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Molecular Dynamics Simulation of Organohalide Perovskite Precursors: solvent effects in the formation of Perovskite solar cells - Electronic Suplementary Information (ESI)

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Table S1. Lennard Jones parameters and point charges for all species.*

Atom types	Epsilon (kJ/mol)	Sigma (nm)	Charge (*e*)
Precursors			
C_$MeNH_3$	0.45773	0.3399	-0.160
N_$MeNH_3$	0.71128	0.325	-0.340
H_C_$MeNH_3$	0.06569	0.1959	0.156
H_N_$MeNH_3$	0.06569	0.1069	0.344
Pb^{++}	0.2394	0.3132*	2.0
I^-	0.4080	0.540*	-1.0
Solvents			
O_water	0.6489	0.3166	-0.8476
H_water	-	-	0.4238
CH_3_pentane	0.8149	0.375	0.0
CH_2_pentane	0.3825	0.395	0.0

* Sigma parameters were modified in some simulations to reproduce the correct crystall estructure of the perosvkite

Table S2. Diffusion coefficient and model parameters of precursors and solvents used in this work. These values were obtained between 10^3 and 2 10^3 ps.

#Precursors	Diffusion Coefficient (m^2/s)	α	Diffusion Coefficient (m^2/s)	α
Solvent	pentane		water	
10	$4.17 10^{-3}$	0.95	$1.13 10^{-3}$	0.98
20	$2.60 10^{-3}$	0.97	$1.05 10^{-3}$	0.97
30	$1.31 10^{-3}$	0.94	$9.06 10^{-4}$	0.97
40	$6.27 10^{-4}$	0.92		
50	$2.47 10^{-4}$	0.89		
$[CH_3NH_3]^+$				
10	$2.54 10^{-4}$	0.80	$8.42 10^{-4}$	0.97
20	$6.80 10^{-5}$	0.95	$6.77 10^{-4}$	0.971
30	$1.53 10^{-5}$	0.74	$5.38 10^{-4}$	0.93
40	$8.88 10^{-6}$	0.72		
50	$2.89 10^{-6}$	0.49		
I^-				
10	$2.31 10^{-4}$	0.84	$7.72 10^{-4}$	1.00
20	$6.64 10^{-5}$	0.98	$6.20 10^{-4}$	0.96
30	$1.51 10^{-5}$	0.85	$4.28 10^{-4}$	0.99
40	$7.53 10^{-6}$	0.80		
50	$1.63 10^{-6}$	0.58		
Pb^{++}				
10	$2.22 10^{-4}$	0.88	$2.54 10^{-4}$	0.87
20	$6.53 10^{-5}$	0.99	$2.61 10^{-4}$	0.99
30	$1.50 10^{-5}$	0.89	$2.01 10^{-4}$	0.94
40	$6.63 10^{-6}$	0.81		
50	$1.40 10^{-6}$	0.63		

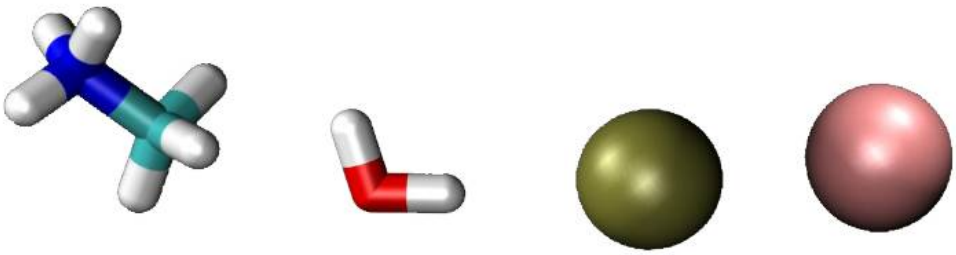


Figure S1. Molecular models used in this work. The key color for atoms is: I pink, Pb tan, C cyan, N blue, and H white.

