2.56	2.56	1.67E-03
$Cs_2NaInCl_4I_2$-b	2.88	2.56	2.58	2.56	2.88	2.58	1.49E-03
$Cs_2NaInCl_3I_3$-a	2.89	2.91	2.59	2.91	2.56	2.56	1.92E-03
$Cs_2NaInCl_3I_3$-b	2.88	2.88	2.59	2.59	2.88	2.59	1.37E-03

Table S3 The bond length in $Cs_2NaInCl_6$ and corresponding substituted structures (Br substitution) supercell containing 40 atoms di (i = 1, 2, 3, 4, 5, 6; Å) and corresponding distortion Δ*d*

Materials	d_1	d_2	d_3	d_4	d_5	d_6	Δ*d*
$Cs_2NaInCl_6$	2.54	2.54	2.54	2.54	2.54	2.54	0.00
$Cs_2NaInCl_5Br$	2.56	2.57	2.56	2.86	2.56	2.56	8.81E-04
$Cs_2NaInCl_4Br_2$-a	2.69	2.55	2.69	2.55	2.55	2.55	3.19E-04
$Cs_2NaInCl_4Br_2$-b	2.68	2.55	2.56	2.55	2.68	2.56	2.72E-04
$Cs_2NaInCl_3Br_3$-a	2.69	2.56	2.69	2.68	2.55	2.55	3.46E-04
$Cs_2NaInCl_3Br_3$-b	2.68	2.56	2.56	2.68	2.68	2.56	2.73E-04

Table S4 The bond length in $Cs_2NaInBr_6$ and corresponding substituted structures (Cl substitution) supercell containing 40 atoms *di* (*i* = 1, 2, 3, 4, 5, 6; Å) and corresponding distortion Δ*d*

Materials	d_1	d_2	d_3	d_4	d_5	d_6	Δ*d*
$Cs_2NaInBr_6$	2.69	2.69	2.69	2.69	2.69	2.69	0.00
$Cs_2NaInBr_5Cl$	2.69	2.69	2.69	2.69	2.56	2.69	1.76E-04
$Cs_2NaInBr_4Cl_2$-a	2.70	2.55	2.70	2.55	2.70	2.70	3.47E-04
$Cs_2NaInBr_4Cl_2$-b	2.69	2.56	2.69	2.68	2.56	2.68	2.72E-04
$Cs_2NaInBr_3Cl_3$-a	2.56	2.55	2.68	2.55	2.69	2.69	3.30E-04
$Cs_2NaInBr_3Cl_3$-b	2.56	2.56	2.68	2.68	2.56	2.68	2.78E-04

Table S5 The bond length in $Cs_2NaInBr_6$ and corresponding substituted structures (I substitution) supercell containing 40 atoms *di* (*i* = 1, 2, 3, 4, 5, 6; Å) and corresponding distortion Δ*d*

Materials	d_1	d_2	d_3	d_4	d_5	d_6	Δ*d*
$Cs_2NaInBr_6$	2.69	2.69	2.69	2.69	2.69	2.69	0.00
$Cs_2NaInBr_5I$	2.70	2.88	2.70	2.72	2.70	2.70	3.00E-04
$Cs_2NaInBr_4I_2$-a	2.70	2.91	2.70	2.91	2.70	2.70	5.91E-04
$Cs_2NaInBr_4I_2$-b	2.70	2.90	2.70	2.72	2.90	2.72	4.83E-04
$Cs_2NaInBr_3I_3$-a	2.90	2.92	2.72	2.92	2.70	2.70	6.53E-04
$Cs_2NaInBr_3I_3$-b	2.90	2.90	2.72	2.72	2.90	2.72	4.70E-04

Table S6 The bond length in Cs_2NaInI_6 and corresponding substituted structures (Cl substitution) supercell containing 40 atoms *di* (*i* = 1, 2, 3, 4, 5, 6; Å) and corresponding distortion Δ*d*

