Supporting Information for:

Localized High Concentrated Electrolyte and its Effects on Polysulfide Structure in Solution

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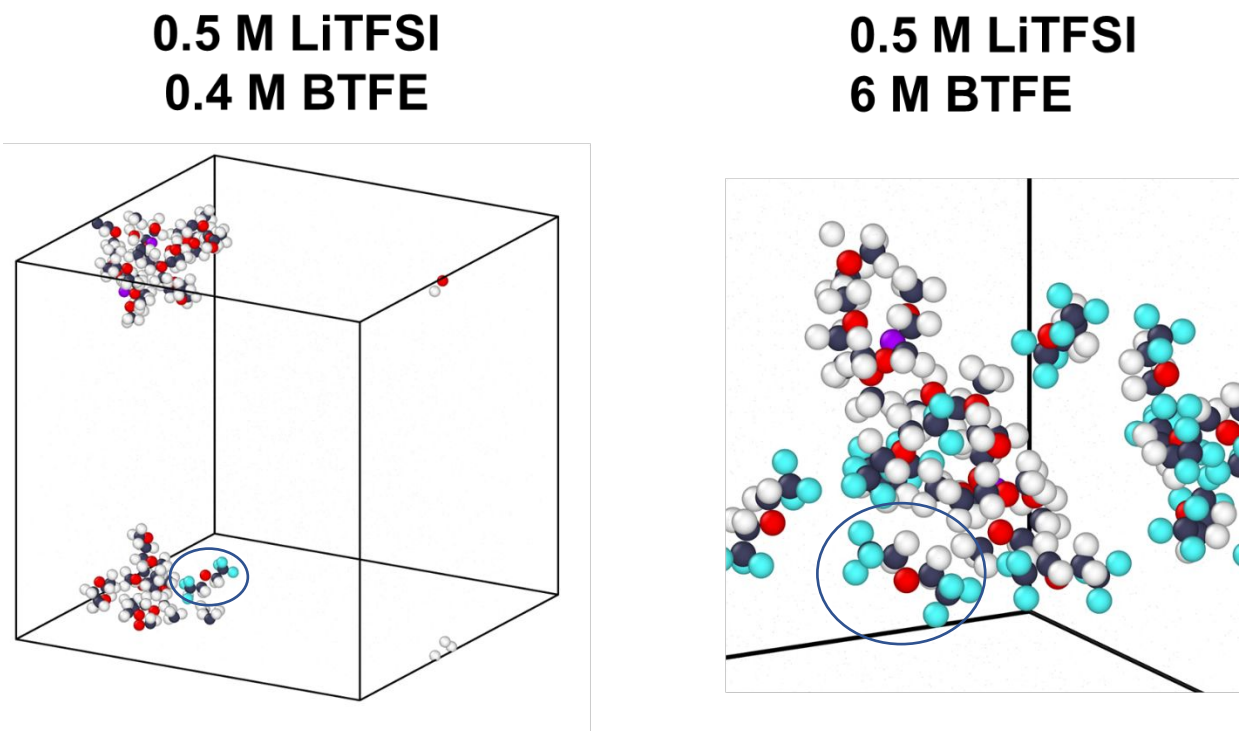

Figure S1 : Snapshot of example Li solvation shell for low and high concentration with 0.5 M LiTFSI concentration. Color code: Li: purple, O: red; C: black; H: white, F: turquoise. The BTFE molecule is encircled to show structure.

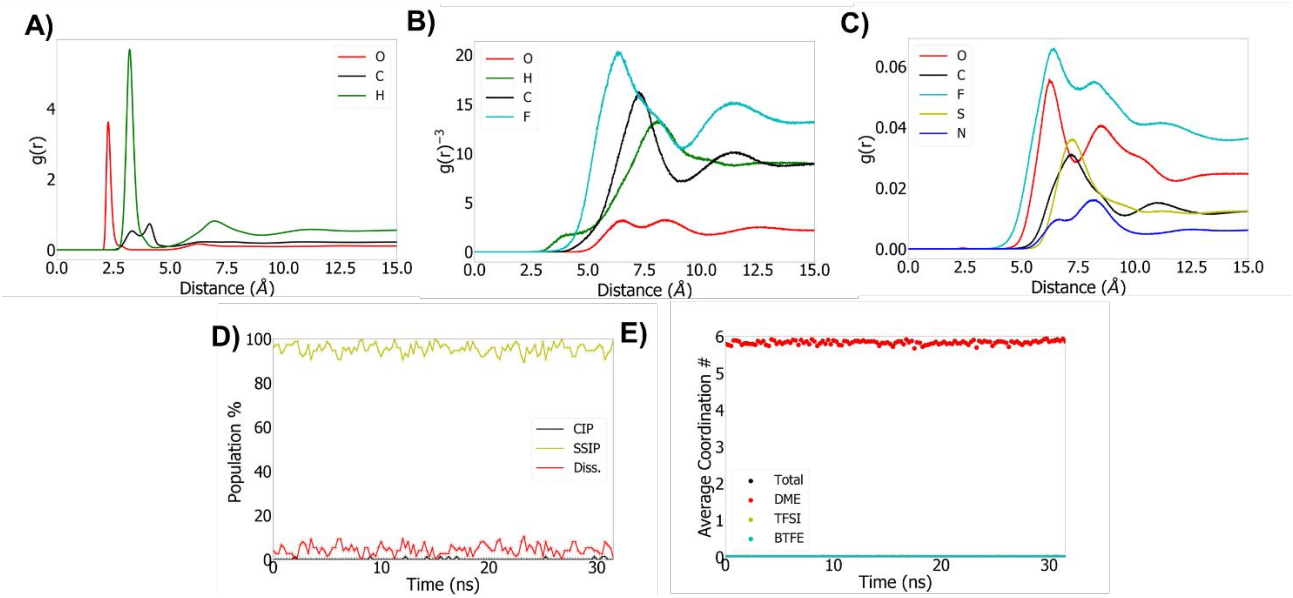

Figure S2: Structural analysis of 1.0 M LiTFSI with low BTFE concentration Radial distribution functions for A) Li-DME B) Li-BTFE C) Li-TFSI. D) Population % of Li-TFSI ionic association as as a function of time. E) Average Li-O coordination number throughout simulation