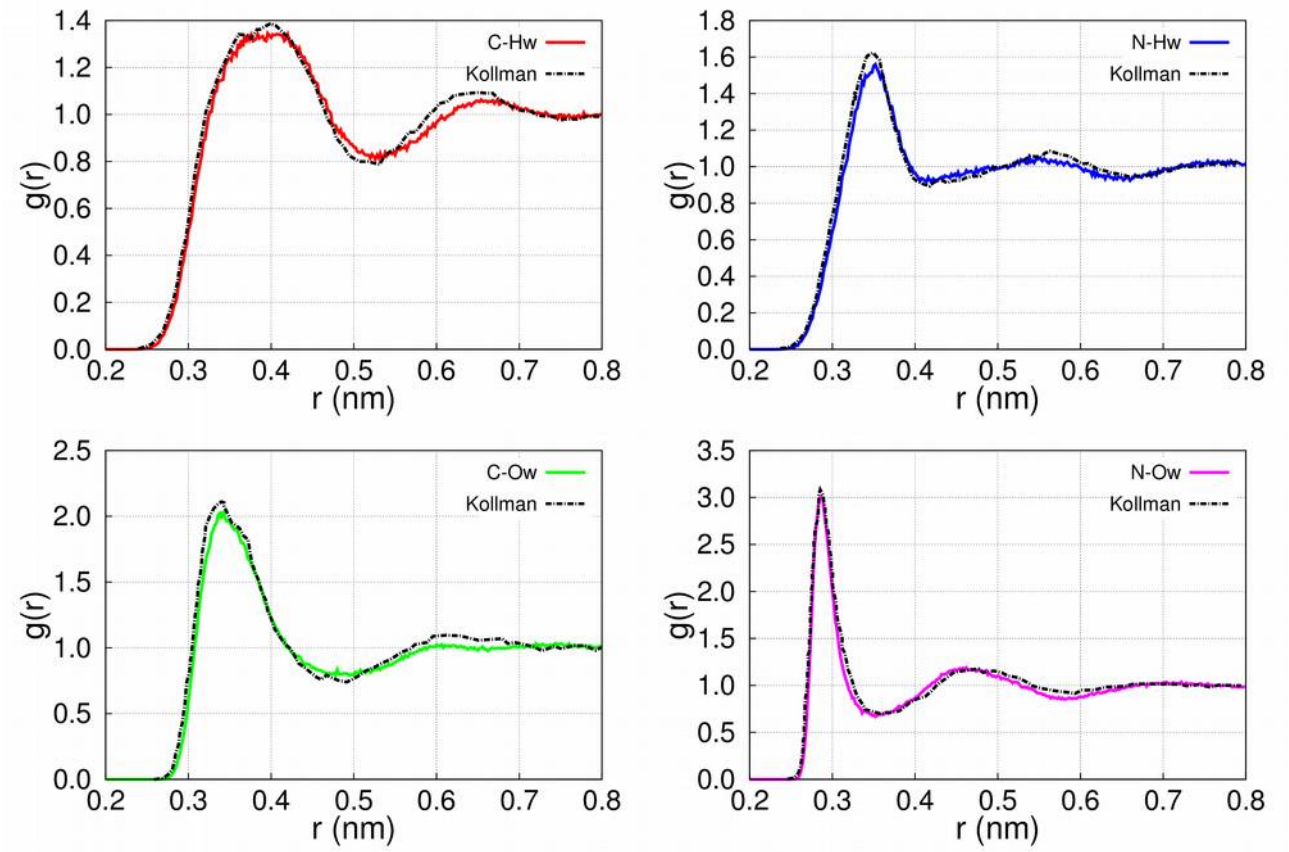


Figure S2. Radial distribution functions as obtained from MD simulations in the NVT ensemble for CH_3NH_3I precursors in water (from left-top to right-bottom: carbon-water hydrogen, nitrogen-water hydrogen, carbon-water oxygen and nitrogen-water oxygen). Results from this work (solid color line) are compared with the data of Meng and Kollman.[1]

