Electronic Supporting Materials

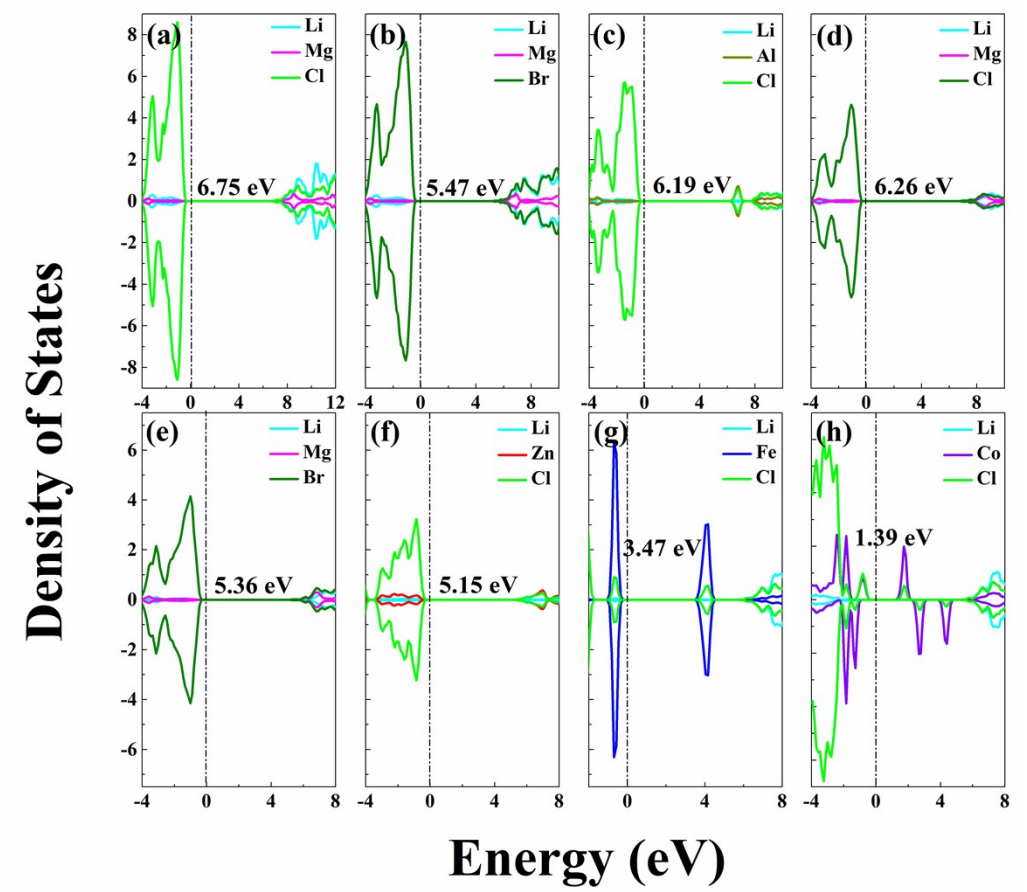

Fig. S1 Projected density of states (PDOS) calculated using the HSE06 functional: (a) Li_6MgCl_8, (b) Li_6MgBr_8, (c) Li_3AlCl_6, (d) Li_2MgCl_4, (e) Li_2MgBr_4, (f) $LiZnCl_3$, (g) Li_6FeCl_8 and (h) Li_6CoCl_8.

