——Supporting Information——

Defect Chemistry and Ion Transport in Low-Dimensional-Networked Li-Rich Anti-Perovskites as Solid Electrolytes for Solid-State Batteries

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Li_3OCl CIF

```
data_VESTA_phase_1


_chemical_name_common                  'Li3 Cl1 O1'
_cell_length_a                         3.908337
_cell_length_b                         3.908337
_cell_length_c                         3.908337
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      90.000000
_cell_volume                           59.700236
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1


loop_
```

```
_space_group_symop_operation_xyz
   'x, y, z'


loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
   Li0       1.0     0.000000     0.500000     0.500000    Uiso  ? Li
   Li1       1.0     0.500000     0.000000     0.500000    Uiso  ? Li
   Li2       1.0     0.500000     0.500000     0.000000    Uiso  ? Li
   Cl3       1.0     0.000000     0.000000     0.000000    Uiso  ? Cl
   O4        1.0     0.500000     0.500000     0.500000    Uiso  ? O
```

Li_3OBr CIF

```
data_VESTA_phase_1


_chemical_name_common                  'New structure'
_cell_length_a                         4.000000
_cell_length_b                         4.000000
_cell_length_c                         4.000000
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      90.000000
_cell_volume                           64.000000
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1

loop_
_space_group_symop_operation_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
```

_atom_site_U_iso_or_equiv

_atom_site_type_symbol

Br1	1.0	0.000000	0.000000	0.000000	Uiso	?	Br
O1	1.0	0.500000	0.500000	0.500000	Uiso	?	O
Li1	1.0	0.500000	0.500000	0.000000	Uiso	?	Li
Li2	1.0	0.500000	0.000000	0.500000	Uiso	?	Li
Li3	1.0	0.000000	0.500000	0.500000	Uiso	?	Li

Li_4OCl_2 CIF

data_cif

_audit_creation_method 'generated by GULP'

_symmetry_space_group_name_H-M 'P 1'

_symmetry_Int_Tables_number 1

_symmetry_cell_setting triclinic

_cell_length_a 3.9043

_cell_length_b 3.9043

_cell_length_c 12.5990

_cell_angle_alpha 90.0000

_cell_angle_beta 90.0000

_cell_angle_gamma 90.0000

loop_

_atom_site_label

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_occupancy

Li 0.00000 0.50000 0.00000 1.0000

Li 0.50000 0.00000 0.00000 1.0000

Li 0.50000 1.00000 0.50000 1.0000

Li	0.00000	0.50000	0.50000	1.0000
Li	1.00000	0.00000	0.15304	1.0000
Li	0.00000	0.00000	0.84696	1.0000
Li	0.50000	0.50000	0.65304	1.0000
Li	0.50000	0.50000	0.34696	1.0000
Cl	0.00000	1.00000	0.34637	1.0000
Cl	0.00000	1.00000	0.65363	1.0000
Cl	0.50000	0.50000	0.84637	1.0000
Cl	0.50000	0.50000	0.15363	1.0000
O	1.00000	0.00000	0.00000	1.0000
O	0.50000	0.50000	0.50000	1.0000

Li_4OBr_2 CIF

```
data_VESTA_phase_1


_chemical_name_common                  'New structure'
_cell_length_a                         3.904336
_cell_length_b                         3.904336
_cell_length_c                         11.599001
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      90.000000
_cell_volume                           176.813308
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1

loop_
_space_group_symop_operation_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
```

