Supporting Information

Unraveling the origin of unusual Cs atom disorder in cesium octahedral molybdenum halide cluster compounds, $Cs_2[\{Mo_6X^i_8\}X^a_6]$ (X = Cl and Br)

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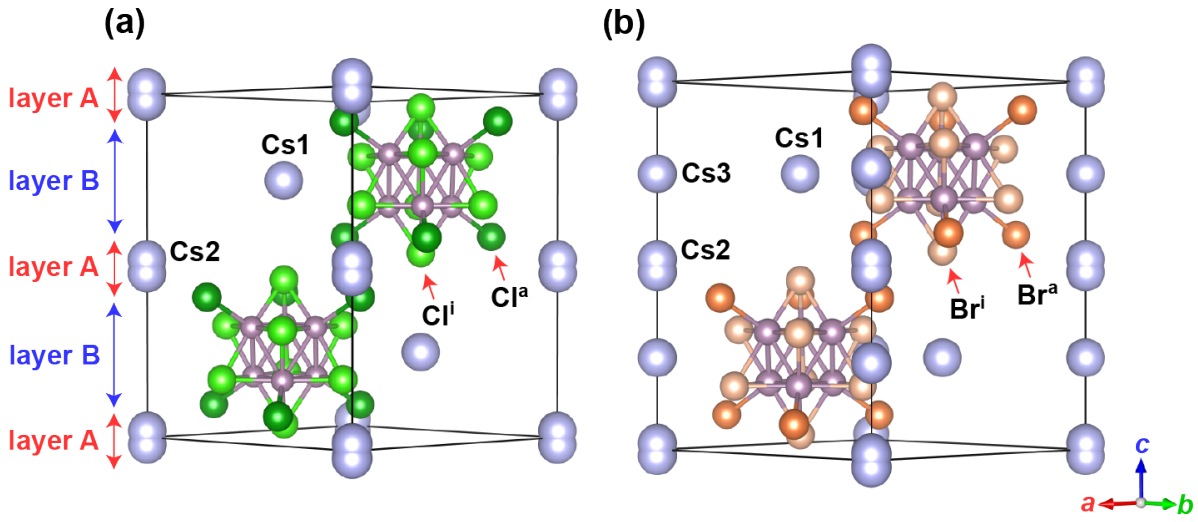

Figure S1. Unit cells of trigonal (a) CMCC and (b) CMBB, representing a A-B-A-B close-packed hexagonal stacking. Each unit cell contains two MC units ($Z = 2$).