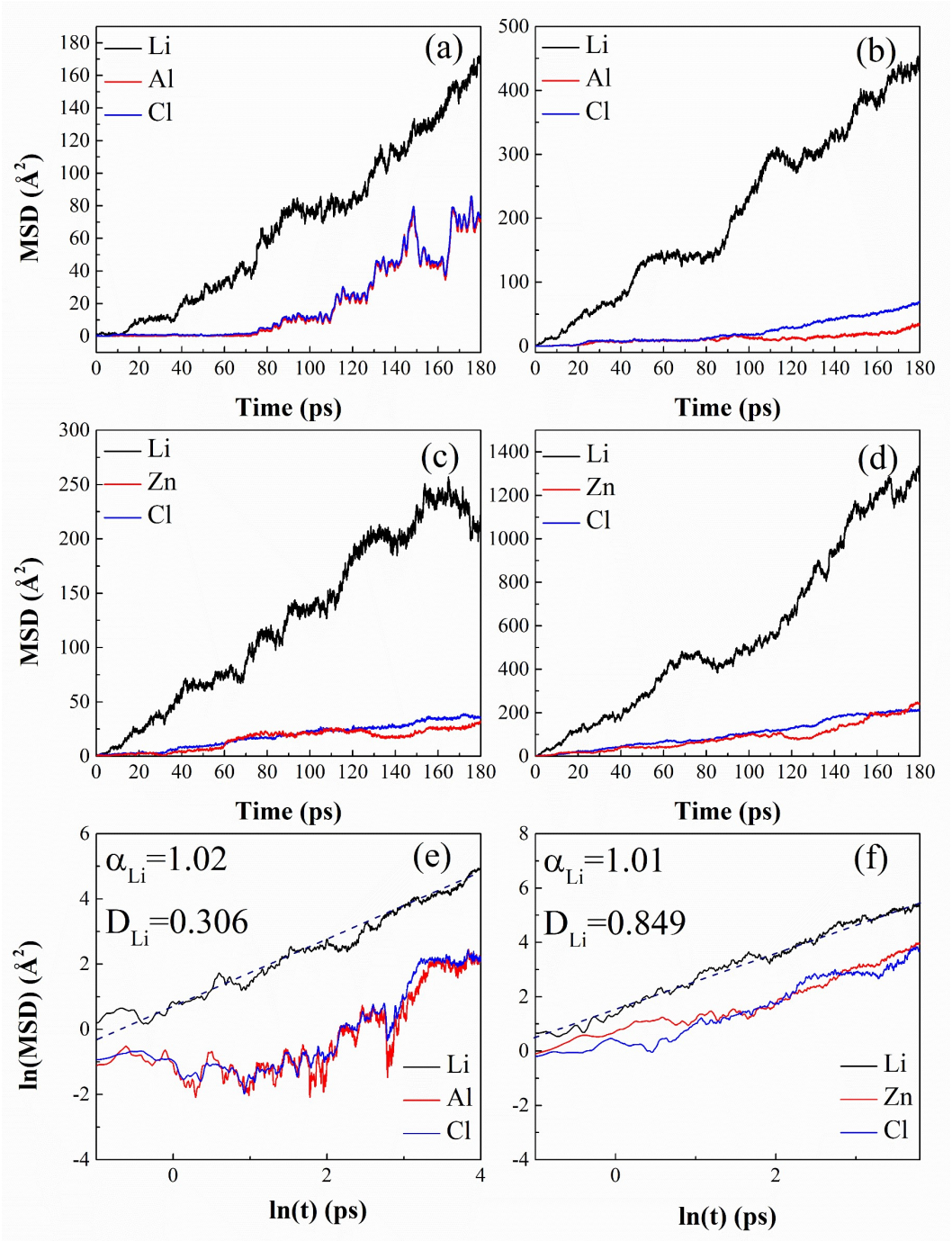

Fig. S2 MSD in Li_3AlCl_6-vac at (a) 650 K and (b) 900 K; and MSD in $LiZnCl_3$ at (c) 600 K and (d) 900 K. (e-f)The ln<MSD>of Li_3AlCl_6-vac and $LiZnCl_3$ at 900 K was plotted against ln (t) to determine the Li^+ diffusion coefficients D (10^{-4} cm^2 s^{-1}) and diffusion exponent α.

Table S1 The summary of the compounds through screening steps.