Materials	d_1	d_2	d_3	d_4	d_5	d_6	Δ*d*
Cs_2NaInI_6	2.92	2.92	2.92	2.92	2.92	2.92	0.00
Cs_2NaInI_5Cl	2.93	2.88	2.93	2.58	2.93	2.93	9.77E-04
$Cs_2NaInI_4Cl_2$-a	2.92	2.55	2.92	2.55	2.92	2.92	1.94E-03
$Cs_2NaInI_4Cl_2$-b	2.94	2.88	2.59	2.59	2.88	2.94	1.47E-03
$Cs_2NaInI_3Cl_3$-a	2.91	2.59	2.56	2.89	2.56	2.91	1.88E-03
$Cs_2NaInI_3Cl_3$-b	2.60	2.88	2.88	2.60	2.60	2.88	1.36E-03

Table S7 The bond length in Cs_2NaInI_6 and corresponding substituted structures (Br substitution) supercell containing 40 atoms *di* (*i* = 1, 2, 3, 4, 5, 6; Å) and corresponding distortion Δ*d*

Materials	d_1	d_2	d_3	d_4	d_5	d_6	Δ*d*
Cs_2NaInI_6	2.92	2.92	2.92	2.92	2.92	2.92	0.00
Cs_2NaInI_5Br	2.92	2.72	2.92	2.90	2.92	2.92	3.31E-04
$Cs_2NaInI_4Br_2$-a	2.92	2.70	2.92	2.70	2.92	2.92	6.37E-04
$Cs_2NaInI_4Br_2$-b	2.92	2.73	2.92	2.90	2.73	2.90	4.43E-04
$Cs_2NaInI_3Br_3$-a	2.70	2.73	2.70	2.90	2.92	2.92	6.29E-04
$Cs_2NaInI_3Br_3$-b	2.73	2.73	2.90	2.90	2.73	2.90	4.73E-04

Table S8 The bond angle in $Cs_2NaInCl_6$ and corresponding substituted structures (Br substitution) supercell containing 40 atoms θi(i = 1, 2, 3, 4, 5, 6,7,8; °) and corresponding distortion $\Delta\theta$

Materials	$\theta 1$	$\theta 2$	$\theta 3$	$\theta 4$	$\theta 5$	$\theta 6$	$\theta 7$	$\theta 8$	$\Delta\theta$
$Cs_2NaInCl_6$	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInCl_5Br$	90.011	89.988	89.988	90.011	90.000	89.988	90.000	90.011	5.10E-09
$Cs_2NaInCl_4Br_2$-a	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInCl_4Br_2$-b	90.067	90.067	89.9328	89.9328	90.0219	90.067	90.111	90.067	2.29E-07
$Cs_2NaInCl_3Br_3$-a	90.001	89.998	89.998	90.001	90.000	89.500	90.000	90.499	1.92E-06
$Cs_2NaInCl_3Br_3$-b	90.389	90.105	89.395	90.105	90.389	90.105	90.105	90.389	5.17E-06

Table S9 The bond angle in $Cs_2NaInCl_6$ and corresponding substituted structures (I substitution) supercell containing 40 atoms θi(i = 1, 2, 3, 4, 5, 6,7,8; °) and corresponding distortion $\Delta\theta$

Materials	$\theta 1$	$\theta 2$	$\theta 3$	$\theta 4$	$\theta 5$	$\theta 6$	$\theta 7$	$\theta 8$	$\Delta\theta$
$Cs_2NaInCl_6$	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00
$Cs_2NaInCl_5I$	90.012	90.012	89.989	89.989	90.000	90.012	90.000	89.989	5.10E-09
$Cs_2NaInCl_4I_2$-a	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInCl_4I_2$-b	90.121	90.121	89.879	89.879	90.001	90.121	90.071	90.121	5.60E-07
$Cs_2NaInCl_3I_3$-a	89.904	90.096	90.096	89.904	90.879	90.002	89.121	90.002	6.26E-06
$Cs_2NaInCl_3I_3$-b	90.778	90.212	88.782	90.212	90.778	90.778	90.212	90.212	1.86E-05

Table S10 The bond angle in $Cs_2NaInBr_6$ and corresponding substituted structures (Cl substitution) supercell containing 40 atoms θi(i = 1, 2, 3, 4, 5, 6,7,8; °) and corresponding distortion $\Delta\theta$