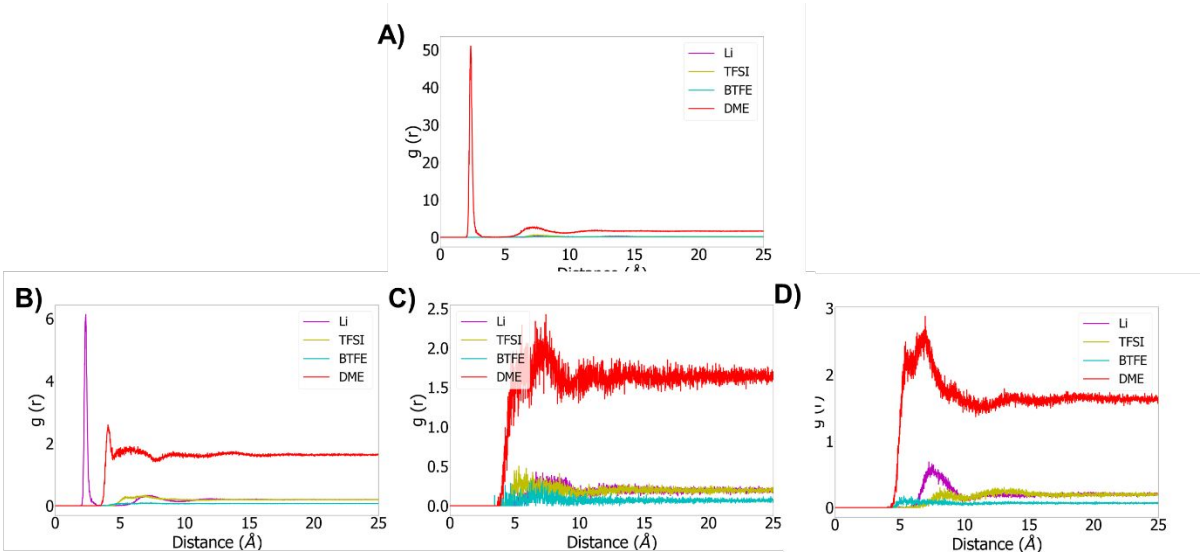

Figure S3: COM-RDF of A) Li B) DME C) BTFE D) TFSI in 1.0 M TFSI low BTFE concentration

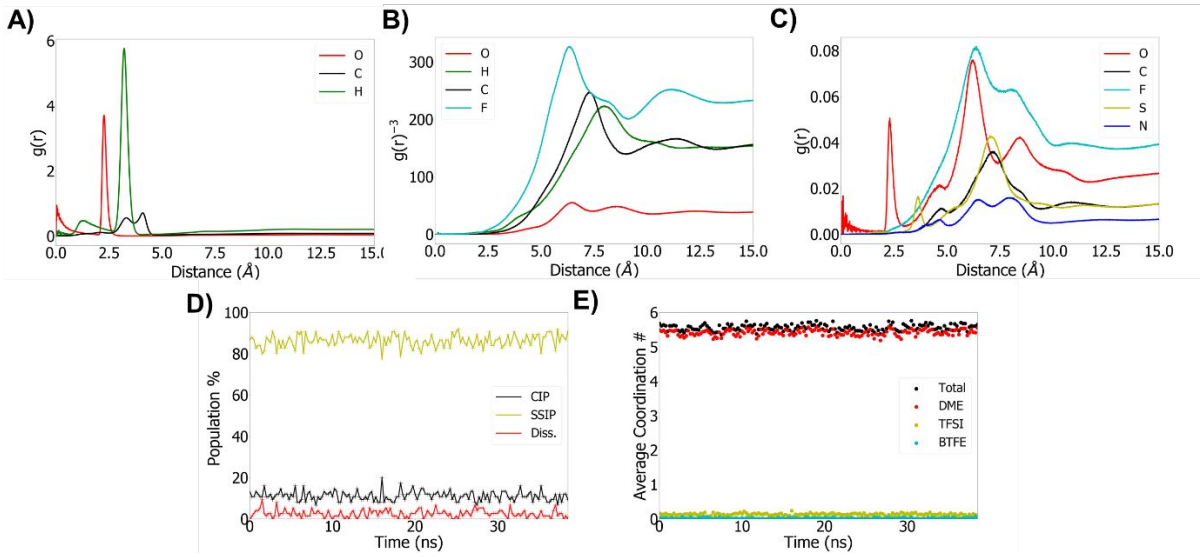

Figure S4: Structural analysis of 1.0 M LiTFSI with high BTFE concentration Radial distribution functions for A) Li-DME B) Li-BTFE C) Li-TFSID) Population % of Li-TFSI ionic association as a function of time. E) Average Li-O coordination number throughout simulation