_atom_site_U_iso_or_equiv

_atom_site_type_symbol

Li1	1.0	0.000000	0.500000	0.000000	Uiso	?	Li
Li2	1.0	0.500000	0.000000	0.000000	Uiso	?	Li
Li3	1.0	0.500000	1.000000	0.500000	Uiso	?	Li
Li4	1.0	0.000000	0.500000	0.500000	Uiso	?	Li
Li5	1.0	1.000000	0.000000	0.153038	Uiso	?	Li
Li6	1.0	0.000000	0.000000	0.846962	Uiso	?	Li
Li7	1.0	0.500000	0.500000	0.653038	Uiso	?	Li
Li8	1.0	0.500000	0.500000	0.346962	Uiso	?	Li
Br1	1.0	0.000000	1.000000	0.346373	Uiso	?	Br
Br2	1.0	0.000000	1.000000	0.653627	Uiso	?	Br
Br3	1.0	0.500000	0.500000	0.846373	Uiso	?	Br
Br4	1.0	0.500000	0.500000	0.153627	Uiso	?	Br
O1	1.0	1.000000	0.000000	0.000000	Uiso	?	O
O2	1.0	0.500000	0.500000	0.500000	Uiso	?	O
Br5	1.0	0.000000	1.000000	0.346550	Uiso	?	Br
Br6	1.0	0.000000	0.000000	0.653450	Uiso	?	Br
Br7	1.0	0.500000	0.500000	0.846550	Uiso	?	Br
Br8	1.0	0.500000	0.500000	0.153450	Uiso	?	Br
O3	1.0	1.000000	0.000000	0.000000	Uiso	?	O
O4	1.0	0.500000	0.500000	0.500000	Uiso	?	O

Li_5OCl_3 CIF

data_cif

_audit_creation_method 'generated by GULP'

_symmetry_space_group_name_H-M 'P 1'

_symmetry_Int_Tables_number 1

_symmetry_cell_setting triclinic

_cell_length_a 7.7384

_cell_length_b 5.9300

_cell_length_c 11.6909

_cell_angle_alpha 90.0013

_cell_angle_beta 89.9993

_cell_angle_gamma 90.0011

loop_

_atom_site_label

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_occupancy

Li	0.63333	0.52653	0.62577	1.0000
Li	0.36204	0.57358	0.36697	1.0000
Li	0.86203	0.02651	0.36699	1.0000

Li	0.13333	0.07357	0.62577	1.0000
Li	0.36204	0.57359	0.12577	1.0000
Li	0.63332	0.52657	0.86696	1.0000
Li	0.13332	0.07358	0.86697	1.0000
Li	0.86204	0.02654	0.12578	1.0000
Li	0.63334	0.07356	0.86697	1.0000
Li	0.36192	0.02659	0.12579	1.0000
Li	0.86191	0.57354	0.12578	1.0000
Li	0.13334	0.52658	0.86696	1.0000
Li	0.36191	0.02659	0.36696	1.0000
Li	0.63335	0.07352	0.62579	1.0000
Li	0.13335	0.52658	0.62578	1.0000
Li	0.86191	0.57351	0.36696	1.0000
Li	0.37856	0.30004	0.74637	1.0000
Li	0.61676	0.80020	0.24638	1.0000
Li	0.11676	0.79991	0.24638	1.0000
Li	0.87855	0.30008	0.74637	1.0000
Cl	0.33582	0.80008	0.74638	1.0000
Cl	0.65951	0.30003	0.24637	1.0000
Cl	0.15951	0.30008	0.24637	1.0000
Cl	0.83582	0.80006	0.74638	1.0000
Cl	0.37884	0.30006	0.97079	1.0000
Cl	0.61647	0.80005	0.02196	1.0000
Cl	0.11647	0.80008	0.02196	1.0000
Cl	0.87884	0.30007	0.97079	1.0000

Cl	0.61647	0.80005	0.47080	1.0000
Cl	0.37884	0.30006	0.52195	1.0000
Cl	0.87885	0.30006	0.52195	1.0000
Cl	0.11647	0.80007	0.47079	1.0000
O	0.62569	0.30005	0.74637	1.0000
O	0.36962	0.80008	0.24638	1.0000
O	0.86962	0.80004	0.24638	1.0000
O	0.12569	0.30007	0.74637	1.0000

Li_5OBr_3 CIF

```
data_VESTA_phase_1


_chemical_name_common                  'New structure'
_cell_length_a                         8.500000
_cell_length_b                         6.300000
_cell_length_c                         13.000000
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      90.000000
_cell_volume                           696.150021
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1

loop_
_space_group_symop_operation_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
```

