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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 and references to be added