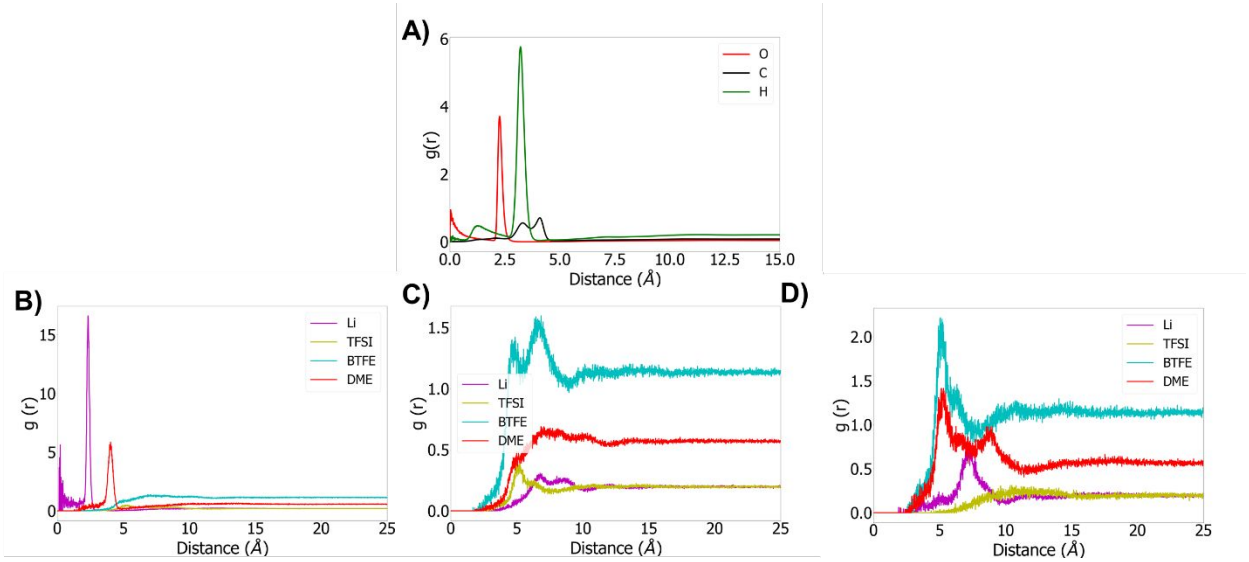

Figure S5: COM-RDF of A) Li B) DME C) BTFE D) TFSI in 1.0 M TFSI high BTFE concentration.

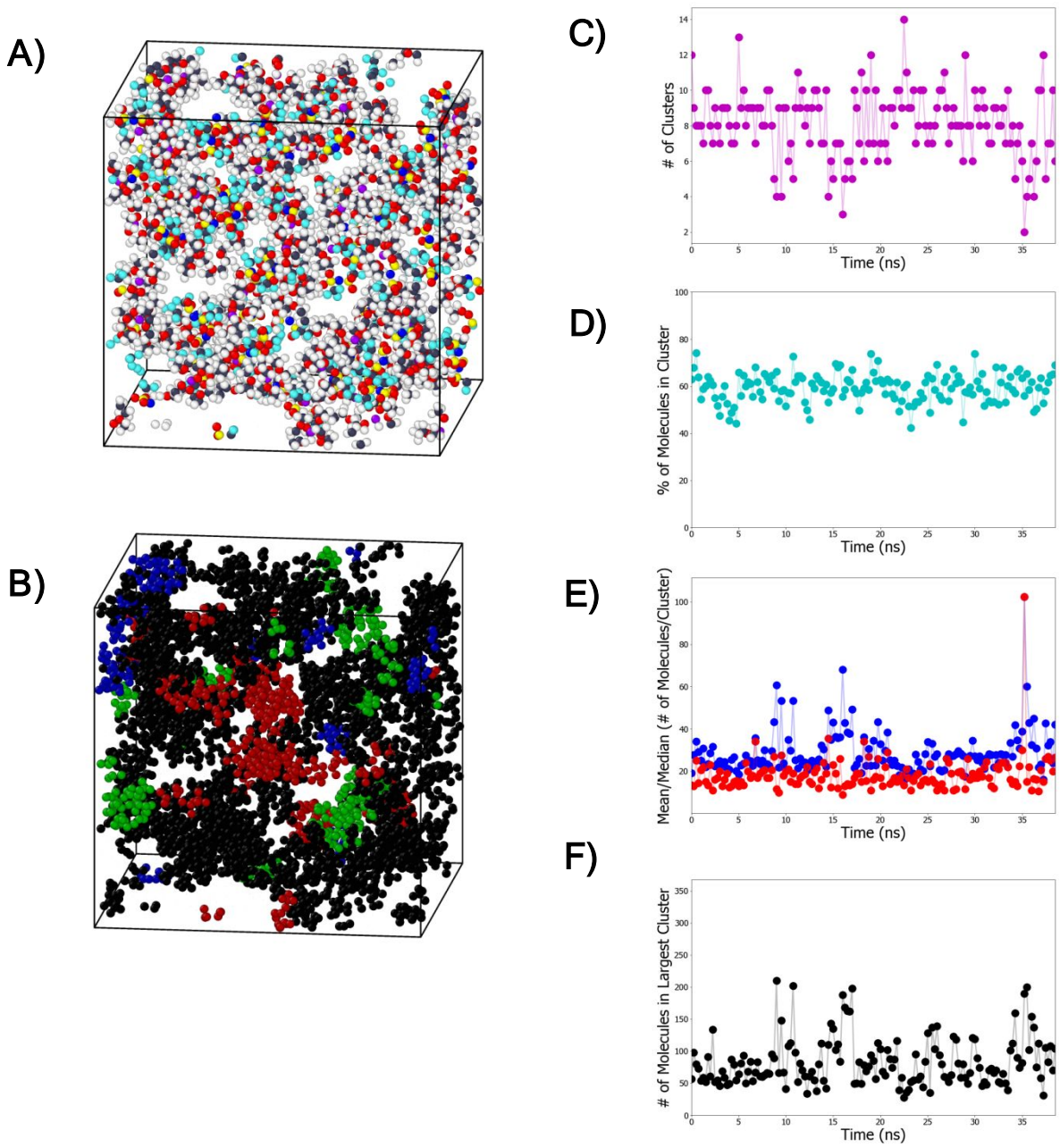

Figure S6: Clustering Analysis of 1.0 M LiTFSI with high BTFE concentration A) System snapshot without BTFE B) System snapshot without BTFE. Green, blue and Red atoms represent molecules in different example clusters. Black regions are other non-BTFE molecules not in those clusters. C) number of clusters over simulation time D) Percent of molecules clustered over time. E) Mean (blue) and median (red) of clusters F) Number of molecules in the largest cluster at a particular timeframe.