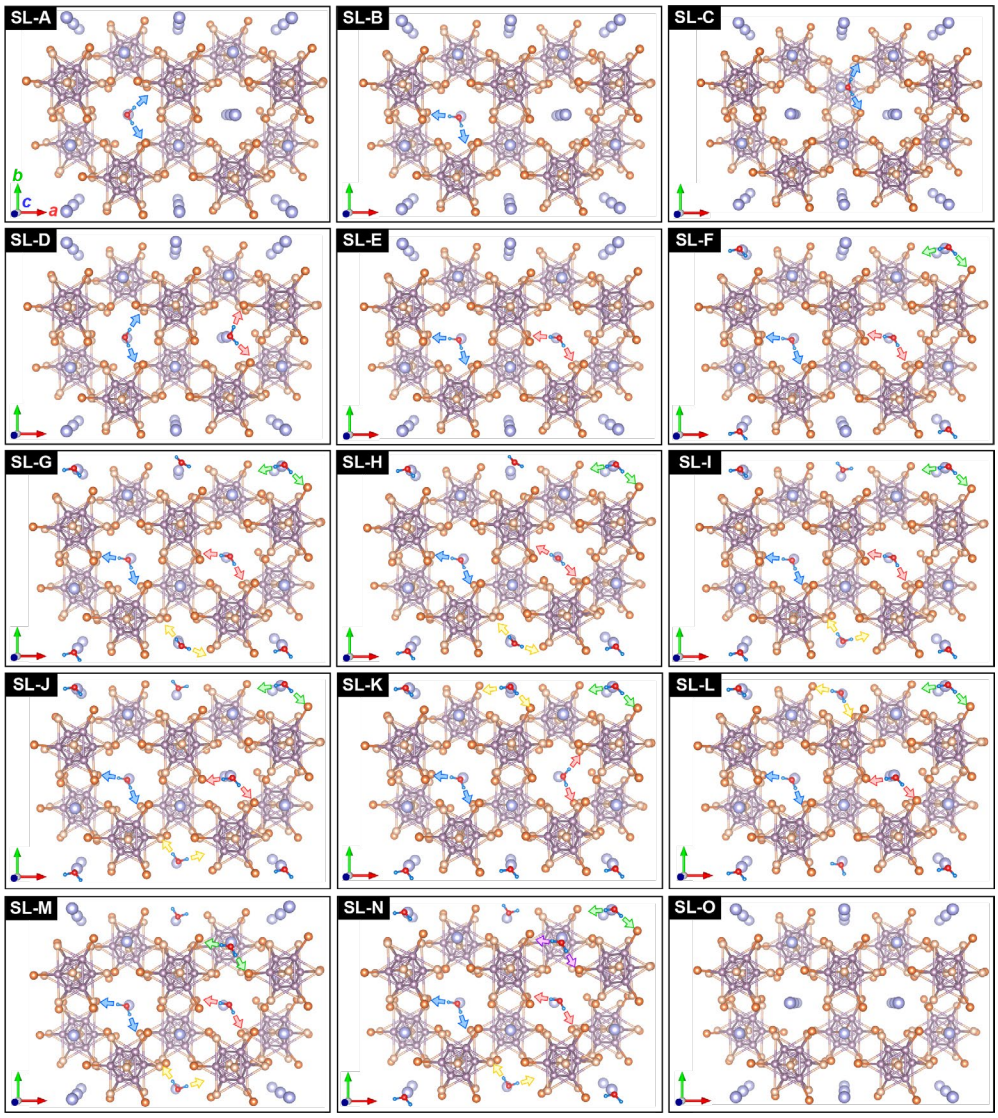

Figure S2. Superlattice models of $Cs_2[\{Mo_6X^i_8\}X^a_6]$ used in DFT-D calculations. Each superlattice contains 1−5 water molecules in the unit cell, with varying positions and orientations. The blue, red, green, yellow, and purple arrows indicate the individual water molecules incorporated into the superlattice and directions of their O−H bonds. The water molecules were arranged in an interstitial space located at the hexagonal channel between Cs2 sites (*i.e.* Cs3 site), and in some models (SL-C, SL-M, and SL-N), between the stacking of the MC unit and Cs1 site. The initial orientations of the water molecules were set so that their O−H bonds point toward X^as of the MC unit.

