Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Close examination of the structure and dynamics of $HC(NH_2)_2PbI_3$ by MD simulations and group theory

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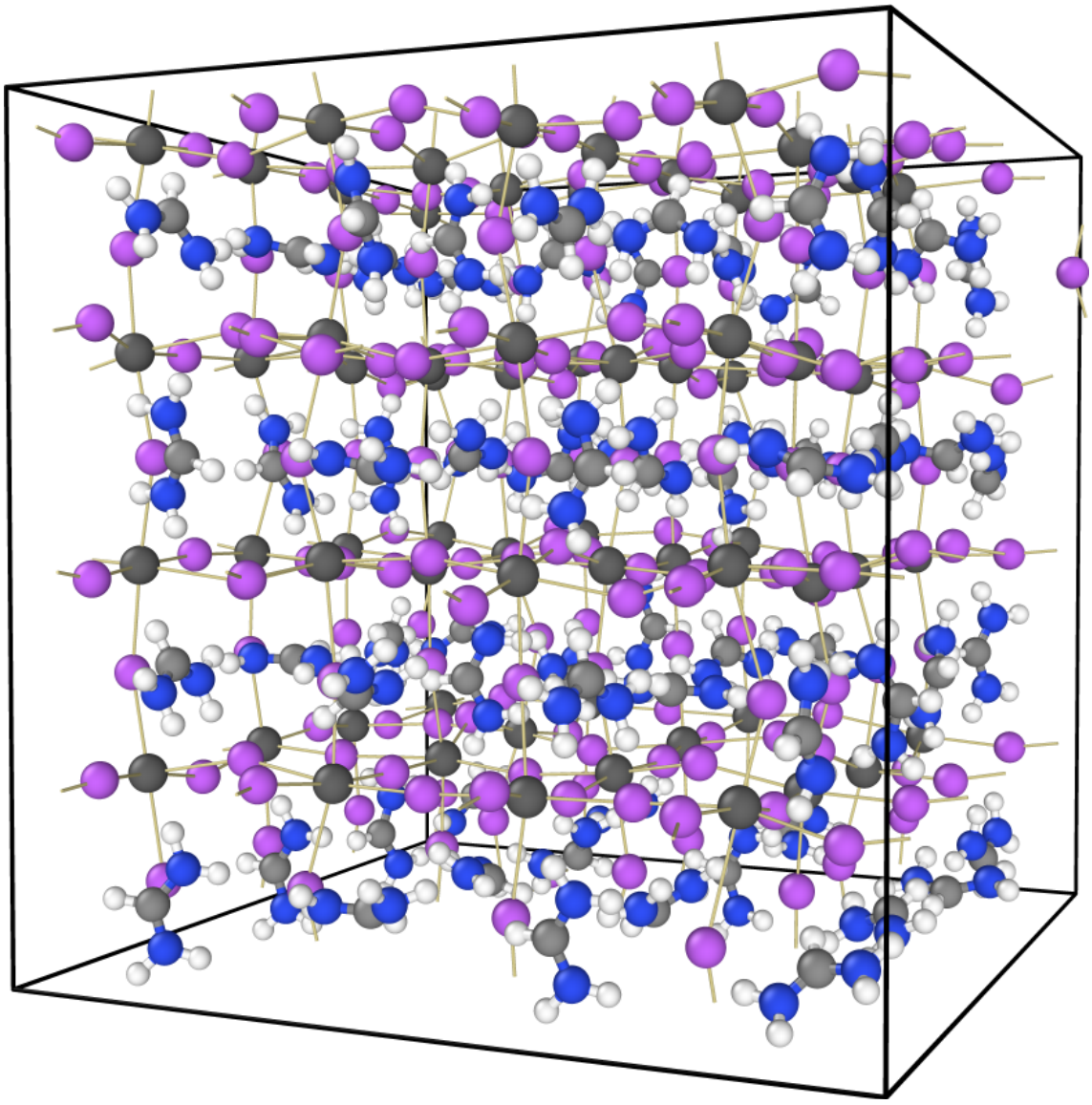
Supporting Information



Rendering of the supercell corresponding to the simulation of the 444 system at 300 K, for t=50.7 ps. The thin pale lines display the Pb-I bonds to facilitate the understanding of the overall structure.