_atom_site_U_iso_or_equiv

_atom_site_type_symbol

Li1	1.0	0.633330	0.526530	0.625770	Uiso	?	Li
Li2	1.0	0.863210	0.609350	0.348160	Uiso	?	Li
Li3	1.0	0.363210	0.026560	0.348160	Uiso	?	Li
Li4	1.0	0.133330	0.109360	0.625760	Uiso	?	Li
Li5	1.0	0.863210	0.609350	0.125770	Uiso	?	Li
Li6	1.0	0.633330	0.526550	0.848160	Uiso	?	Li
Li7	1.0	0.133330	0.109360	0.848160	Uiso	?	Li
Li8	1.0	0.363210	0.026560	0.125760	Uiso	?	Li
Li9	1.0	0.633360	0.109320	0.848160	Uiso	?	Li
Li10	1.0	0.863210	0.026560	0.125770	Uiso	?	Li
Li11	1.0	0.363210	0.609340	0.125760	Uiso	?	Li
Li12	1.0	0.133360	0.526580	0.848150	Uiso	?	Li
Li13	1.0	0.863210	0.026560	0.348160	Uiso	?	Li
Li14	1.0	0.633340	0.109310	0.625770	Uiso	?	Li
Li15	1.0	0.133360	0.526580	0.625770	Uiso	?	Li
Li16	1.0	0.363210	0.609340	0.348160	Uiso	?	Li
Li17	1.0	0.383820	0.317900	0.736960	Uiso	?	Li
Li18	1.0	0.112740	0.817950	0.236960	Uiso	?	Li
Li19	1.0	0.612720	0.817950	0.236960	Uiso	?	Li
Li20	1.0	0.883810	0.318000	0.736960	Uiso	?	Li
Br1	1.0	0.291370	0.817980	0.736960	Uiso	?	Br
Br2	1.0	0.205170	0.317950	0.236960	Uiso	?	Br
Br3	1.0	0.705180	0.317950	0.236960	Uiso	?	Br

Br4	1.0	0.791370	0.817920	0.736960	Uiso	?	Br
Br5	1.0	0.379280	0.317960	0.942690	Uiso	?	Br
Br6	1.0	0.117280	0.817950	0.031230	Uiso	?	Br
Br7	1.0	0.617280	0.817950	0.031230	Uiso	?	Br
Br8	1.0	0.879280	0.317950	0.942690	Uiso	?	Br
Br9	1.0	0.117280	0.817950	0.442690	Uiso	?	Br
Br10	1.0	0.379280	0.317940	0.531230	Uiso	?	Br
Br11	1.0	0.879280	0.317950	0.531230	Uiso	?	Br
Br12	1.0	0.617280	0.817950	0.442690	Uiso	?	Br
O1	1.0	0.620340	0.317930	0.736960	Uiso	?	O
O2	1.0	0.876210	0.817950	0.236960	Uiso	?	O
O3	1.0	0.376200	0.817950	0.236960	Uiso	?	O
O4	1.0	0.120360	0.317970	0.736960	Uiso	?	O
Br13	1.0	0.291370	0.817980	0.736960	Uiso	?	Br
Br14	1.0	0.205170	0.317950	0.236960	Uiso	?	Br
Br15	1.0	0.705180	0.317950	0.236960	Uiso	?	Br
Br16	1.0	0.791370	0.817920	0.736960	Uiso	?	Br
Br17	1.0	0.379280	0.317960	0.942690	Uiso	?	Br
Br18	1.0	0.117280	0.817950	0.031230	Uiso	?	Br
Br19	1.0	0.617280	0.817950	0.031230	Uiso	?	Br
Br20	1.0	0.879280	0.317950	0.942690	Uiso	?	Br
Br21	1.0	0.117280	0.817950	0.442690	Uiso	?	Br
Br22	1.0	0.379280	0.317940	0.531230	Uiso	?	Br
Br23	1.0	0.879280	0.317950	0.531230	Uiso	?	Br
Br24	1.0	0.617280	0.817950	0.442690	Uiso	?	Br

O5	1.0	0.620340	0.317930	0.736960	Uiso	?	O
O6	1.0	0.876210	0.817950	0.236960	Uiso	?	O
O7	1.0	0.376200	0.817950	0.236960	Uiso	?	O
O8	1.0	0.120360	0.317970	0.736960	Uiso	?	O