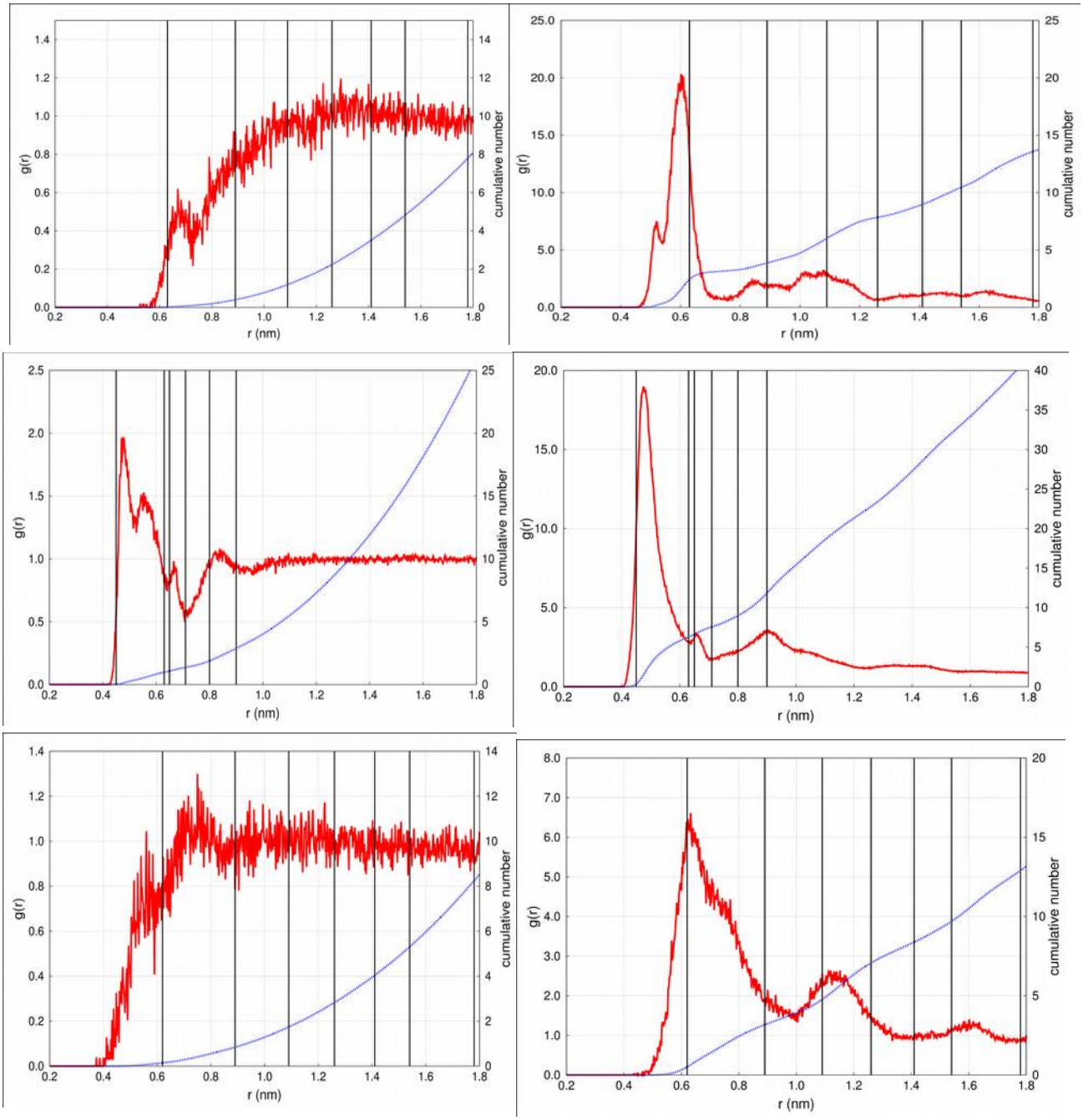
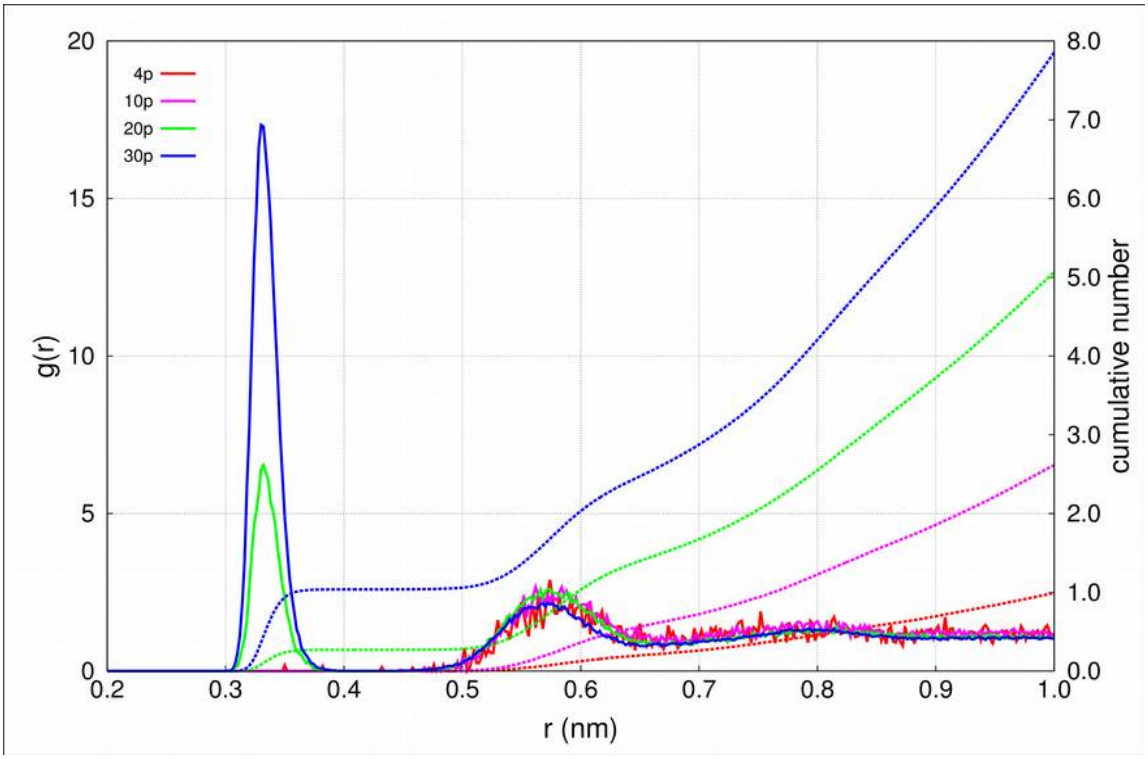


Figure S3. RDFs (red line) and coordination number (blue dotted line) for Pb++-Pb++ (top), I--I- (center), and [CH3NH3]+ (bottom) extracted from equilibrated MD simulations with 20 CH3NH3PbI3 precursors in water (left) and in pentane (right). Vertical lines stand for the crystallographic positions of solid CH3NH3PbI3 as extracted from Ref.[2]