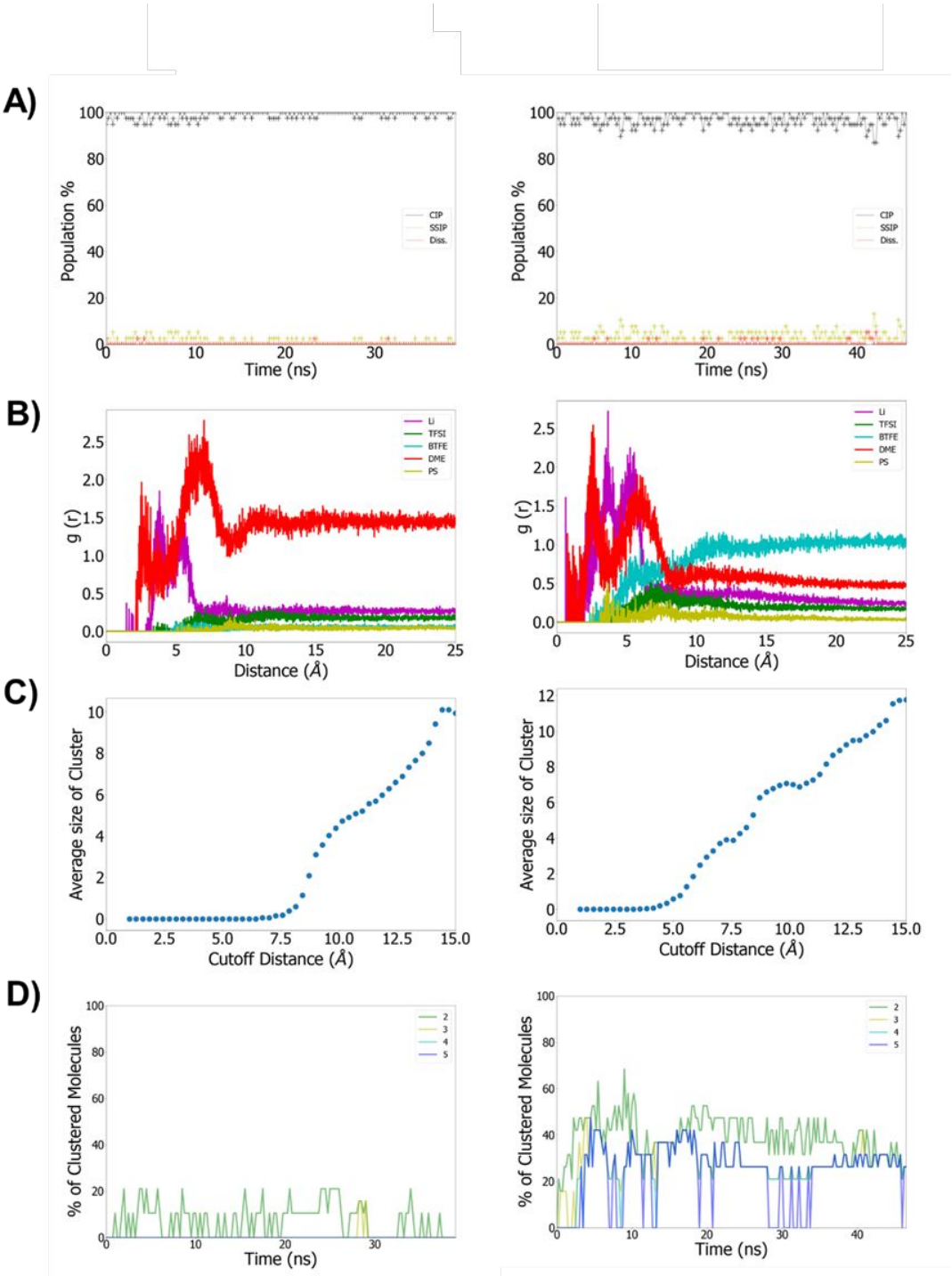

Figure S7 : Li_2S_6 in DME with *high (right) and low (left) BTFE concentrations.* A) Population % of Li_2S_6 ionic association as a function of time. B) Li_2S_6 COM RDF C) Average size of Li_2S_6-Li_2S_6 clusters as a function of cutoff distance for nearest neighbors D) The percent of Li_2S_6 in a cluster with one, two , three, four, and 5 other Li_2S_6 for a cutoff distance of 7.5 Å

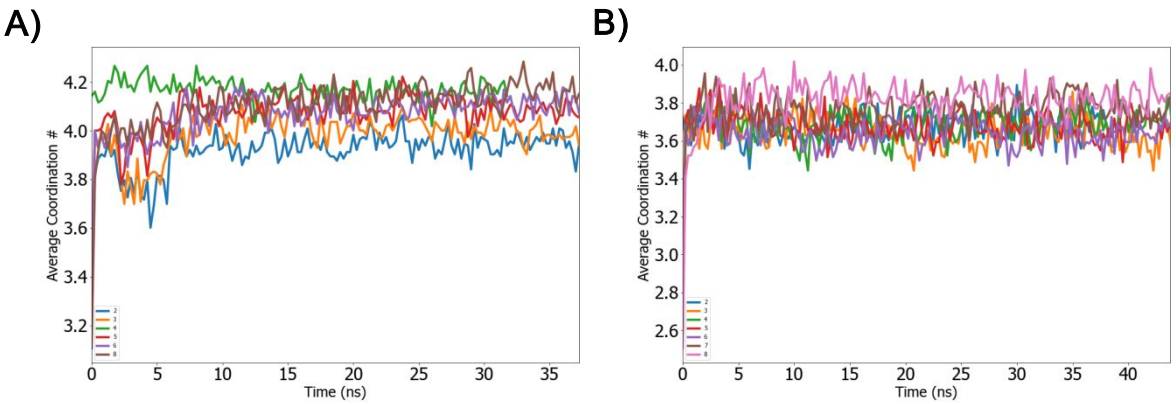

Figure S8: Average Li-O total coordination for all polysulfide systems for A) low BTFE B) high BTFE concentrations.