Compounds	Octahedral factors	Structure	Band Gap	PHONON	Formation Energy	AIMD	Voltage Plateau	Mechanical Property
Li_6BaCl_8	×							
Li_6BaBr_8	×							
Li_6CaCl_8	×							
Li_6CaBr_8	×							
Li_6CoCl_8	√	USPEX(MP-505391)	1.388					
Li_6CoBr_8	√	USPEX	0.97					
Li_6CuCl_8	√	USPEX	0.919					
Li_6CuBr_8	√	USPEX	0.43					
Li_6FeCl_8	√	USPEX(MP-28828)	3.469					
Li_6FeBr_8	√	USPEX	3.236					
Li_6MgCl_8	√	USPEX	6.753(√)	√	√	√	0-4.0116	√
Li_6MgBr_8	√	USPEX(MP-29008)	5.474(√)	√	√	√	0-4.77	√
Li_6MnCl_8	√	USPEX	3.126					
Li_6MnBr_8	√	USPEX	2.794					
Li_6NiCl_8	√	MP-1211124	3.518					
Li_6NiBr_8	×							
Li_6TiCl_8	√	USPEX	0					
Li_6TiBr_8	√	USPEX	0					
Li_6ZnCl_8	×							
Li_6ZnBr_8	×							
Li_4BaCl_6	×							
Li_4BaBr_6	×							
Li_4CaCl_6	×							
Li_4CaBr_6	×							
Li_4CoCl_6	×							
Li_4CoBr_6	×							
Li_4CuCl_6	×							
Li_4CuBr_6	×							
Li_4FeCl_6	√	USPEX	4.338					
Li_4FeBr_6	√	USPEX	2.535					
Li_4MgCl_6	×							
Li_4MgBr_6	×							
Li_4MnCl_6	√	USPEX	3.655					
Li_4MnBr_6	√	USPEX	3.653					

Li_4NiCl_6	×							
Li_4NiBr_6	×							
Li_4TiCl_6	√	USPEX	0					
Li_4TiBr_6	√	USPEX	0					
Li_4ZnCl_6	×							
Li_4ZnBr_6	×							
Li_3AlCl_6	√	USPEX	6.19(√)	√	√	√	0-4.639	√
Li_3AlBr_6	×							
Li_3FeCl_6	√	USPEX	2363					
Li_3FeBr_6	√	USPEX	1.19					
Li_2BaCl_4	×							
Li_2BaBr_4	×							
Li_2CaCl_4	×							
Li_2CaBr_4	×							
Li_2CoCl_4	√	MP-22980	2.045					
Li_2CoBr_4	√	USPEX	1.119					
Li_2CuCl_4	√	USPEX	1.755					
Li_2CuBr_4	√	USPEX	0.93					
Li_2FeCl_4	√	MP-1222745	3.66					
Li_2FeBr_4	√	USPEX(MP-22967)	3.17					
Li_2MgCl_4	√	MP-38684	6.257(√)	√	√	√	0-4.86	√
Li_2MgBr_4	√	USPEX(MP-29009)	5.36(√)	√	√	√	0-4.014	√
Li_2MnCl_4	√	MP-34148	2.163					
Li_2MnBr_4	√	USPEX(MP-28250)	1.872					
Li_2NiCl_4	×							
Li_2NiBr_4	×							
Li_2TiCl_4	√	USPEX	0.88					
Li_2TiBr_4	√	USPEX	0.933					
Li_2ZnCl_4	×							
Li_2ZnBr_4	×							
$LiAlCl_4$	×							
$LiAlBr_4$	×							
$LiFeCl_4$	√	MP-1210931						
$LiFeBr_4$	√	MP-1211043						
$LiBaCl_3$	×							
$LiBaBr_3$	×							
$LiCaCl_3$	×							

$LiCaBr_3$	×							
$LiCoCl_3$	×							
$LiCoBr_3$	×							
$LiCuCl_3$	√		0.384					
$LiCuBr_3$	√		0					
$LiFeCl_3$	×							
$LiFeBr_3$	×							
$LiMgCl_3$	×							
$LiMgBr_3$	×							
$LiMnCl_3$	×							
$LiMnBr_3$	×							
$LiNiCl_3$	√		0					
$LiNiBr_3$	√		0					
$LiTiCl_3$	√	MP-676210	0					
$LiTiBr_3$	×							
$LiZnCl_3$	√	USPEX	5.15(√)	√	√	√	0-4.722	√
$LiZnBr_3$	×							

Table S2 Ionic radius data and calculated octahedral factors in MX_6.