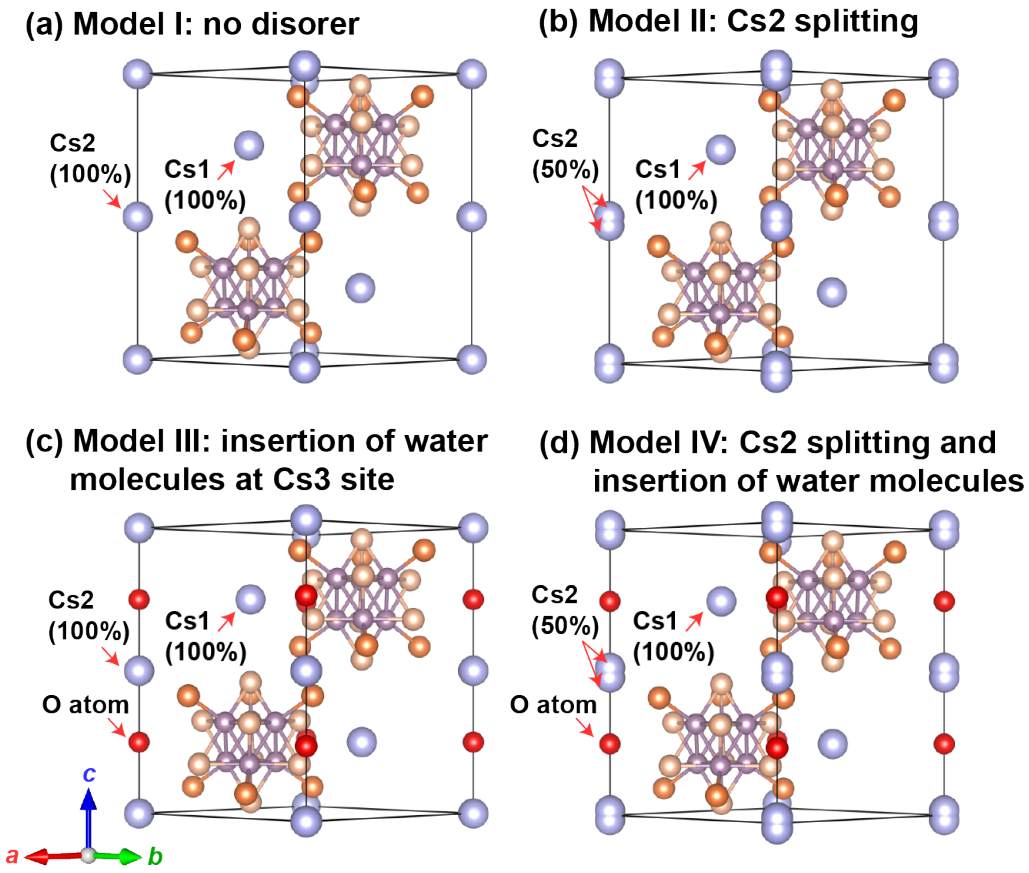

Figure S3. Crystal structure models of $Cs_2[\{Mo_6X^i_8\}X^a_6]$ adopted in SR-XRD structure refinements: (a) Model I: Trigonal phase without any disorder, (b) Model II: Trigonal phase with Cs2 splitting, (c) Model III: Trigonal phase with an O atom (water molecule) in Cs3 site, (d) Model IV: Trigonal phase with Cs2 splitting and an O atom in Cs3 site.