SYSTEM 444, 300 K

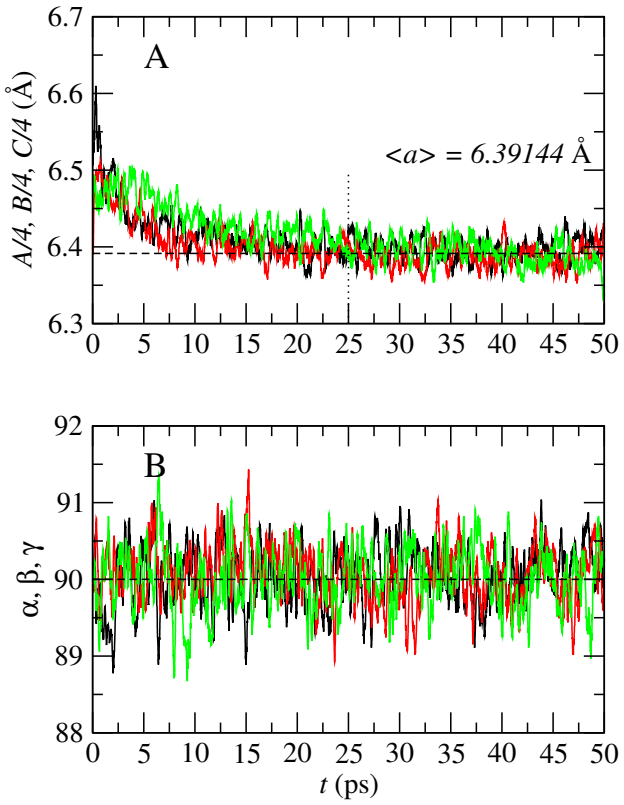


Figure S1
Time evolution of the cell box lengths (A) and cell angles (B) from the first principles MD simulation of FAPI at **T=300 K**. The curves are actually running averages over 100 points and each point is registered every 1 fs. The cell lengths are divided by 4 in order to represent the lattice constants. The dashed horizontal line in black in panel A is calculated by taking the cubic root of the volume averaged in the lapse that goes from 25 ps to 50 ps, which then results in an average lattice parameter for the cubic cell of <*a*> = 6.39144 Å.

Average supercell parameters calculated for the interval [25,50] ps. All lengths in Å

```
AX     =  25.583796016097363
AY     =  -3.1977746112904520E-002
AZ     =   6.3049604326348915E-002
BX     =   1.3993368675381215E-002
BY     =  25.550948993404027
BZ     =  -2.9383099599535063E-002
CX     =  -6.9101855250702698E-002
CY     =  -1.0196078077670988E-002
CZ     =  25.564264115623978

VOL               =   16710.021694296240
VOL**(1./3.)      =      25.565779949477143
```