Li_6OCl_4 CIF

```
data_cif

_audit_creation_method            'generated by GULP'

_symmetry_space_group_name_H-M    'P 1'
_symmetry_Int_Tables_number       1
_symmetry_cell_setting            triclinic

_cell_length_a                    7.1969
_cell_length_b                    6.7647
_cell_length_c                    7.2117
_cell_angle_alpha                 90.0135
_cell_angle_beta                  95.4091
_cell_angle_gamma                 89.9876

loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
 Cl      0.83052    0.24256    0.33877  1.0000
 Cl      0.07518    0.74173    0.58339  1.0000
 Cl      0.65751    0.74257    0.16663  1.0000
```

Cl	0.41334	0.24175	0.92257	1.0000
Cl	0.84469	0.39024	0.80678	1.0000
Cl	0.18998	0.59319	0.15281	1.0000
Cl	0.64402	0.89034	0.69877	1.0000
Cl	0.29815	0.09325	0.35333	1.0000
Li	0.99042	0.91930	0.26672	1.0000
Li	0.97148	0.04064	0.73786	1.0000
Li	0.49788	0.41944	0.23898	1.0000
Li	0.51727	0.54052	0.76812	1.0000
Li	0.26018	0.94145	0.02721	1.0000
Li	0.73027	0.06574	0.00569	1.0000
Li	0.22842	0.44137	0.47892	1.0000
Li	0.75805	0.56585	0.50000	1.0000
Li	0.05944	0.26296	0.06553	1.0000
Li	0.93037	0.72051	0.93939	1.0000
Li	0.42871	0.76297	0.44061	1.0000
Li	0.55837	0.22051	0.56611	1.0000
O	0.00104	0.99172	0.99635	1.0000
O	0.48748	0.49178	0.50954	1.0000

Li_6OBr_4 CIF

```
data_VESTA_phase_1


_chemical_name_common                  'New structure'
_cell_length_a                         7.776548
_cell_length_b                         7.305370
_cell_length_c                         7.776600
_cell_angle_alpha                      90.000000
_cell_angle_beta                       94.241402
_cell_angle_gamma                      90.000000
_cell_volume                           440.583043
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1

loop_
_space_group_symop_operation_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
```

_atom_site_U_iso_or_equiv

_atom_site_type_symbol

Br1	1.0	0.830520	0.242564	0.338774	Uiso	?	Br
Br2	1.0	0.181879	0.742550	0.690134	Uiso	?	Br
Br3	1.0	0.681879	0.742564	0.190134	Uiso	?	Br
Br4	1.0	0.330520	0.242550	0.838774	Uiso	?	Br
Br5	1.0	0.822528	0.375991	0.830790	Uiso	?	Br
Br6	1.0	0.189874	0.609122	0.198121	Uiso	?	Br
Br7	1.0	0.689874	0.875992	0.698120	Uiso	?	Br
Br8	1.0	0.322528	0.109122	0.330790	Uiso	?	Br
Li1	1.0	0.004155	0.931049	0.254962	Uiso	?	Li
Li2	1.0	0.008244	0.054063	0.773953	Uiso	?	Li
Li3	1.0	0.508244	0.431051	0.273953	Uiso	?	Li
Li4	1.0	0.504155	0.554065	0.754962	Uiso	?	Li
Li5	1.0	0.246697	0.931002	0.012467	Uiso	?	Li
Li6	1.0	0.765703	0.054108	0.016453	Uiso	?	Li
Li7	1.0	0.265703	0.431006	0.516453	Uiso	?	Li
Li8	1.0	0.746697	0.554112	0.516453	Uiso	?	Li
Li9	1.0	0.071128	0.258908	0.079351	Uiso	?	Li
Li10	1.0	0.941271	0.726206	0.949569	Uiso	?	Li
Li11	1.0	0.441271	0.758908	0.449569	Uiso	?	Li
Li12	1.0	0.571128	0.226206	0.579351	Uiso	?	Li
O1	1.0	0.006200	0.992555	0.014458	Uiso	?	O
O2	1.0	0.506200	0.492559	0.514458	Uiso	?	O
Br9	1.0	0.828744	0.242560	0.336999	Uiso	?	Br