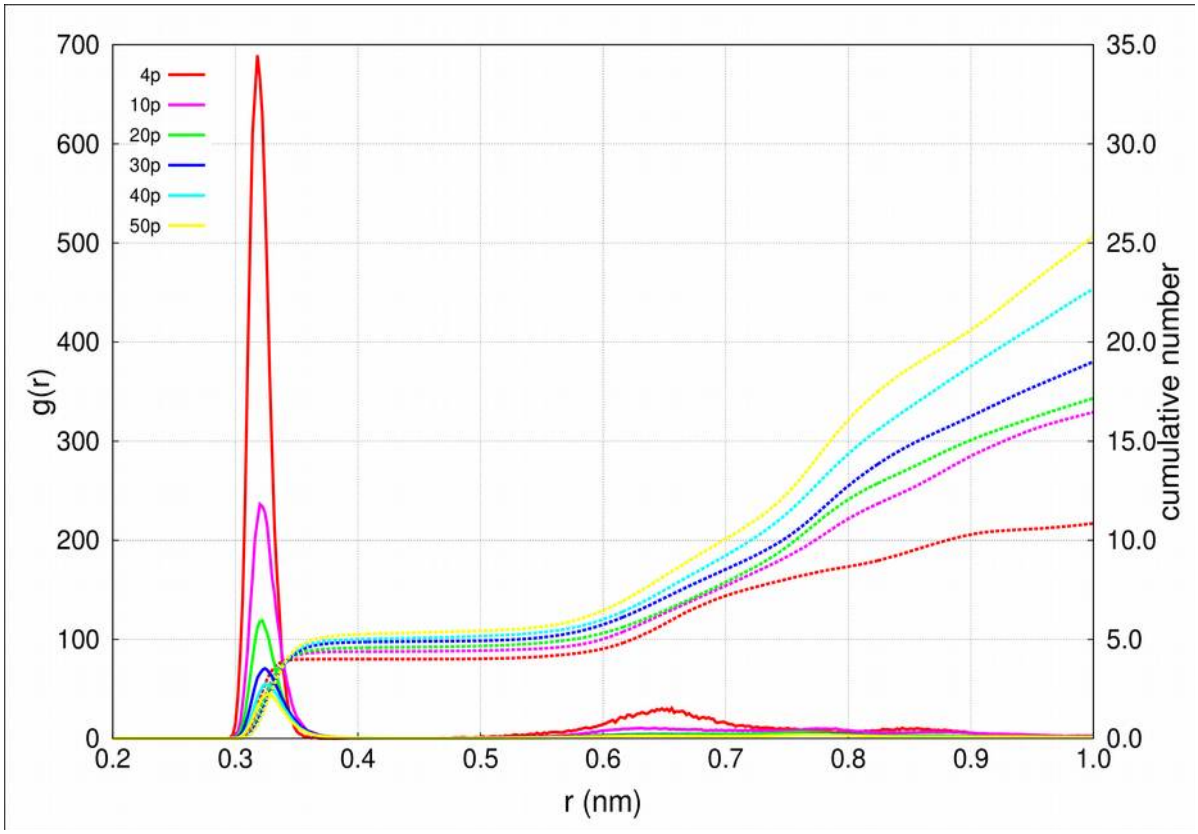


Figure S4. Pb^{++}-I^{-} RDFs (solid line) and coordination number (dotted line) for different number of precursor units in water (top) and in pentane (bottom).