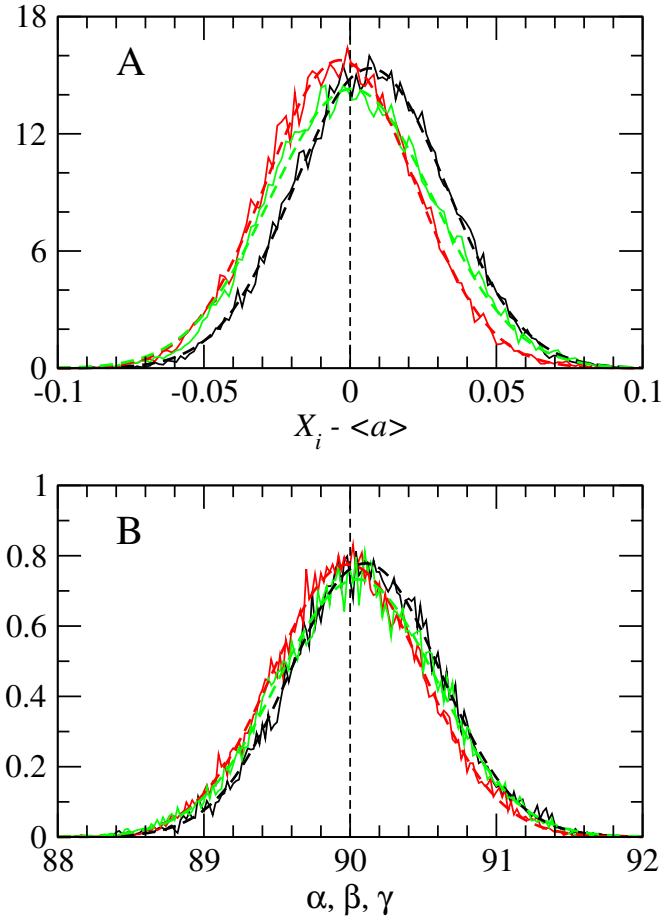


Figure S2
Histograms corresponding to the cell dimensions (A) and cell angles (B) from the first principles MD simulation of FAPI at **T=300 K**. The histograms are calculated taking every frame from 25 ps to 50 ps. The dashed lines are fits with a normal distribution. For panel A, <*a*> = 6.39144 Å.

Cell Dimensions:

```
Fitting formula:
y = 1/sqrt(2*3.14159)/A1*exp(-((x-A0)^2)/(2*A1^2))
Tolerance = 1e-05

A:
Computed values:
     A0 = 0.00691737
     A1 = 0.0259778
Chi-square: 17.4181
Correlation coefficient: 0.998318
Theil U coefficient: 0.0487635
```

B:
Computed values:
     A0 = 0.00691737
     A1 = 0.0259778
Chi-square: 17.4181
Correlation coefficient: 0.998318
Theil U coefficient: 0.0487635

C:
Computed values:
     A0 = 0.000503465
     A1 = 0.0278935
Chi-square: 23.5542
Correlation coefficient: 0.997488
Theil U coefficient: 0.0586736

Angles:

alpha:
Computed values:
     A0 = 90.1038
     A1 = 0.512617
Chi-square: 0.112141
Correlation coefficient: 0.996805
Theil U coefficient: 0.0638638

beta:
Computed values:
     A0 = 89.9859
     A1 = 0.514745
Chi-square: 0.0870482
Correlation coefficient: 0.997509
Theil U coefficient: 0.0563111

gamma:
Computed values:
     A0 = 90.0504
     A1 = 0.54451
Chi-square: 0.129474
Correlation coefficient: 0.996000
Theil U coefficient: 0.0703622