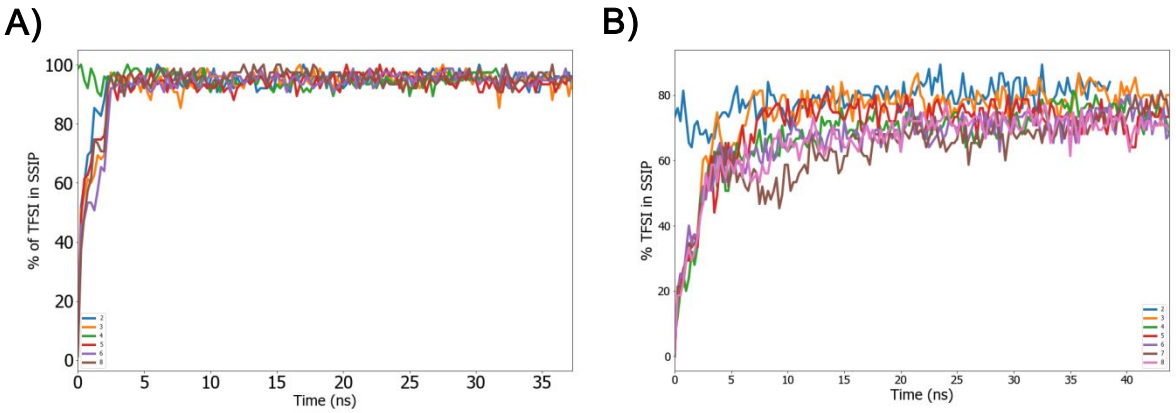

Figure S9: % of LiTFSI in SSIP configuration for all polysulfide systems in A) low BTFE B) high BTFE concentrations.

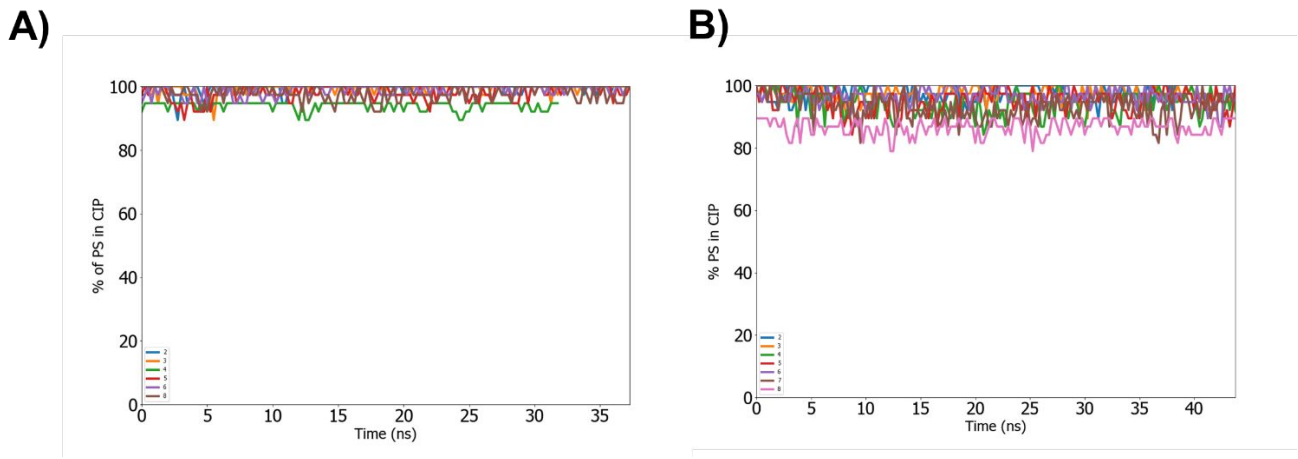

Figure S10: % of PS in CIP configuration for all polysulfide systems in A) low BTFE B) high BTFE concentrations.