Br10	1.0	0.183656	0.742552	0.691908	Uiso	?	Br
Br11	1.0	0.683656	0.742561	0.191908	Uiso	?	Br
Br12	1.0	0.328744	0.242554	0.836999	Uiso	?	Br
Br13	1.0	0.821463	0.373942	0.829728	Uiso	?	Br
Br14	1.0	0.190938	0.611171	0.199182	Uiso	?	Br
Br15	1.0	0.690938	0.873943	0.699183	Uiso	?	Br
Br16	1.0	0.321463	0.111172	0.329728	Uiso	?	Br
O3	1.0	0.006200	0.992555	0.014458	Uiso	?	O
O4	1.0	0.506200	0.492559	0.514458	Uiso	?	O

Example LAMMPS input file

```
############################################################
#------------Variables and cell-------------------------#
############################################################

    clear
    units          metal       #eV,atomic charge,angstroms,ps,kelvin,bars,g/mol
    dimension 3
    boundary p p p
    atom_style full
    #processors * * * grid numa
    read_data Li4OCl2.lammps
    group lithium type 1
    #replicate 2 2 2
    variable T1 equal 500
    variable Timer equal step*dt

############################################################
#---------- Pair styles and electrostatics--------------#
############################################################

    pair_style buck/coul/long 12.0
    pair_coeff * *  0.0 1.0 0.0
    pair_coeff 1 1  360.5269 0.1609 0
    pair_coeff 1 2  292.3 0.3472 0
```

```
pair_coeff 1 3  421.0366 0.33364 0
pair_coeff 2 2  22764.3 0.149 13.185
pair_coeff 2 3  8287 0.259 62.2
pair_coeff 3 3  1227.2 0.3214 14.53

#pair_style buck/coul/long 10.0
#pair_coeff * *  0.0 1.0 0.0
#pair_coeff 1 4  2088.79 0.346 23.25
#pair_coeff 2 4  1453.8 0.35 0
#pair_coeff 3 4  632.1018 0.2906 0
#pair_coeff 4 4  22764.3 0.149 27.869

kspace_style pppm 1e-05

############################################################
# ---------- Run Minimization ----------#
############################################################

reset_timestep 0
timestep 0.5
thermo 10
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000
############################################################
```

```
# ---------- Relax Cell ----------#
############################################################


    reset_timestep 0
    timestep 0.5
    fix 1 all box/relax aniso 1.0 vmax 0.003
    thermo 1
    thermo_style custom step enthalpy fmax lx ly lz vol press
    min_style cg
    minimize 1e-25 1e-25 5000 10000
    unfix 1


############################################################
# ---------- Run NPT T1----------#
############################################################


    reset_timestep 0
    timestep 0.002
    velocity all create ${T1} 4928459 rot yes dist gaussian
    fix            2 all npt temp ${T1} ${T1} 0.01 aniso 1.0 1.0 0.1
    thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
    thermo 1000
    run 2000
    unfix 2
```

```
reset_timestep 0
timestep 0.002
compute         mymsd lithium msd com yes
variable        msdx equal "c_mymsd[1]"
variable        msdy equal "c_mymsd[2]"
variable        msdz equal "c_mymsd[3]"
variable        msdtot equal "c_mymsd[4]"
fix             msdT1 lithium ave/time 1 1 10000 v_msdx v_msdy v_msdz v_msdtot
file msd${T1}
fix             3 all nvt temp ${T1} ${T1} 0.01
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
thermo 5000
#dump dynamics all xyz 100 dynamics.xyz
#dump 4 all atom 100 traj.dat
run             5000000
unfix 3
unfix msdT1
```