Ionic radius (Å)	Octahedral factor	
	M/Cl	M/Br
Li^+	0.42	0.388
Al^{3+}(0.535)	0.3	0.273
Ba^{2+}(1.35)	0.746	0.689
Ca^{2+}(1.0)	0.55	0.51
Co^{2+}(0.745)	0.412	0.38
Cu^{2+}(0.73)	0.4	0.37
Fe^{3+}(0.55)	0.304	0.281
Fe^{2+}(0.61)	0.337	0.311
Mg^{2+}(0.72)	0.398	0.367
Mn^{2+}(0.67)	0.37	0.342
Ni^{2+}(0.69)	0.38	0.352
Ti^{2+}(0.86)	0.475	0.439
Zn^{2+}(0.86)	0.475	0.439

Table S3 Lattice parameters and space groups of various minimal energy compounds from USPEX

Confs	**a**	**b**	**c(Å)**	**α**	**β**	**γ(°)**	**Symmetry**	**Average Octahedral Factor**
Li_6CoCl_8	10.22	10.22	10.22	90	90	90	$FM\bar{3}M(225)$	0.419
Li_6CoBr_8	10.92	10.92	10.92	90	90	90	$FM\bar{3}M(225)$	0.387
Li_6CuCl_8	10.27	10.27	10.27	90	90	90	$FM\bar{3}M(225)$	0.417
Li_6CuBr_8	10.97	10.97	10.97	90	90	90	$FM\bar{3}M(225)$	0.385
Li_6FeCl_8	10.22	10.22	10.22	90	90	90	$FM\bar{3}M(225)$	0.408
Li_6FeBr_8	10.92	10.92	10.92	90	90	90	$FM\bar{3}M(225)$	0.377
Li_6MgCl_8	10.35	10.35	10.35	90	90	90	$FM\bar{3}M(225)$	0.417
Li_6MgBr_8	11.06	11.06	11.06	90	90	90	$FM\bar{3}M(225)$	0.385
Li_6MnCl_8	10.24	10.24	10.24	90	90	90	$FM\bar{3}M(225)$	0.413
Li_6MnBr_8	11.06	11.06	11.06	90	90	90	$FM\bar{3}M(225)$	0.381
Li_6NiCl_8	10.27	10.27	10.27	90	90	90	$FM\bar{3}M(225)$	0.414
Li_6TiCl_8	24.99	3.71	6.68	90	84.8	90	$CM(8)$	0.428
Li_6TiBr_8	26.76	3.97	7.11	90	84.69	90	$CM(8)$	0.395
Li_4FeCl_6	16.53	3.53	7.19	90	104.12	90	$C2/M(12)$	0.403
Li_4FeBr_6	17.64	3.81	7.76	90	76.50	90	$C2/M(12)$	0.373
Li_4MnCl_6	16.69	3.54	7.18	90	104.29	90	$C2/M(12)$	0.41
Li_4MnBr_6	17.48	3.87	7.81	90	103.35	90	$C2/M(12)$	0.379

Li_4TiCl_6	16.84	3.56	7.26	90	103.31	90	$C2/M(12)$	0.431
Li_4TiBr_6	17.97	3.80	7.74	90	103.11	90	$C2/M(12)$	0.398
Li_3AlCl_6	6.26	6.26	6.24	90	90	120	$P\bar{3}1M(162)$	0.39
Li_3FeCl_6	6.21	6.21	6.15	90	90	120	$P\bar{3}1M(162)$	0.391
Li_3FeBr_6	6.62	6.62	6.54	90	90	120	$P\bar{3}1M(162)$	0.361
Li_2CoCl_4	10.26	7.32	3.63	90	90	90	$CMMM(65)$	0.417
Li_2CoBr_4	7.903	5.395	3.665	90	90	90	$PMMM(47)$	0.385
Li_2CuCl_4	7.999	9.712	3.983	90	104.05	90	*CM*(8)	0.413
Li_2CuBr_4	8.559	10.22	4.243	90	75.299	90	*CM*(8)	0.382
Li_2FeCl_4	7.48	7.37	10.30	90	90	90	$IMMA(74)$	0.392
Li_2FeBr_4	7.95	7.87	10.98	90	90	90	$IMMA(74)$	0.362
Li_2MgCl_4	7.39	7.46	10.52	90	90	90	$IMMA(74)$	0.417
Li_2MgBr_4	7.89	11.13	3.89	90	90	90	$CMMM(65)$	0.381
Li_2MnCl_4	7.42	7.516	10.51	90	90	90	$IMMA(74)$	0.403
Li_2MnBr_4	7.88	11.13	3.89	90	90	90	$CMMM(65)$	0.373
Li_2TiCl_4	7.38	10.62	3.56	90	90	90	$CMMM(65)$	0.438
Li_2TiBr_4	7.86	11.28	3.79	90	90	90	$CMMM(65)$	0.405
$LiFeCl_4$	6.63	8.41	13.16	90	90.76	90	$P2_1/C(14)$	0.362
$LiFeBr_4$	7.55	7.44	14.13	90	93.55	90	$P2_1/C(14)$	0.335
$LiNiCl_3$	3.99	3.99	21.22	90	90	120	*R3M*(160)	0.4
$LiNiBr_3$	4.25	4.25	22.61	90	90	120	*R3M*(160)	0.37
$LiCuCl_3$	11.74	4.70	4.08	90	90.47	90	*CM*(8)	0.41
$LiCuBr_3$	12.44	5.03	4.39	90	91.41	90	*CM*(8)	0.379
$LiTiCl_3$	13.08	7.16	12.90	90	114.02	90	*CM*(8)	0.448
$LiZnCl_3$	6.09	3.70	6.34	90	115.34	90	*PM*(6)	0.448