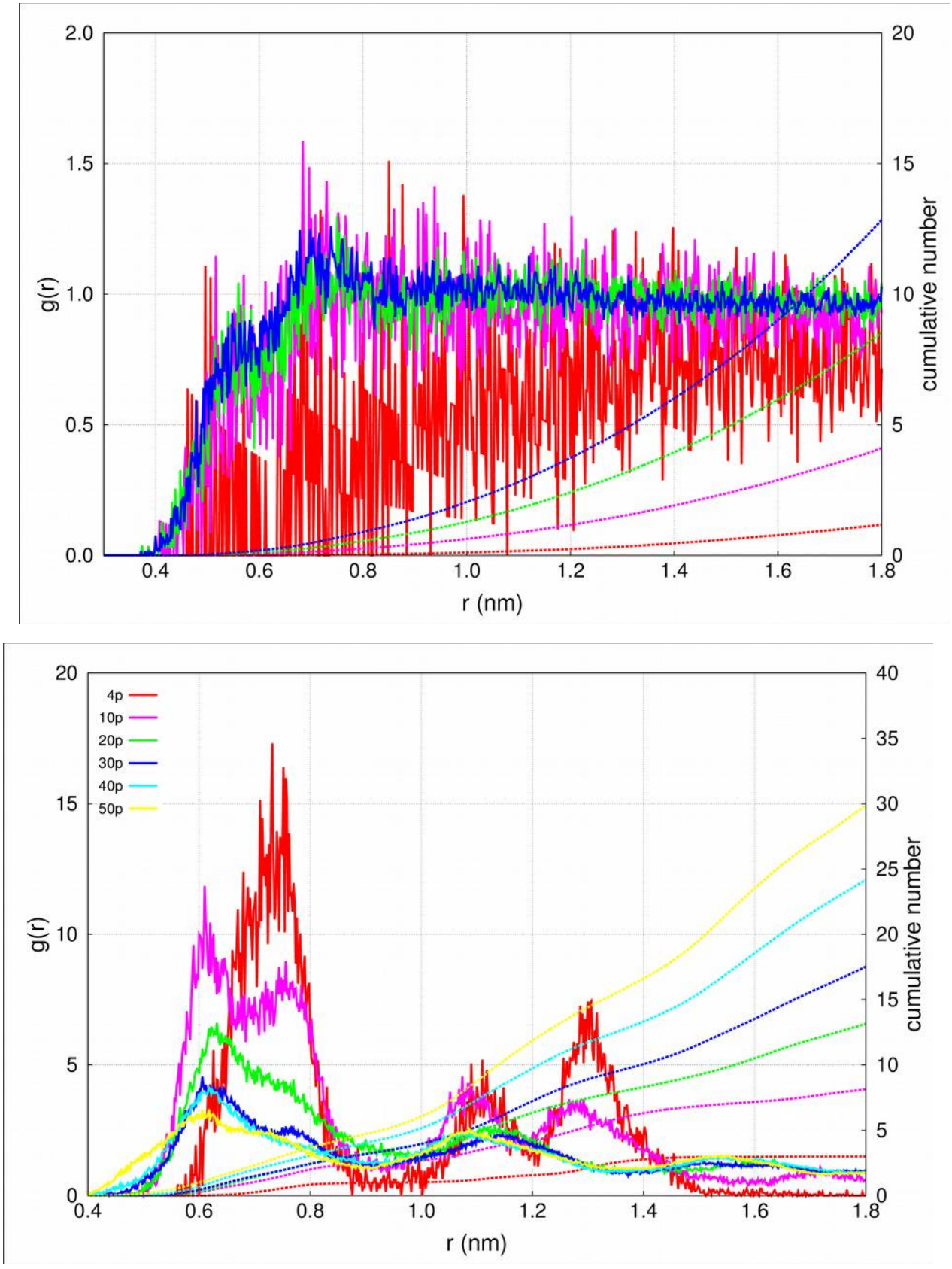


Figure S5. $[CH_3NH_3]^+$-$[CH_3NH_3]^+$ RDFs (solid line) and coordination number (dotted line) for different number of precursor units in water (top) and in pentane (bottom).

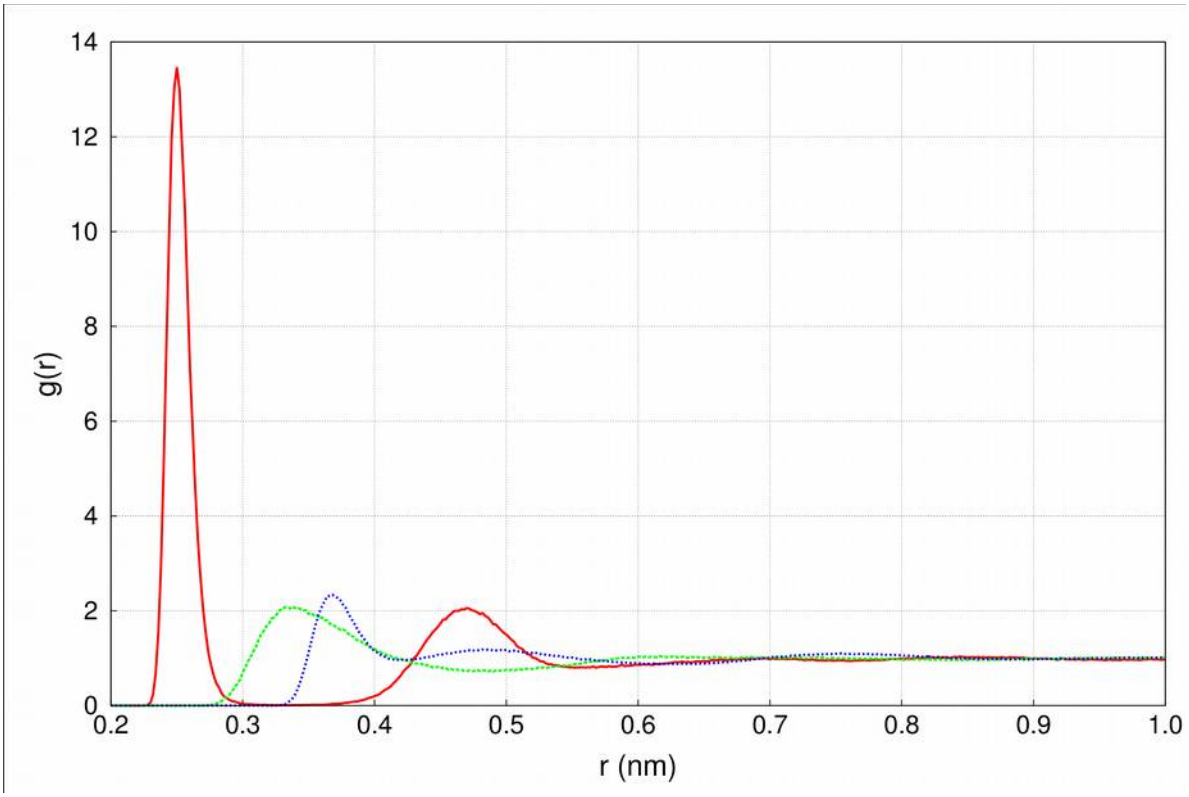


Figure S6. RDFs of Pb^{++}-O_{wate}r (red line), $[CH_3NH_3]^+$-O_{water} (gren line), and I^--O_{water} (blue line), from simulations with 20 $CH_3NH_3PbI_3$ precursors in water.