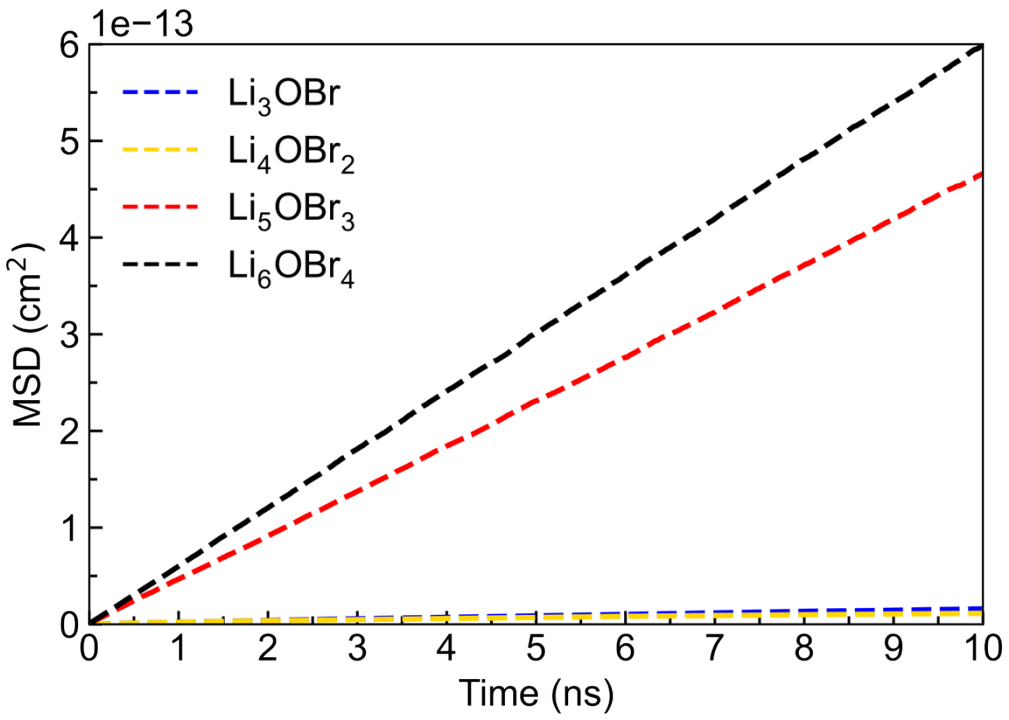

Figure S1. MSD plots for Li_xOBr_{x-2} (x = 3–6) anti-perovskites at 700 K with an alkali-halide partial Schottky defect concentration of ~2%.