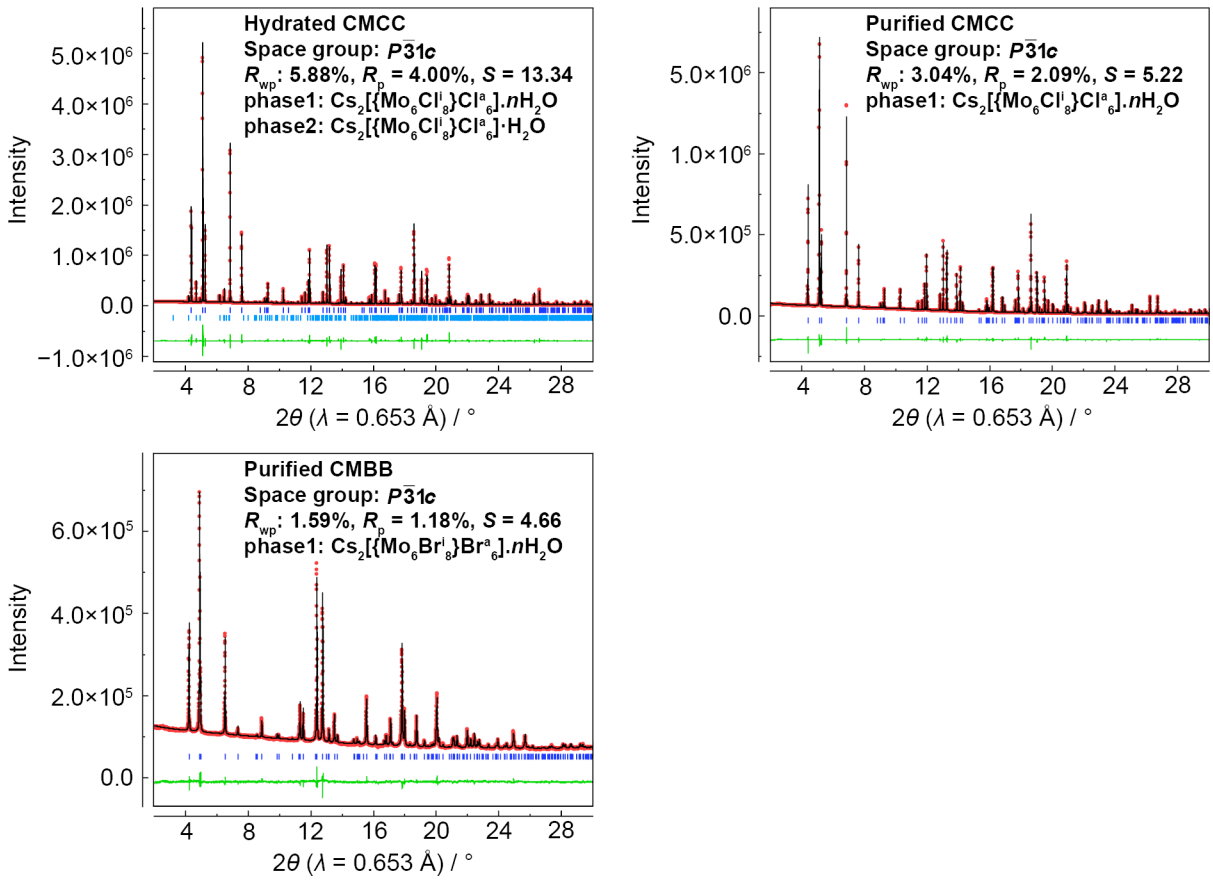

Figure S4. SR-XRD Rietveld refinements of hydrated CMCC, purified CMCC, and purified CMBB. Red circles and black line show the observed and simulated profiles, respectively. Green line indicates the difference between the observed and simulated profiles. Blue marks show the diffraction positions in the simulated profile.

Table S1. Summary of the SR-XRD Rietveld refinements of the MC-based compounds.

	Hydrated CMCC	Purified CMCC	Purified CMBB
Radiation source		Synchrotron X-ray	
Wavelength / Å		0.653	
Chemical formula	$CsMo_3Cl_7O_{0.45}$	$CsMo_3Cl_7O_{0.17}$	$CsMo_3Br_7O_{0.41}$
Formula weight	676.1	671.6	986.61
Temperature / K		300	
Crystal system		Trigonal	
Space group		$P\bar{3}1c$ (no. 163)	
Lattice parameters / Å	a = 9.830(8)	a = 9.790(4)	a = 10.175(33)
	c = 14.176(8)	c = 14.221(5)	c = 15.045(36)
	V = 1186.2(15)	V = 1180.4(9)	V = 1349.0(70)
Z		2	
Goodness of fit (S)	13.34	5.22	4.66
R_p / %	4.00	2.09	1.18
R_{wp} / %	5.88	3.04	1.59

Table S2. Refined structure factors of the MC-based compounds assuming the model IV illustrated in Fig. S3d:

(a) Hydrated CMCC (Space group: $P\bar{3}1c$, R_{wp} = 5.88%, R_p = 4.00%, and S = 13.34)