Table S4 Formation energies for the compounds of interest with respect to the corresponding reference phases

Compounds	Reference phase	Formation energy (eV/atom)
$LiMgCl_3$	$LiCl+MgCl_2$	0.0267
Li_2MgCl_4	$LiCl+2MgCl_2$	-0.006565
Li_4MgCl_6	$LiCl+Li_2MgCl_4$	0.00637649
Li_6MgCl_8	$LiCl+Li_2MgCl_4$	0.00202287
$LiMgBr_3$	$LiBr+MgBr_2$	0.0385
Li_2MgBr_4	$LiBr+MgBr_2$	-0.000020476
Li_4MgBr_6	$LiBr+Li_2MgBr_4$	0.00075745
Li_6MgBr_8	$LiBr+Li_2MgBr_4$	-0.00049766
$LiAlCl_4$	$LiCl+AlCl_3$	-0.05549
Li_3AlCl_6	$LiCl+LiAlCl_4$	0.0243
$LiZnCl_3$	$LiCl+ZnCl_2$	0.012713
Li_2ZnCl_4	$LiCl+ZnCl_2$	-0.015131754
Li_4ZnCl_6	$LiCl+Li_2ZnCl_4$	-0.004744
Li_6ZnCl_8	$LiCl+Li_4ZnCl_6$	0.0229

POSCAR files of identified in this work:

$LiZnCl_3$

```
6.0928001404          0.0000000000          0.0000000000
0.0000000000          3.6989998817          0.0000000000
-2.7120750913         0.0000000000          5.7261047277
   Li   Cl   Zn
    1    3    1
Direct
      0.504620016          0.500000000          0.663339972
      0.408890009          0.500000000          0.028170001
      0.810270011          0.000000000          0.779879987
      0.218960002          0.000000000          0.434350014
      0.189349994          0.000000000          0.066930003
```

Li_2MgCl_4

```
7.3668999672          0.0000000000          0.0000000000
0.0000000000         10.4561996460          0.0000000000
0.0000000000          0.0000000000          3.6547000408
   Li   Mg   Cl
    4    2    8
Direct
      0.750000000          0.750000000          0.500000000
      0.250000000          0.250000000          0.500000000
      0.250000000          0.750000000          0.500000000
```

0.750000000	0.250000000	0.500000000
0.000000000	0.000000000	0.000000000
0.500000000	0.500000000	0.000000000
0.265879989	0.500000000	0.500000000
0.734120011	0.500000000	0.500000000
0.765879989	0.000000000	0.500000000
0.234120011	0.000000000	0.500000000
0.000000000	0.760859966	0.000000000
0.000000000	0.239140004	0.000000000
0.500000000	0.260859996	0.000000000
0.500000000	0.739140034	0.000000000

Li_2MgBr_4

7.8871998787	0.0000000000	0.0000000000
0.0000000000	11.1295003891	0.0000000000
0.0000000000	0.0000000000	3.8891999722