SYSTEM 444, 450 K

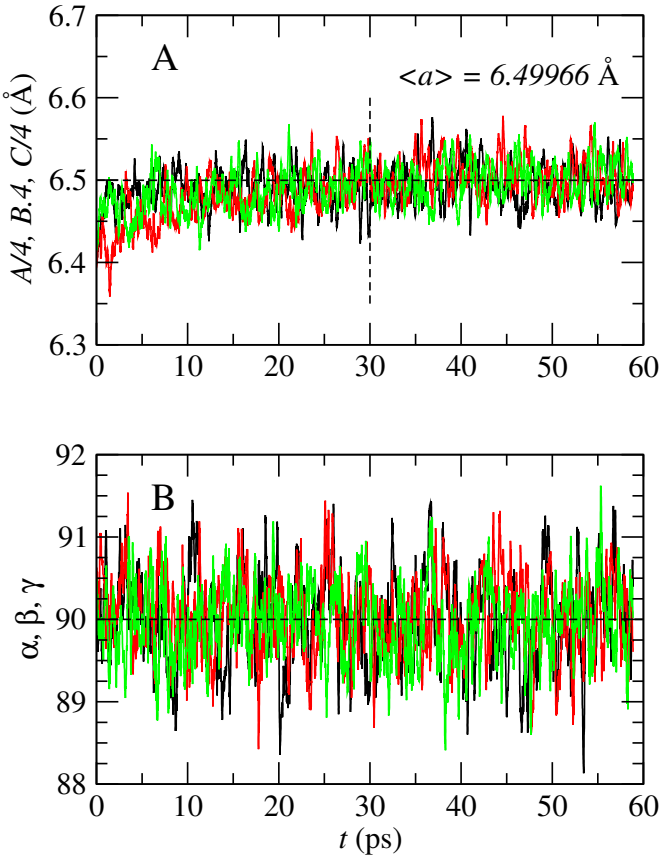


Figure S3
Time evolution of the cell box lengths (A) and cell angles (B) from the first principles MD simulation of FAPI at **T=450 K**. The curves are actually running averages over 100 points and each point is registered every 1 fs. The cell lengths are divided by 4 in order to represent the lattice constants. The dashed horizontal line in black in panel A is calculated by taking the cubic root of the volume averaged in the lapse that goes from 30 ps to 58.9 ps, which then results in an average lattice parameter for the cubic cell of $\langle a \rangle$ = 6.49966 Å.

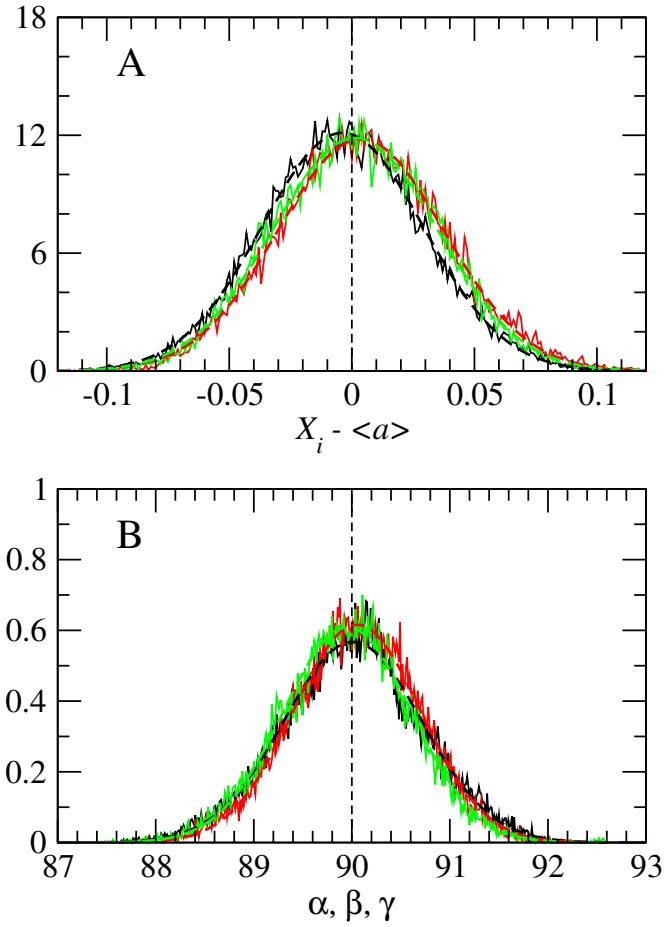


Figure S4
Histograms corresponding to the cell dimensions (A) and cell angles (B) from the first principles MD simulation of FAPI at **T=450 K**. The histograms are calculated taking every frame from 230 ps to 58.9 ps. The dashed lines are fits with a normal distribution. For panel A, <*a*> = 6.39144 Å.

Cell Dimensions:

```
Fitting formula:
y = 1/sqrt(2*3.14159)/A1*exp(-((x-A0)^2)/(2*A1^2))
Tolerance = 1e-05

A:
Computed values:
     A0 = -0.00379283
     A1 = 0.0329111
Chi-square: 33.8019
Correlation coefficient: 0.997231
Theil U coefficient: 0.0626726
```

B:
Computed values:
A0 = 0.00363547
A1 = 0.0337745

Chi-square: 41.2574
Correlation coefficient: 0.996508
Theil U coefficient: 0.0700441

C:
Computed values:
A0 = 0.00139695
A1 = 0.0336066

Chi-square: 51.4399
Correlation coefficient: 0.995783
Theil U coefficient: 0.077564

Angles:

alpha:
Computed values:
A0 = 90.0101
A1 = 0.70345

Chi-square: 0.34543
Correlation coefficient: 0.991168
Theil U coefficient: 0.101673

beta:
Computed values:
A0 = 90.0527
A1 = 0.647799

Chi-square: 0.256629
Correlation coefficient: 0.994359
Theil U coefficient: 0.0836695

gamma:
Computed values:
A0 = 89.9542
A1 = 0.655574

Chi-square: 0.302291
Correlation coefficient: 0.993144
Theil U coefficient: 0.0917068