Atom	Site	Occup.	x	y	z	U_{iso} / Å^2
Mo	12*i*	1.0	0.6554(1)	0.1794(1)	0.1752(1)	0.0144(2)
Cl1	4*f*	1.0	2/3	1/3	0.0401(3)	0.0352(13)
Cl2	12*i*	1.0	0.9553(2)	0.3292(2)	0.1779(2)	0.0315(7)
Cl3	12*i*	1.0	0.6542(2)	−0.0370(2)	0.0871(2)	0.0307(7)
Cs1	2*c*	1.0	2/3	1/3	3/4	0.0534(6)
Cs2	4*e*	0.50	0	0	0.0268(1)	0.0209(7)
O1	2*a*	0.89	0	0	1/4	0.0331(52)

(b) Purified CMCC (Space group: $P\bar{3}1c$, R_{wp} = 3.04%, R_p = 2.09%, and S = 5.22)

Atom	Site	Occup.	x	y	z	U_{iso} / Å^2
Mo	12*i*	1.0	0.6658(1)	0.1793(1)	0.1756(1)	0.0156(2)
Cl1	4*f*	1.0	2/3	1/3	0.0394(2)	0.0235(8)
Cl2	12*i*	1.0	0.9563(2)	0.3291(2)	0.1777(1)	0.0236(5)
Cl3	12*i*	1.0	0.6534(2)	−0.0375(2)	0.0856(1)	0.0311(5)
Cs1	2*c*	1.0	2/3	1/3	3/4	0.0501(5)
Cs2	4*e*	0.50	0	0	0.0160(2)	0.0248(5)
O1	2*a*	0.34	0	0	1/4	1.020(97)

(c) Purified CMBB (Space group: $P\bar{3}1c$, R_{wp} = 1.59%, R_p = 1.18%, and S = 4.66)

Atom	Site	Occup.	x	y	z	U_{iso} / Å^2
Mo	12*i*	1.0	0.6685(3)	0.1861(2)	0.1799(1)	0.0124(5)
Br1	4*f*	1.0	2/3	1/3	0.0415(2)	0.0136(6)
Br2	12*i*	1.0	0.9573(2)	0.3279(2)	0.1773(1)	a)
Br3	12*i*	1.0	0.6551(2)	−0.0357(2)	0.0867(1)	0.0250(7)
Cs1	2*c*	1.0	2/3	1/3	3/4	0.0558(15)
Cs2	4*e*	0.50	0	0	0.0228(4)	0.0182(20)
O1	2*a*	0.81	0	0	1/4	0.412(44)

a) U_{iso} is constrained to be the same as that of Br1.

Table S3. Summary of the lattice parameters (Å) of the (a) CMBB and (b) CMCC superlattices optimized by DFT-D calculations. The #H_2O column shows the number (n) of the water molecules incorporated in the superlattice, and the Sym. column indicates assumable space group of the fully relaxed superlattice. ΔV (%) indicates a difference between the lattice volumes of the water-incorporated superlattice and the original one (no water molecule). $\Delta H/n$ (eV) normalizes the enthalpy difference in both superlattices (ΔH) by n of the water-incorporated superlattice. $\Delta H/nV$ (eV/Å^3) shows $\Delta H/n$ normalized by the lattice volume (V) of the water-incorporated superlattice. Atomic arrangement of each superlattice is shown in Fig. S2.

(a) CMBB:

Model	#H_2O	Sym.	Lattice parameters								Enthalpy	
			a	b	c	α	β	γ	V	ΔV	$\Delta H/n$	$\Delta H/nV$
SL-A	1	$P1$	19.851	17.119	14.793	90.09	90.27	90.15	5027.0	+0.04	467.77	0.093
SL-B	1	$P1$	19.801	17.128	14.807	89.73	90.04	89.70	5021.9	−0.06	468.00	0.093
SL-C	1	$P1$	19.802	17.123	14.934	90.14	90.11	90.07	5063.8	+0.77	467.51	0.092
SL-D	2	$P1$	19.871	17.113	14.753	89.70	90.21	89.65	5016.6	−0.17	468.07	0.093
SL-E	2	$P1$	19.791	17.175	14.760	89.74	89.90	89.60	5016.8	−0.16	468.07	0.093
SL-F	3	$P1$	19.745	17.232	14.738	89.60	89.62	89.50	5014.2	−0.22	468.06	0.093
SL-G	4	$P1$	19.757	17.255	14.642	89.19	89.58	89.07	4990.2	−0.69	468.10	0.094
SL-H	4	$P1$	19.764	17.237	14.595	88.83	89.59	88.75	4969.9	−1.10	468.13	0.094
SL-I	4	$P1$	19.677	17.309	14.719	89.32	89.18	89.23	5011.7	−0.27	468.05	0.093
SL-J	4	$P1$	19.644	17.306	14.748	89.07	89.07	89.14	5011.9	−0.26	468.03	0.093
SL-M	4	$P1$	19.684	17.279	14.871	89.59	89.31	89.53	5057.1	+0.64	467.92	0.093
SL-N	5	$P1$	19.656	17.326	14.845	89.23	89.12	89.23	5053.9	+0.58	467.95	0.093
SL-O	0	$P\bar{3}1c$	19.780	17.133	14.828	90.00	90.01	90.00	5025.1	–	–	–

(b) CMCC:

Model	#H_2O	Sym.	Lattice parameters								Enthalpy	
			a	*b*	*c*	*α*	*β*	*γ*	*V*	Δ*V*	Δ*H*/*n*	Δ*H*/*nV*
SL-A	1	*P*1	19.119	16.563	13.362	89.68	89.93	89.67	4316.6	−0.01	468.09	0.108
SL-B	1	*P*1	19.095	16.571	13.833	89.67	90.05	89.76	4376.8	1.38	467.30	0.107
SL-D	2	*P*1	19.088	16.610	13.617	89.90	89.74	89.87	4317.2	0	468.08	0.108
SL-G	4	*P*1	19.052	16.669	13.584	89.36	89.41	89.33	4313.4	−0.09	468.09	0.109
SL-H	4	*P*1	19.046	16.673	13.580	89.43	89.31	89.39	4311.5	−0.13	468.09	0.109
SL-I	4	*P*1	19.055	16.706	13.564	89.18	89.27	89.16	4316.6	−0.01	468.08	0.108
SL-J	4	*P*1	19.081	16.718	13.535	89.67	89.40	89.69	4317.3	0.01	468.06	0.108
SL-K	4	*P*1	19.092	16.618	13.576	89.38	89.76	89.52	4306.9	−0.24	468.11	0.109
SL-L	4	*P*1	19.051	16.654	13.580	89.01	89.41	89.06	4307.0	−0.24	468.11	0.109
SL-O	0	$P\bar{3}1c$	19.117	16.557	13.640	90.00	90.00	90.00	4317.2	–	–	–