Li	Mg	Br
4	2	8

Direct

0.750000000	0.750000000	0.500000000
0.250000000	0.250000000	0.500000000
0.250000000	0.750000000	0.500000000
0.750000000	0.250000000	0.500000000
0.000000000	0.500000000	0.000000000
0.500000000	0.000000000	0.000000000
0.000000000	0.741129994	0.000000000
0.000000000	0.258870006	0.000000000
0.500000000	0.241129994	0.000000000
0.500000000	0.758870006	0.000000000
0.763490021	0.500000000	0.500000000
0.236509994	0.500000000	0.500000000
0.263490021	0.000000000	0.500000000
0.736509979	0.000000000	0.500000000

Li_3AlCl_6

6.2641000748	0.0000000000	0.0000000000
-3.1320500374	5.4248697966	0.0000000000
0.0000000000	0.0000000000	6.2431998253

Li	Al	Cl
3	1	6

Direct

0.333333343	0.666666687	0.500000000
0.666666627	0.333333313	0.500000000
0.000000000	0.000000000	0.000000000
0.000000000	0.000000000	0.500000000
0.303730011	0.303730011	0.719079971
0.696269989	0.696269989	0.280920029
0.696269989	0.000000000	0.719079971
0.303730011	0.000000000	0.280920029

0.000000000 0.696269989 0.719079971
0.000000000 0.303730011 0.280920029

Li_6MgCl_8
10.3517999649 0.0000000000 0.0000000000
0.0000000000 10.3517999649 0.0000000000
0.0000000000 0.0000000000 10.3517999649
Li Mg Cl
24 4 32
Direct
0.250000000 0.500000000 0.250000000
0.750000000 0.500000000 0.750000000
0.750000000 0.500000000 0.250000000
0.250000000 0.500000000 0.750000000
0.250000000 0.250000000 0.500000000
0.750000000 0.750000000 0.500000000
0.250000000 0.750000000 0.500000000
0.750000000 0.250000000 0.500000000
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0.500000000 0.500000000 0.241469994
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0.500000000 0.000000000 0.741469979
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0.241469994 0.000000000 0.000000000
0.000000000 0.758530021 0.000000000

0.000000000 0.241469994 0.000000000
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0.000000000 0.500000000 0.741469979
0.258530021 0.500000000 0.000000000
0.741469979 0.500000000 0.000000000
0.000000000 0.258530021 0.500000000
0.000000000 0.741469979 0.500000000
0.000000000 0.000000000 0.758530021
0.000000000 0.000000000 0.241469994
0.258530021 0.000000000 0.500000000
0.741469979 0.000000000 0.500000000
0.750000000 0.250000000 0.750000000
0.250000000 0.750000000 0.250000000
0.250000000 0.750000000 0.750000000
0.750000000 0.250000000 0.250000000
0.250000000 0.250000000 0.250000000
0.750000000 0.750000000 0.750000000
0.750000000 0.750000000 0.250000000
0.250000000 0.250000000 0.750000000

Li_6MgCl_8
11.0615997314 0.0000000000 0.0000000000
0.0000000000 11.0615997314 0.0000000000
0.0000000000 0.0000000000 11.0615997314
Li Mg Br
24 4 32
Direct
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0.500000000 0.250000000 0.750000000
0.500000000 0.250000000 0.250000000
0.500000000 0.750000000 0.750000000
0.250000000 0.500000000 0.750000000
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0.000000000 0.750000000 0.750000000
0.000000000 0.250000000 0.250000000
0.000000000 0.250000000 0.750000000
0.000000000 0.750000000 0.250000000

0.000000000	0.000000000	0.000000000
0.000000000	0.500000000	0.500000000
0.500000000	0.000000000	0.500000000
0.500000000	0.500000000	0.000000000
0.750000000	0.250000000	0.750000000
0.250000000	0.750000000	0.250000000
0.250000000	0.750000000	0.750000000
0.750000000	0.250000000	0.250000000
0.250000000	0.250000000	0.250000000
0.750000000	0.750000000	0.750000000
0.750000000	0.750000000	0.250000000
0.250000000	0.250000000	0.750000000
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0.757319987	0.500000000	0.500000000
0.500000000	0.242679998	0.500000000
0.500000000	0.757319987	0.500000000
0.500000000	0.500000000	0.242679998
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0.500000000	0.000000000	0.257319987
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