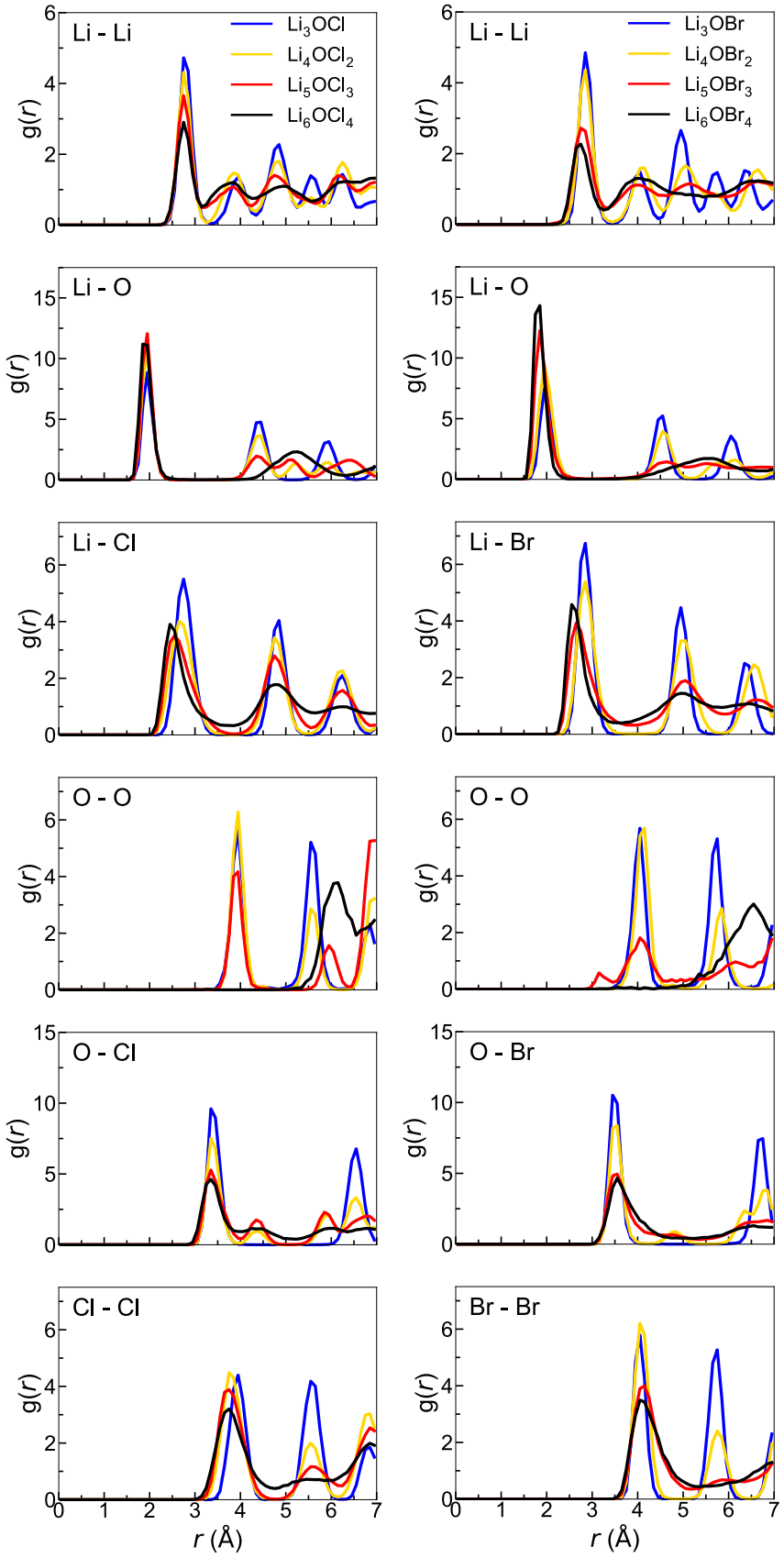

Figure S2. Radial distribution functions for Li_xOX_{x-2} (X = Cl (left) or Br (right); x = 3–6) anti-perovskites at 300 K.