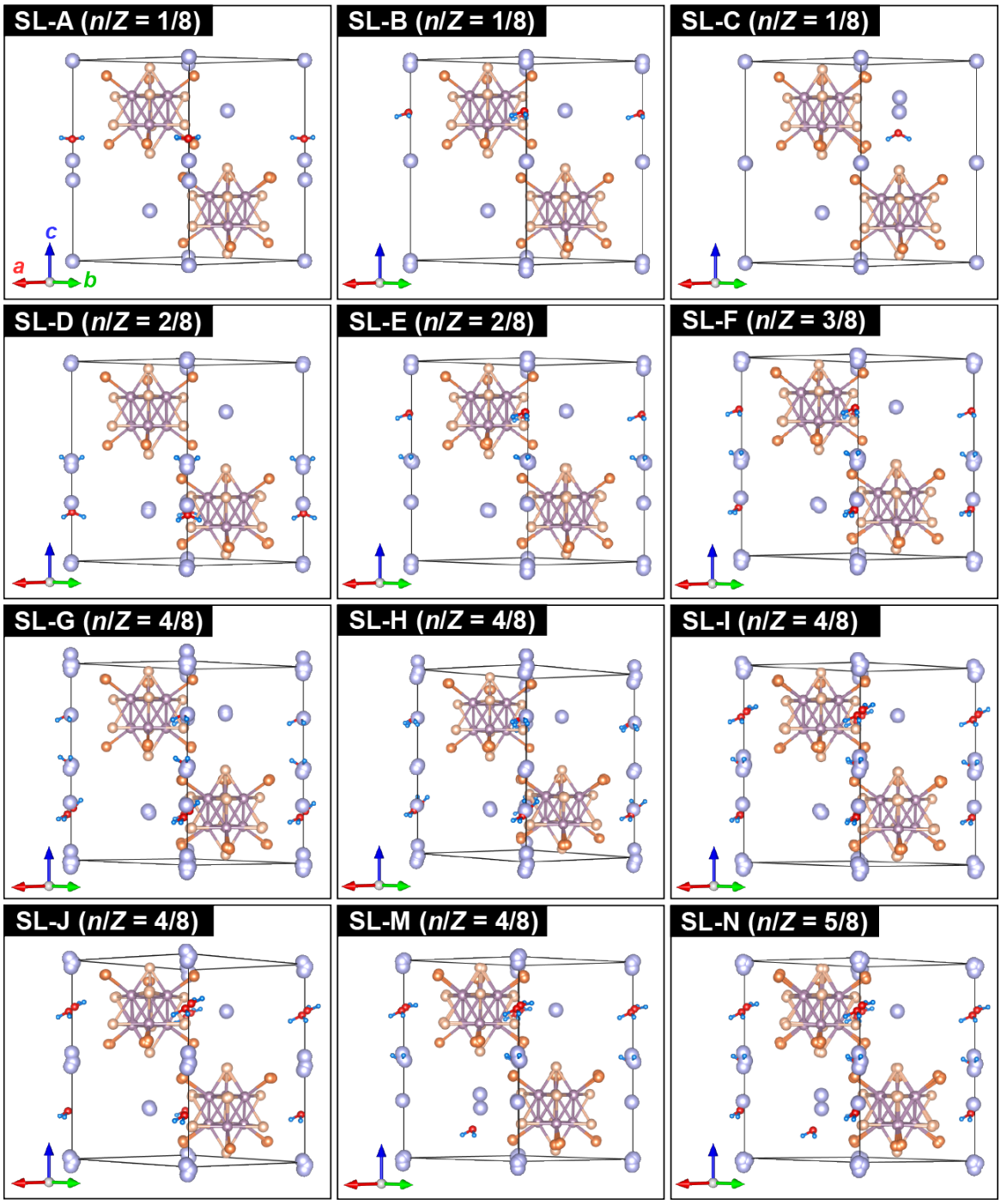

Figure S5. Projection of the water-incorporated CMBB superlattice ($Z = 8$), optimized by DFT-D calculations, into trigonal unit cell with $Z = 2$. n/Z indicates the amount of water molecules (n) per the MC units in the original superlattice. During the lattice projection, duplicate atoms are regarded as the same position using a threshold distance of 0.15 Å to obtain simple structural representation.

Table S4. Refined structure factors of the MC-based compounds assuming the disorders of the Cs atoms illustrated in Fig. 6:

(a) Hydrated CMCC (Space group: $P31c$, R_{wp} = 5.21%, R_p = 3.60%, and S = 11.82)