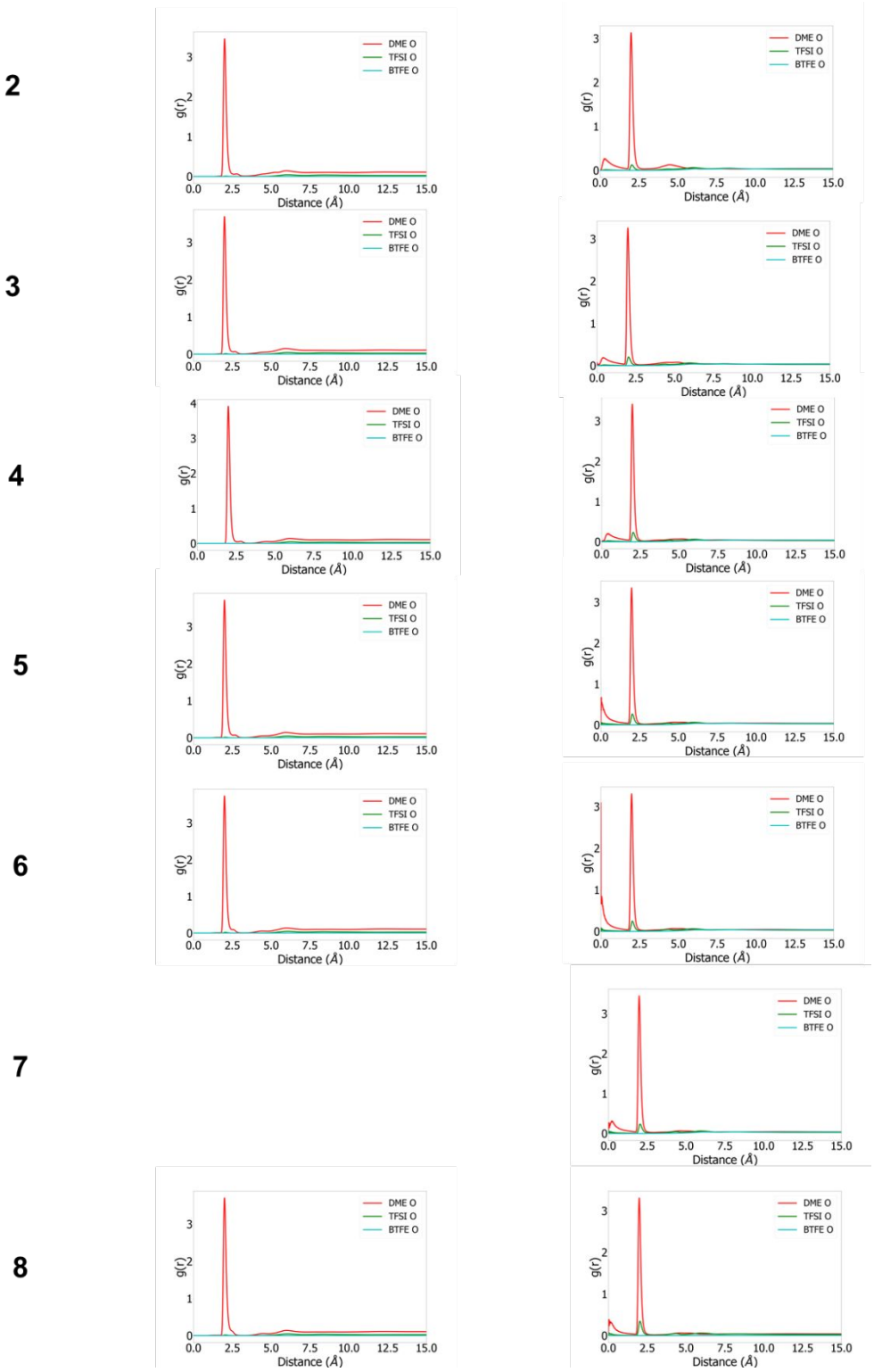

Figure S11: Li-O RDFS for Polysulfides of chain length 2-8 in low (Left) and high (right) BTFE concentrations

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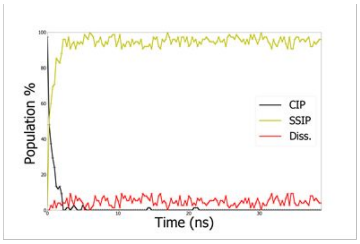
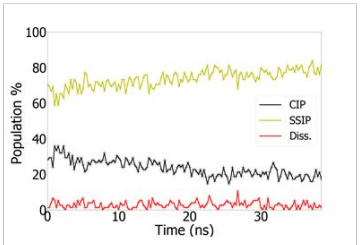

Population %
Time (ns)
CIP
SSIP
Diss.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Time (ns)
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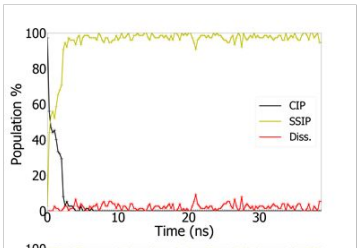
Population %
Time (ns)
CIP
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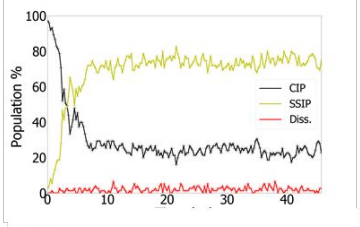
Population %
Time (ns)
CIP
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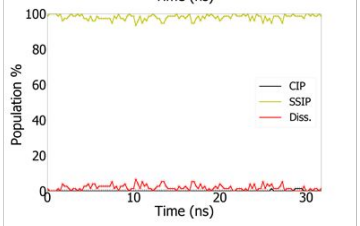
Population %
Time (ns)
CIP
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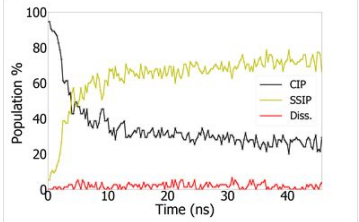
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Time (ns)
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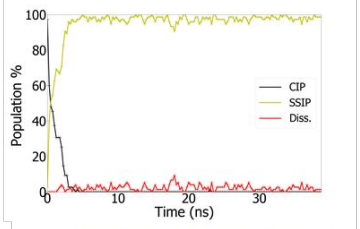
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Time (ns)
CIP
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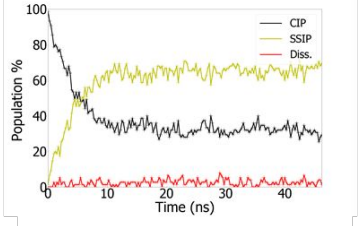
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Time (ns)
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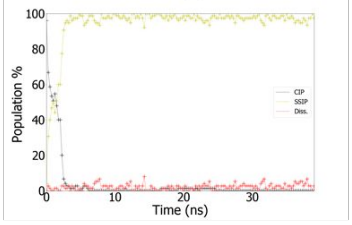
Population %
Time (ns)
CIP
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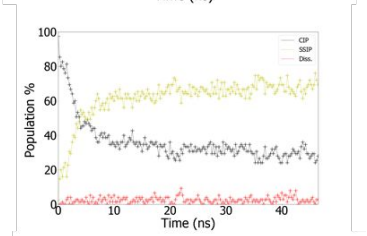
Population %
Time (ns)
CIP
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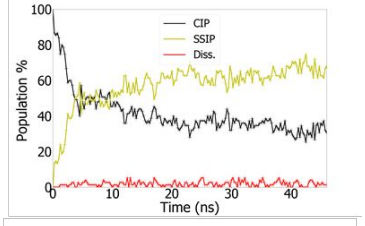
Population %
Time (ns)
CIP
SSIP
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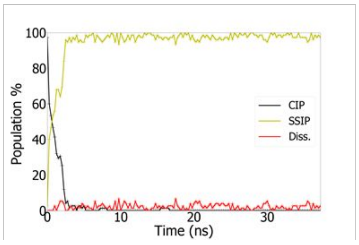
Population %
Time (ns)
CIP
SSIP
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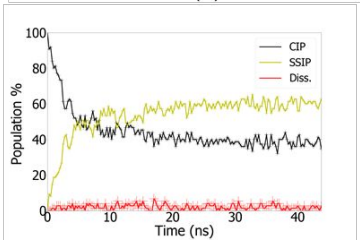
Population %
Time (ns)
CIP
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Figure S12: TFSI ionic association for Polysulfides of chain length 2-8 in low (Left) and high (right) BTFE concentrations . Population % of Li-TFSI as Contact ion pair (black), Solvent-separated ion pair (yellow) and dissociated (red) as a function of time.