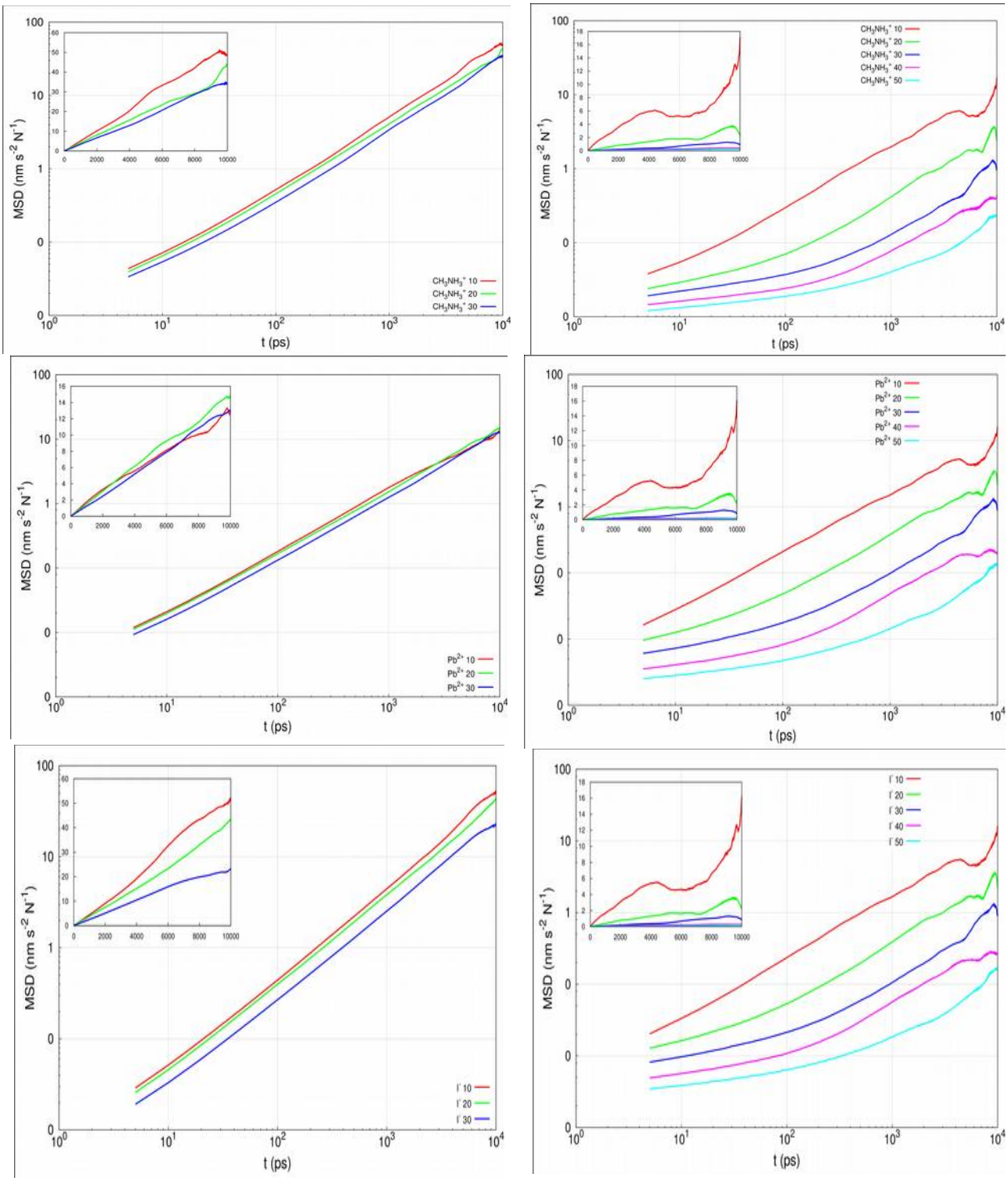


Figure S7. MSDs of $[CH_3NH_3]^+$ (top), Pb^{++} (center), and I^- (bottom) from MD simulations as a function of the number of precursors for water (left) and pentane (right).