SYSTEM 222, 300 K

In order to check the stability of our model system with respect to system size we performed two simulations based on the 96 atoms, 222 system.
In the first case, the setting were exactly the same as in the NPT_F simulations of the system 444. The magnitude of the fluctuations makes are excessively large to perform any meaningful analysis.
In the second case we restricted the supercell fluctuations to isotropic expansions and/ or contractions by using the NPT_I keyword in the CP2K input. In this case the model behaves in a more stable way, although showing very large fluctuation resulting directly from the small number of atoms in the system. The summation was extended for a total of 24 ps.
The average lattice parameter resulting from averaging last 10 ps of simulation is <a>=6.6145 Å, which is 3.5 % larger than the value obtained with the 444 system under NPT_F conditions. The inspection of the radial distribution functions is interesting in order to further asses the importance of the system size and the resulting fluctuation affecting the local organization.

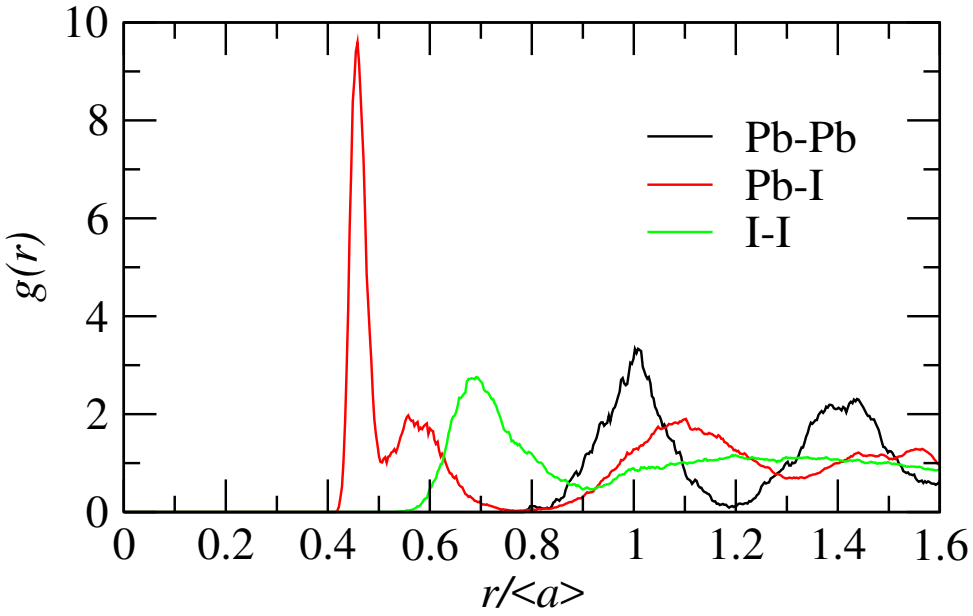


Figure S5
Radial distribution function for the atoms pairs forming the inorganic framework of the FAPI obtained from NPT_I simulations on a 222 system at 300 K.

Average relaxation of r+ and r-. SYSTEM 444, 300 K and 450 K. Fits.