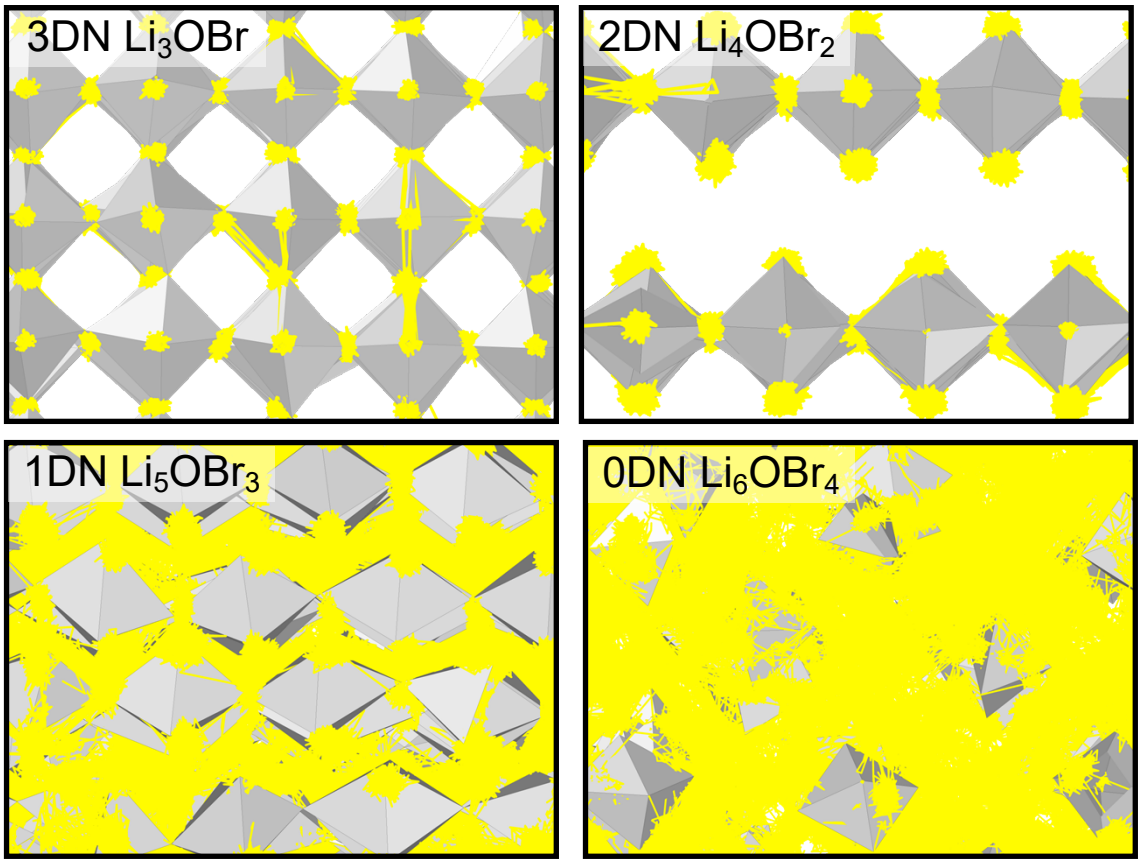

Figure S3. Diffusion density plots of Li ions (yellow) overlaid on OLi_6 (grey) octahedra in Li_xOBr_{x-2} (x = 3–6) anti-perovskites at 300 K. Br ions have been omitted for clarity.

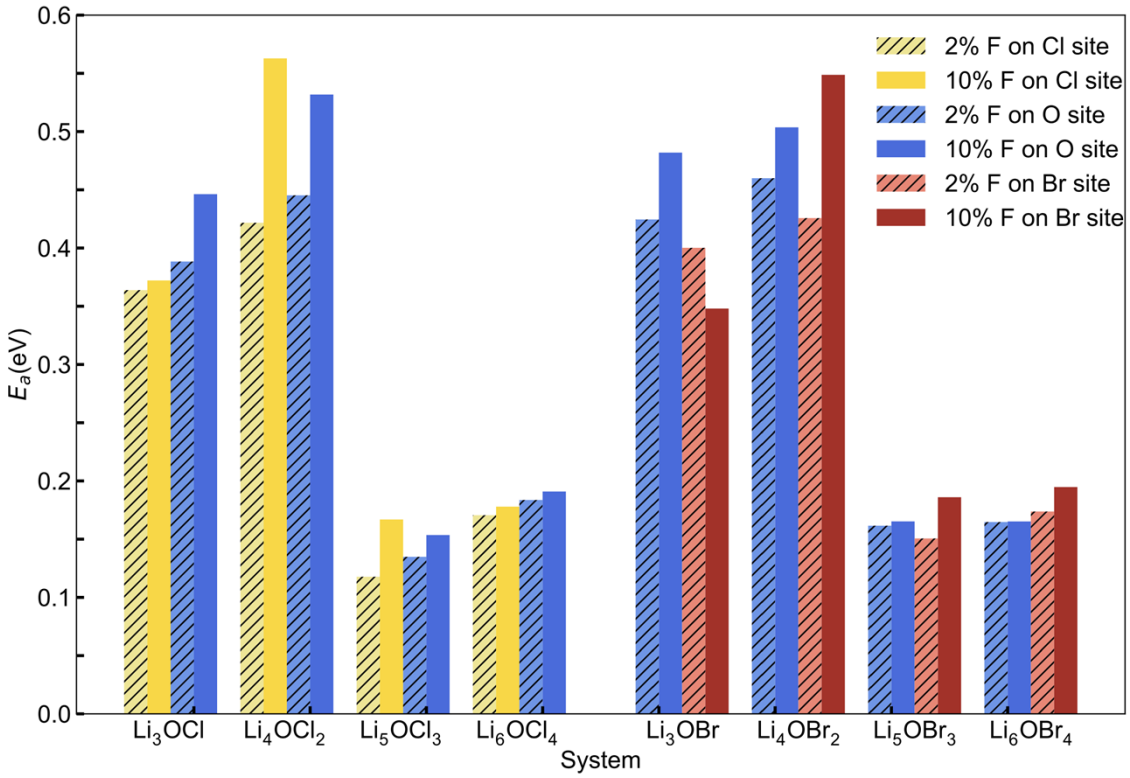

Figure S4. Comparison of activation energies (E_a) for Li-ion diffusion in 2% and 10% F-doped (a) Li_xOCl_{x-2} and (b) Li_xOBr_{x-2} (x = 3–6) anti-perovskites.