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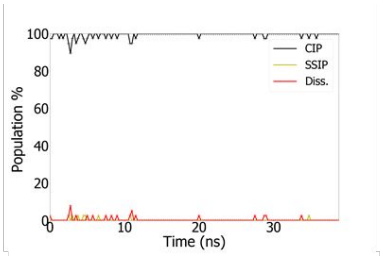
Population %
Time (ns)
CIP
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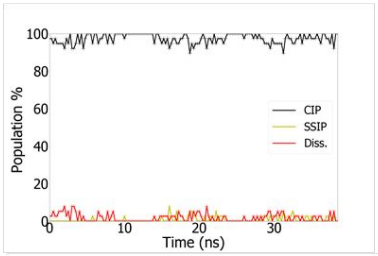
Population %
Time (ns)
CIP
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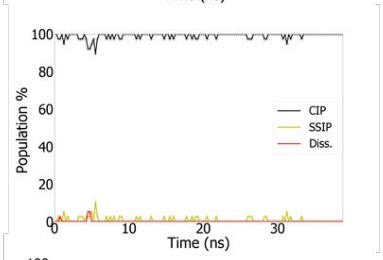
Population %
Time (ns)
CIP
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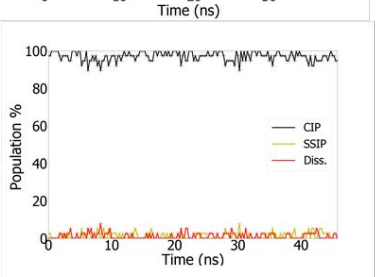
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Time (ns)
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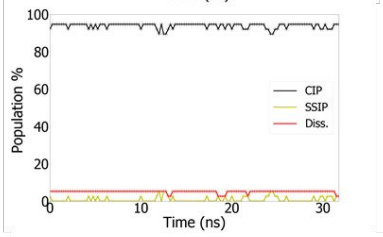
Population %
Time (ns)
CIP
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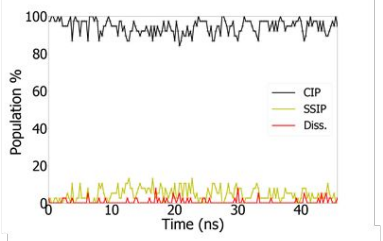
Population %
Time (ns)
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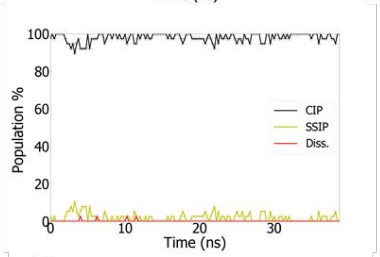
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Time (ns)
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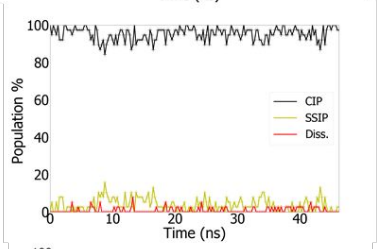
Population %
Time (ns)
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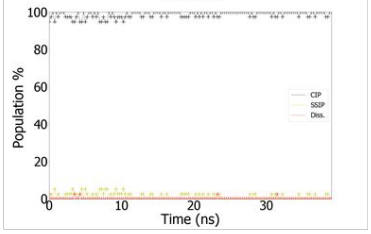
Population %
Time (ns)
CIP
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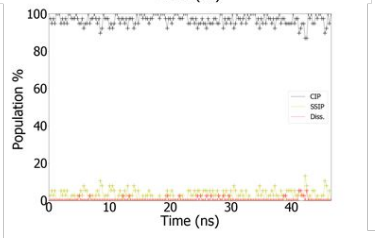
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Time (ns)
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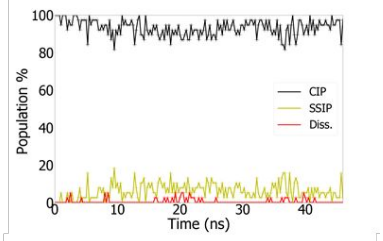
Population %
Time (ns)
CIP
SSIP
Diss.

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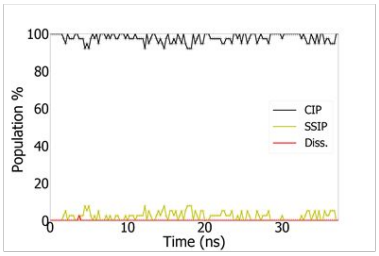
Population %
Time (ns)
CIP
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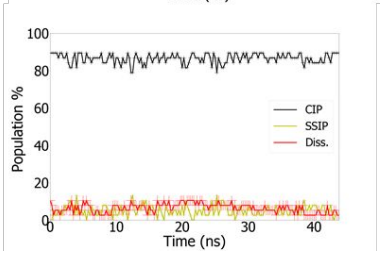
Population %
Time (ns)
CIP
SSIP
Diss.