Materials	$\theta 1$	$\theta 2$	$\theta 3$	$\theta 4$	$\theta 5$	$\theta 6$	$\theta 7$	$\theta 8$	$\Delta\theta$
$Cs_2NaInBr_6$	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00
$Cs_2NaInBr_5Cl$	90.000	90.000	90.000	90.000	89.832	89.832	89.832	89.832	3.26E-07
$Cs_2NaInBr_4Cl_2$-a	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInBr_4Cl_2$-b	89.776	89.776	90.223	90.223	89.776	89.428	89.776	90.085	2.37E-06
$Cs_2NaInBr_3Cl_3$-a	89.863	90.137	90.137	89.863	89.924	90.000	90.077	90.000	6.25E-07
$Cs_2NaInBr_3Cl_3$-b	89.668	89.901	90.527	89.901	89.668	89.668	89.901	89.901	3.51E-06

Table S11 The bond angle in $Cs_2NaInBr_6$ and corresponding substituted structures (I substitution) supercell containing 40 atoms θi(i = 1, 2, 3, 4, 5, 6,7,8; °) and corresponding distortion $\Delta\theta$

Materials	$\theta 1$	$\theta 2$	$\theta 3$	$\theta 4$	$\theta 5$	$\theta 6$	$\theta 7$	$\theta 8$	$\Delta\theta$
$Cs_2NaInBr_6$	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00
$Cs_2NaInBr_5I$	90.626	90.626	89.373	89.373	89.993	90.626	89.993	89.373	1.51E-05
$Cs_2NaInBr_4I_2$-a	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInBr_4I_2$-b	90.433	90.433	89.561	89.561	90.433	90.362	90.433	90.319	7.59E-06
$Cs_2NaInBr_3I_3$-a	90.468	89.532	89.532	90.468	91.173	89.990	88.827	89.990	1.73E-05
$Cs_2NaInBr_3I_3$-b	90.756	90.092	89.047	90.092	90.756	90.756	90.092	90.092	1.31E-05

Table S12 The bond angle in Cs_2NaInI_6 and corresponding substituted structures (Cl substitution) supercell containing 40 atoms θi(i = 1, 2, 3, 4, 5, 6,7,8; °) and corresponding distortion $\Delta\theta$

Materials	$\theta 1$	$\theta 2$	$\theta 3$	$\theta 4$	$\theta 5$	$\theta 6$	$\theta 7$	$\theta 8$	$\Delta\theta$
Cs_2NaInI_6	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00
Cs_2NaInI_5Cl	88.371	91.629	91.629	88.371	88.371	89.954	91.629	89.954	1.03E-04
$Cs_2NaInI_4Cl_2$-a	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInI_4Cl_2$-b	90.058	90.058	89.946	89.946	90.058	85.624	90.058	90.118	1.50E-05
$Cs_2NaInI_3Cl_3$-a	89.045	90.955	90.955	89.045	90.089	90.002	89.911	90.002	2.82E-05
$Cs_2NaInI_3Cl_3$-b	90.801	90.223	88.735	90.223	90.801	90.801	90.223	90.223	2.00E-05

Table S13 The bond angle in Cs_2NaInI_6 and corresponding substituted structures (Br substitution) supercell containing 40 atoms θi(i = 1, 2, 3, 4, 5, 6,7,8; °) and corresponding distortion $\Delta\theta$

Materials	$\theta 1$	$\theta 2$	$\theta 3$	$\theta 4$	$\theta 5$	$\theta 6$	$\theta 7$	$\theta 8$	$\Delta\theta$
Cs_2NaInI_6	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00
Cs_2NaInI_5Br	89.171	89.171	90.829	90.829	89.988	89.171	89.988	90.829	2.65E-05
$Cs_2NaInI_4Br_2$-a	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	0.00E+00
$Cs_2NaInI_4Br_2$-b	89.597	89.597	90.389	90.389	89.597	87.659	89.597	90.371	1.26E-05
$Cs_2NaInI_3Br_3$-a	88.815	88.815	91.185	91.185	89.995	89.751	89.995	90.249	4.38E-05
$Cs_2NaInI_3Br_3$-b	89.056	90.115	90.704	90.115	89.056	89.056	90.115	90.115	1.39E-05