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Figure X. Potentials of mean force (PMF) for the formation of [PbX]+ and PbX2

complexes in DMF and in DMSO upon successive halide addition at 300 K.

The formation of lead halide perovskites starts with the formation of lead-halide prenucleation clusters in solution. We have characterized the initial steps in this process by calculating the potentials of mean force (PMFs) for the first two additions of halide ions to Pb2+ in both DMF and DMSO at 300 K. The resulting PMFs are shown in Figure X. All the potentials exhibit a broad outer minimum, a barrier, and a narrow inner minimum, where the halide is directly coordinated to Pb2+. The outer minima correspond to solvent separated states, whereas the barriers near 4.5 Å are due to displacement of solvent molecules from the inner coordination shell as the halides approach. The PMFs indicate a preference in both solvents for Pb2+ to form complexes with the halides in the order Cl– > Br– > I–. This is likely the reason why chloride-containing crystals initially form in the presence of MACl, despite the Br– and I– containing perovskites being thermodynamically more stable.

**Methods**

Potential of mean force calculations:

Molecular Dynamics (MD) simulations were performed using the AMOEBA polarizable force field with the OpenMM package.[A] Unaltered AMOEBA09 parameters were used for DMF, DMSO, Cl−, Br− and I−, while the Pb2+ parameters, developed and tested for solid perovskites and their precursors in solution, were taken from Ref. B. Initial equilibrations were performed in the NPT ensemble at 1 atm and 300 K using an Andersen thermostat and a Monte Carlo barostat with a leap-frog Verlet integrator with 1 fs timestep. The non-bonding cutoffs was set to 12 Å. Periodic Boundary Conditions and the Particle Mesh Ewald (PME) method were used. Mutual polarization was imposed with 10−5 tolerance.

Constrained MD simulations were used to calculate the potential of mean force (PMF) as a function of the lead-halide ion separation, using simulation boxes containing 500 solvent molecules (DMF or DMSO). Simulations were performed at Pb–X separations (in Angstroms) of 2.6–4.6 (in increments of 0.1), 4.8–6.8 (in increments of 0.2), 7.0–12.5 (in increments of 0.5), and 13–16 (in increments of 1). When adding the second halide ion, a loose harmonic spring [K = 1.2 (kcal/mol)/Å2] was used to keep the first ion bonded to lead, with the equilibrium bond lengths taken from crystallographic data; 3.12, 2.96 and 2.84 Å for Pb–I, Pb-Br and Pb–Cl, respectively. An NVT simulation of 2 ns was performed for each value of the reaction coordinate, with the last 1.2 ns used to calculate the PMF. The free energy difference, Δ*F*(*zs*), between a state where the halide ion is positioned at *zs* and a reference state where the halide ion is at *z*0 is given by Eq. (X), where *fz*(*z’s*) is the *z* component of the force exerted by the solvent and lead ion on the halide ion at the position *z’s*. The average forces at each step were then interpolated and integrated to obtain the PMF,[C]

(X)

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