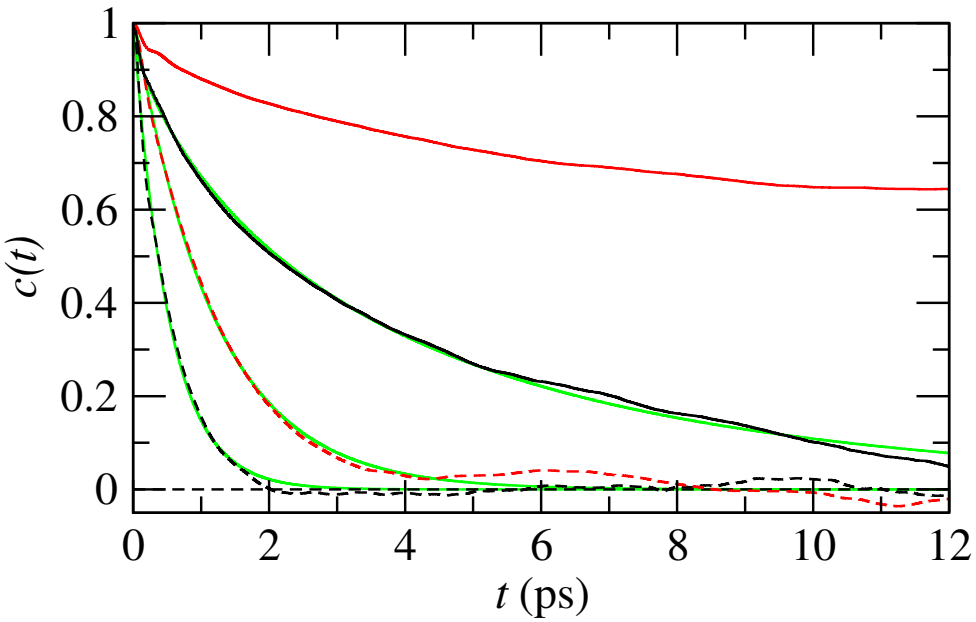


Figure S6
Time dependent self correlation function for r+ (black lines) and r- (red lines) at 300 K (solid lines) and 450 K (dashed lines). The green lines are fits as described below.

r+, 450 K

```
Fitting with formula: y = A0*exp(-x/A1)
Tolerance = 1e-05
Computed values:
     a0 = 1.0048
     a1 = 0.521643

Chi-square: 1.92515
Correlation coefficient: 0.996082
RMS relative error: 7.42554
Theil U coefficient: 0.0851113
```

r-, 450 K

```
Fitting with formula: y = A0*exp(-x/A1)
Tolerance = 1e-05
Computed values:
     a0 = 1.02171
     a1 = 1.1698

Chi-square: 4.08357
Correlation coefficient: 0.996016
RMS relative error: 1.40925
Theil U coefficient: 0.0814744
```

r+, 300 K

```
Fitting with formula: y = A0*exp(-(x/A1)^A2)
Computed values:
      a0 = 0.97758
      a1 = 3.57843
      a2 = 0.765959

Chi-square: 1.93498
Correlation coefficient: 0.998353
RMS relative error: 0.181207
Theil U coefficient: 0.0347234
```

Relaxation of individual molecules, r+, 300 K, System 444.

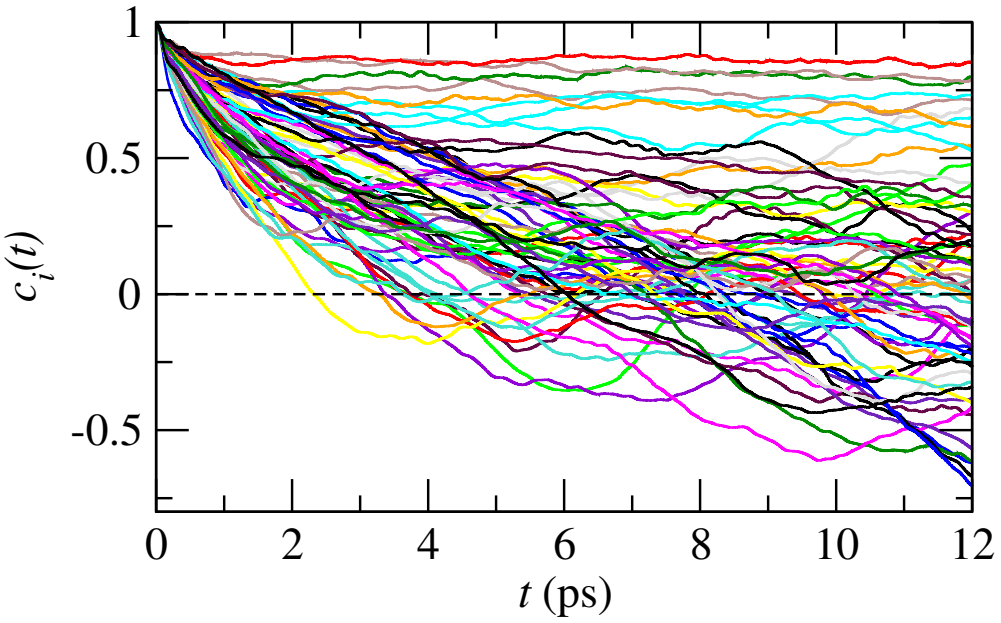


Figure S7
The relaxation of the individual FA molecules, as displayed by the r+ vector, shows heterogeneity in the same way that the MA does, for 300 K.