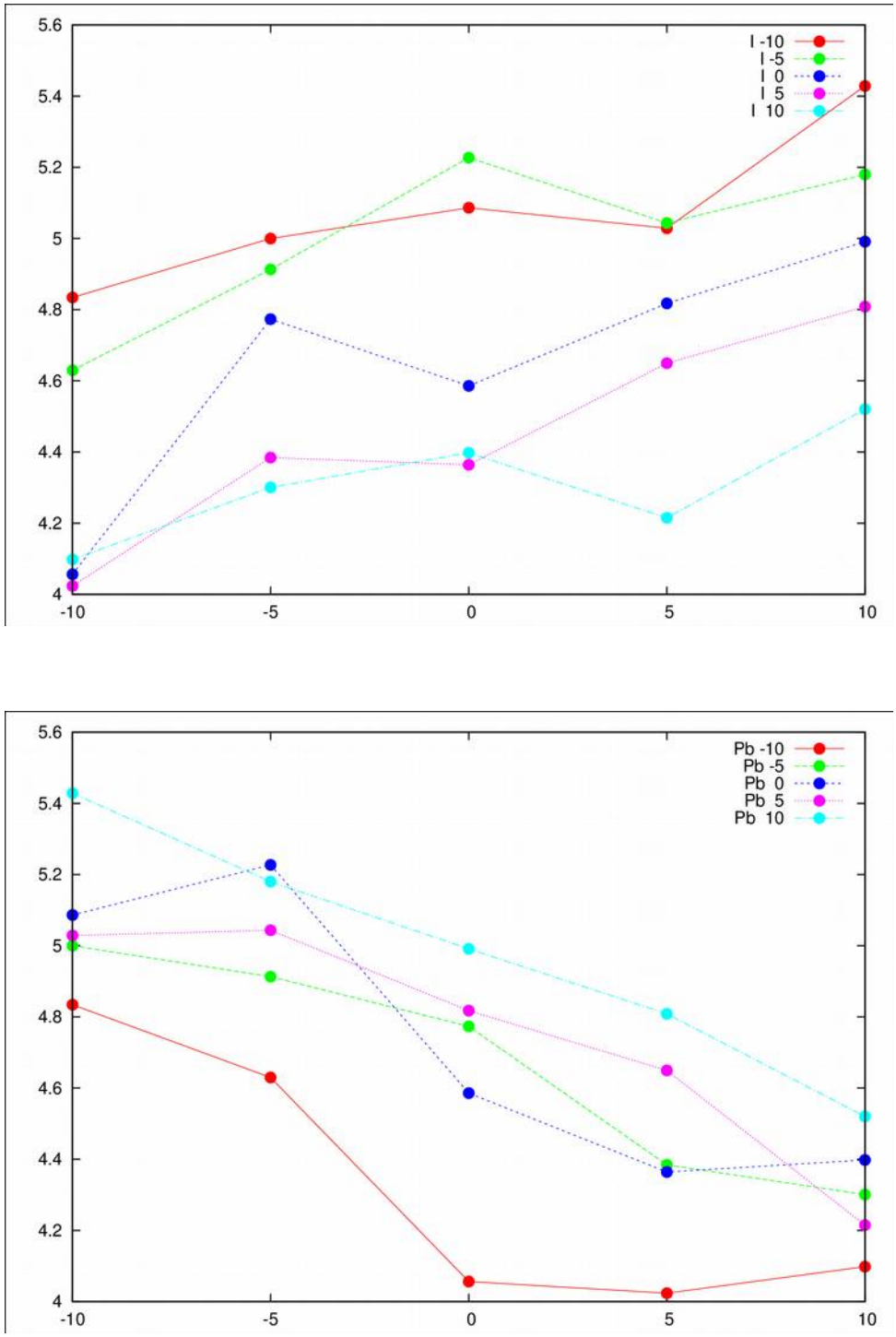


Figure S8. Pb-I coordination number as a function of the percentage variation of the σ-parameter of Pb (top) and I (bottom) keeping the other parameter fixed.