Atom	Site	Occup.	x	y	z	U_{iso} / Å^2
Mo1	6*c*	1.0	0.5124	0.1823	0.1792	0.0147
Mo2	6*c*	1.0	0.5154	0.3380	0.3286	a)
Cl1	6*c*	1.0	0.0292	0.3268	0.0895	0.0262
Cl2	6*c*	1.0	0.3216	0.3631	0.4161	b)
Cl3	6*c*	1.0	0.3736	0.0491	0.3315	0.0273
Cl4	6*c*	1.0	0.3764	0.3370	0.1861	c)
Cl5	2*b*	1.0	1/3	2/3	−0.0327	c)
Cl6	2*b*	1.0	1/3	2/3	0.5453	c)
Cs1A	2*b*	0.62	1/3	2/3	0.2658	0.0313
Cs1B	2*b*	0.04	1/3	2/3	0.2458	d)
Cs1C	2*b*	0.34	1/3	2/3	0.2287	d)
Cs2A	2*a*	0.21	0	0	0.0250	0.0304
Cs2B	2*a*	0.58	0	0	−0.0225	e)
Cs2C	2*a*	0.21	0	0	−0.0356	e)
O1	2*a*	0.88	0	0	0.2360	0.0319

U_{iso} is constrained to be the same as that of Mo1 for a), Cl1 for b), Cl3 for c), Cs1A for d), and Cs2A for e).

(b) Purified CMCC (Space group: $P31c$, R_{wp} = 2.80%, R_p = 1.95%, and S = 4.83)

Atom	Site	Occup.	x	y	z	U_{iso} / Å^2
Mo1	6*c*	1.0	0.5130	0.1798	0.1691	0.0155
Mo2	6*c*	1.0	0.5138	0.3349	0.3180	a)
Cl1	6*c*	1.0	0.0340	0.3317	0.0810	0.0259
Cl2	6*c*	1.0	0.3201	0.3604	0.4092	b)
Cl3	6*c*	1.0	0.3742	0.0437	0.3231	0.0213
Cl4	6*c*	1.0	0.3705	0.3265	0.1779	c)
Cl5	2*b*	1.0	1/3	2/3	−0.0483	c)
Cl6	2*b*	1.0	1/3	2/3	0.5303	c)
Cs1A	2*b*	0.33	1/3	2/3	0.2646	0.0324
Cs1B	2*b*	0.36	1/3	2/3	0.2413	d)
Cs1C	2*b*	0.31	1/3	2/3	0.2223	d)
Cs2A	2*a*	0.44	0	0	0.0131	0.0289
Cs2B	2*a*	0.56	0	0	−0.0164	e)
O1	2*a*	0.20	0	0	0.3291	0.1780

U_{iso} is constrained to be the same as that of Mo1 for a), Cl1 for b), Cl3 for c), Cs1A for d), and Cs2A for e).

(c) Purified CMBB (Space group: $P31c$, R_{wp} = 1.56%, R_p = 1.15%, and S = 4.57)

Atom	Site	Occup.	x	y	z	U_{iso} / Å^2
Mo1	6*c*	1.0	0.5139	0.1814	0.1909	0.0107
Mo2	6*c*	1.0	0.5204	0.3287	0.3307	a)
Br1	6*c*	1.0	0.0381	0.3431	0.1039	0.0269
Br2	6*c*	1.0	0.3124	0.3456	0.4306	b)
Br3	6*c*	1.0	0.3617	0.0404	0.3397	0.0109
Br4	6*c*	1.0	0.3792	0.3347	0.1940	c)
Br5	2*b*	1.0	1/3	2/3	−0.0353	c)
Br6	2*b*	1.0	1/3	2/3	0.5465	c)
Cs1A	2*b*	0.50	1/3	2/3	0.2791	0.0354
Cs1B	2*b*	0.50	1/3	2/3	0.2544	d)
Cs2A	2*a*	0.13	0	0	0.0525	0.0271
Cs2B	2*a*	0.87	0	0	−0.0084	e)
O1	2*a*	0.72	0	0	0.2832	0.1853

U_{iso} is constrained to be the same as that of Mo1 for a), Br1 for b), Br3 for c), Cs1A for d), and Cs2A for e).