Coefficients of fitting r+ colormap at 300 and 450 K using cubic harmonics. System 444.

(i)	300 K C_i	400 K C_i
4	0.898123	0.157817
6	0.307109	0.015817
8	0.399998	0.041476
10	0.130961	0.005785
12	0.045936	0.008149

COUPLING BETWEEN MOLECULAR ORIENTATIONS AND LATTICE DISTORTIONS

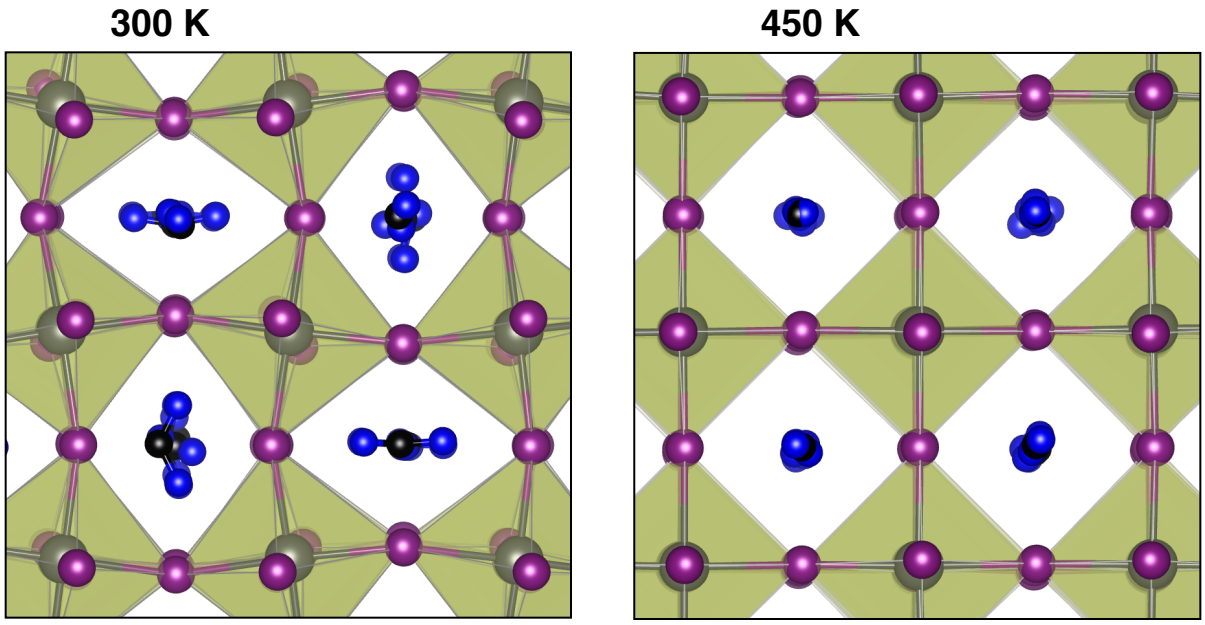


Figure S8
Qualitative assessment of the interplay between the deformations of the inorganic cage and the orientation of the molecules. This figure was done by taking the average position, over the whole production run, of the N and C atoms of the molecules. For 300 K, since the rotational dynamics is slow, the average results in configurations that roughly retain the molecular architecture. For the case corresponding to 450 K, since the rotational dynamic is fast, the average position of the atoms are all located approximately in the center of the inorganic cage. The figure displays a section of the system 444 at both temperatures. The molecules are in average oriented parallel to the long axis of the cavities at 300 K, but no particular correlation is observed at 450 K.