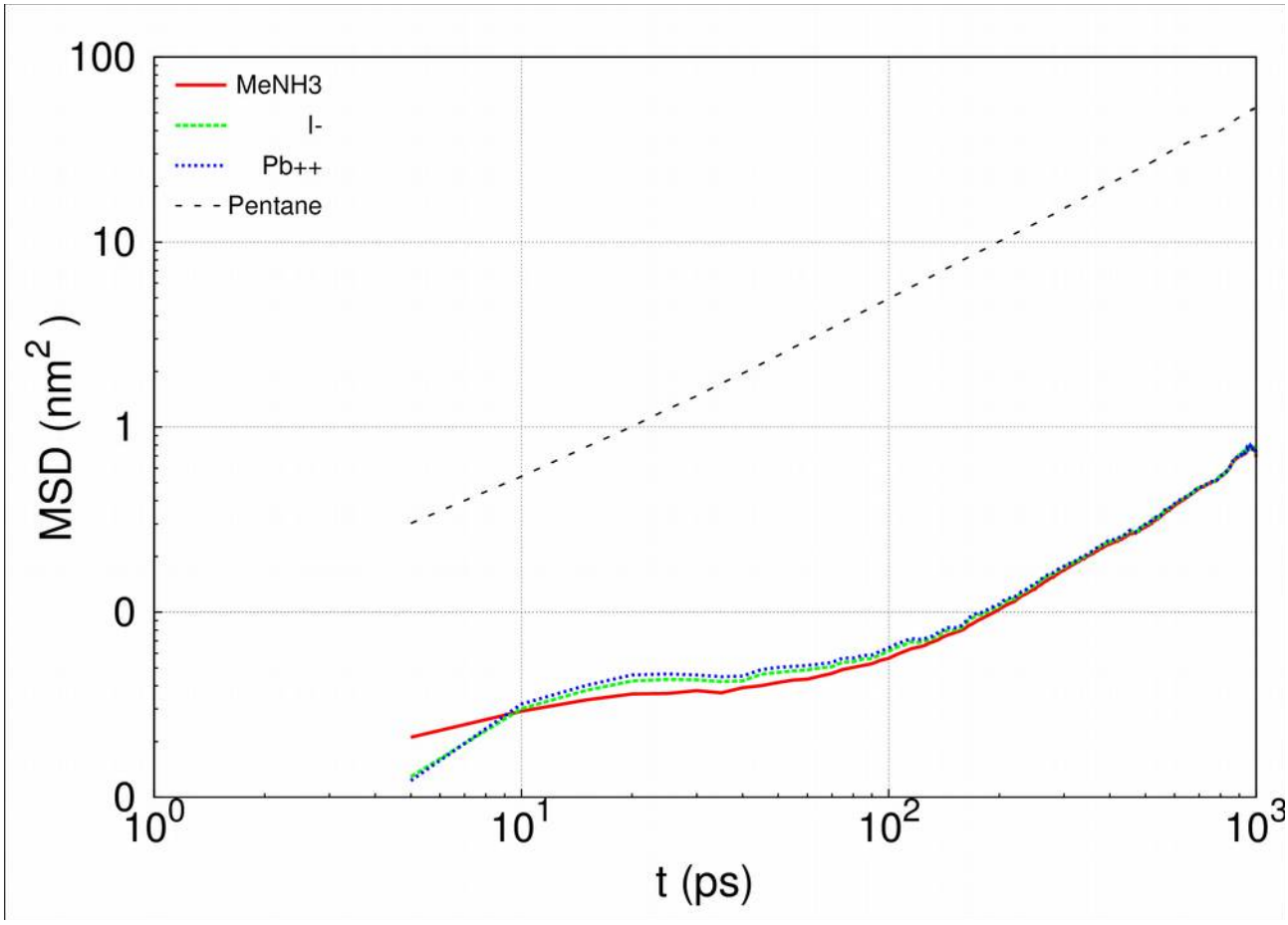


Figure S9. MSDs from the MD of the solid in the presence of pentante molecules.

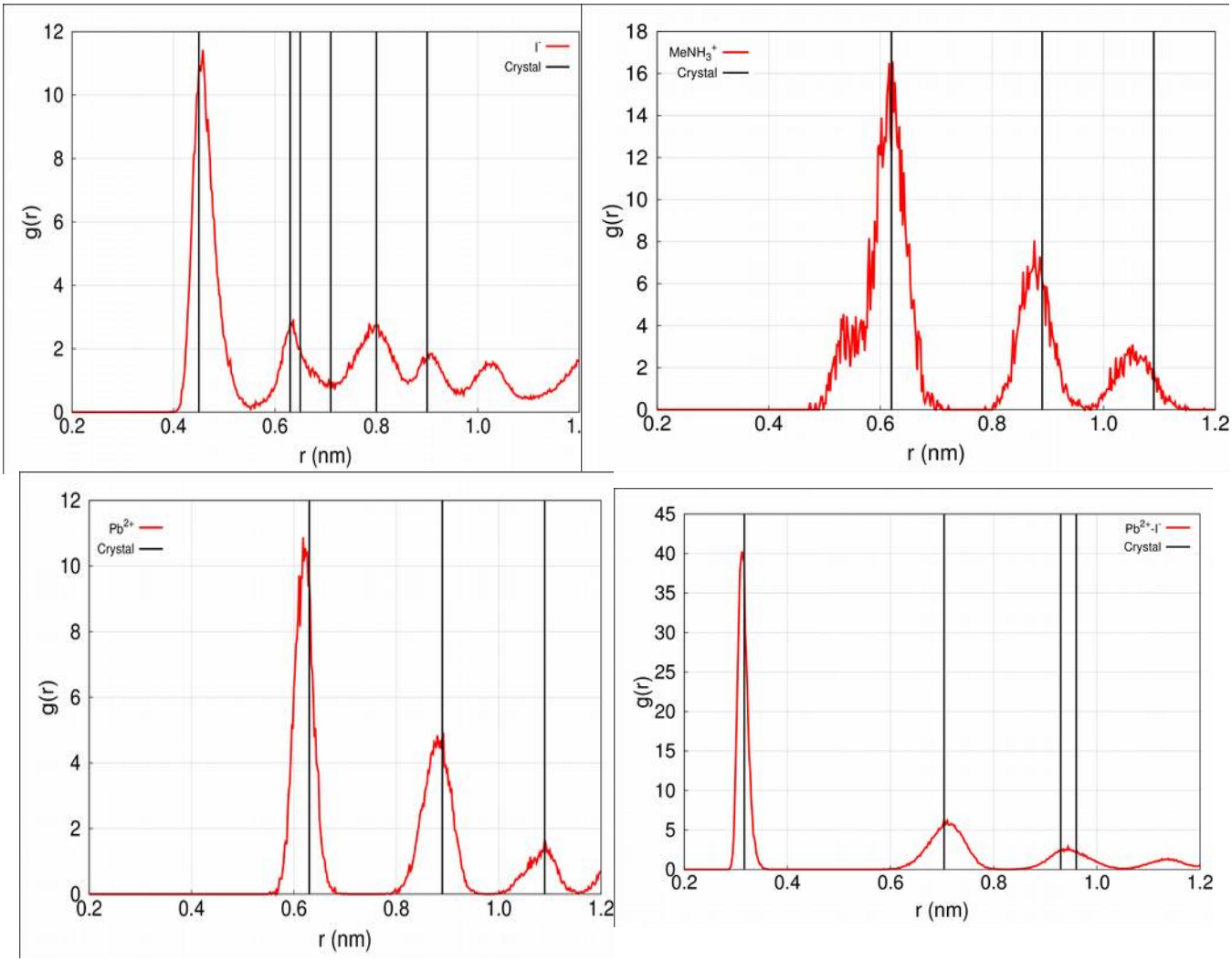


Figure S10. RDF extracted from simulations of the solid-perovskite in the presence of pentane molecules

References

(1) Meng, E. C.; Kollman, P. A. Molecular Dynamics Studies of the Properties of Water around Simple Organic Solutes. *J. Phys. Chem.* **1996**, *100* (27), 11460–11470.

(2) Dang, Y.; Liu, Y.; Sun, Y.; Yuan, D.; Liu, X.; Lu, W.; Liu, G.; Xia, H.; Tao, X. Bulk Crystal Growth of Hybrid Perovskite Material CH3NH3PbI3. *CrystEngComm* **2014**, *17* (3), 665–670.