Figure S13: Polysulfide ionic association for Polysulfides of chain length 2-8 in low (Left) and high (right) BTFE concentrations. Population % of Li2Sx (2<=x<=8) as Contact ion pair (black), Solvent-separated ion pair (yellow) and dissociated (red) as a function of time.

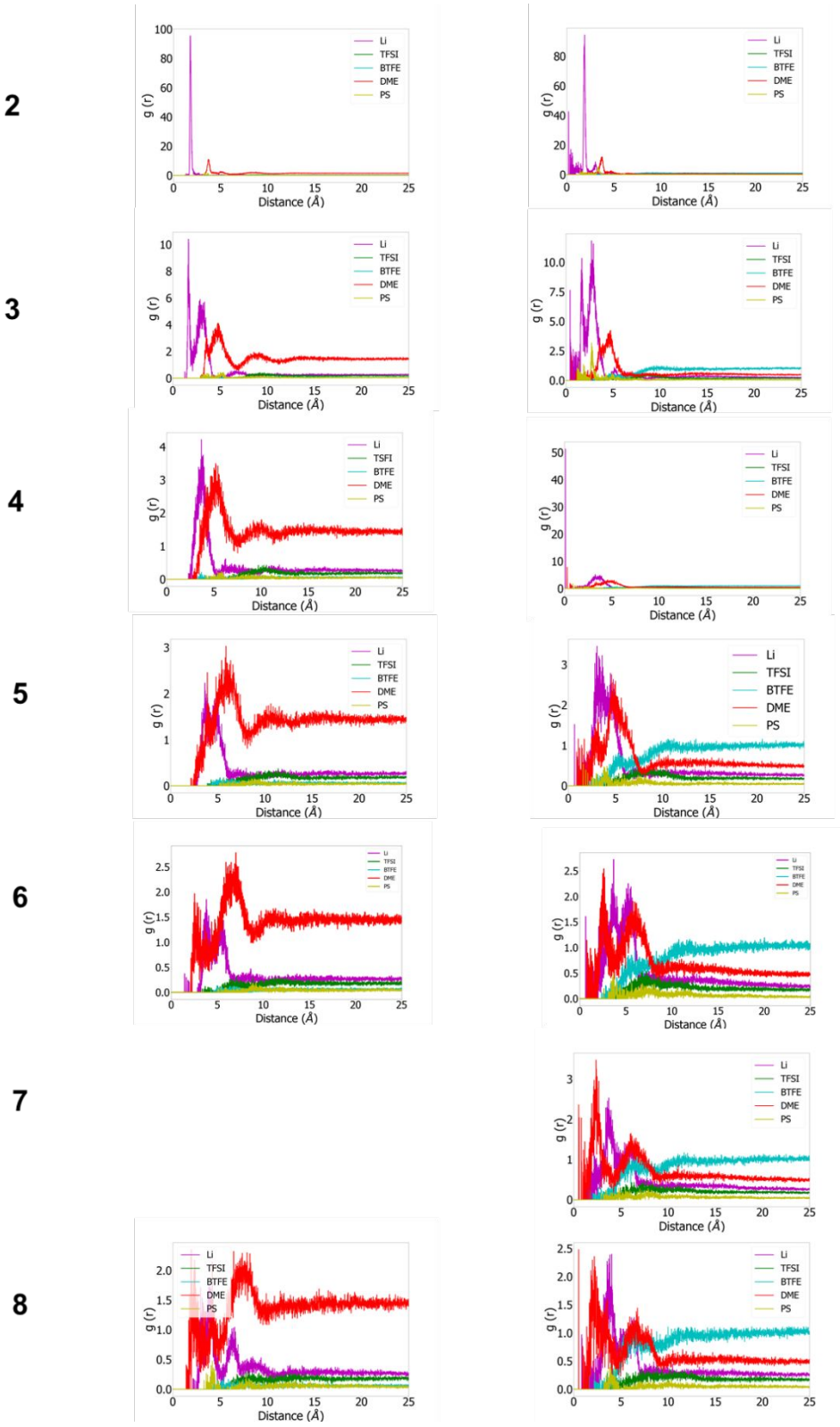

Figure S14: Polysulfide COM RDFS for Polysulfides of chain length 2-8 in low (Left) and high (right) BTFE concentrations.

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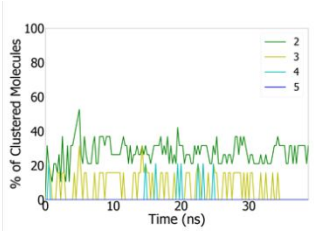
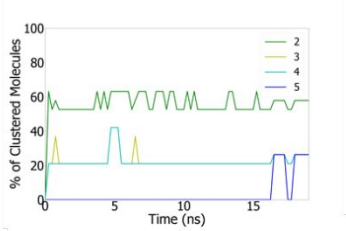

% of Clustered Molecules
Time (ns)
2
3
4
5


% of Clustered Molecules
Time (ns)
2
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4
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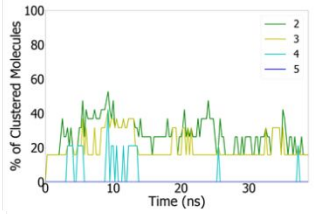
% of Clustered Molecules
Time (ns)
2
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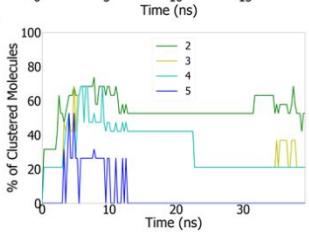
% of Clustered Molecules
Time (ns)
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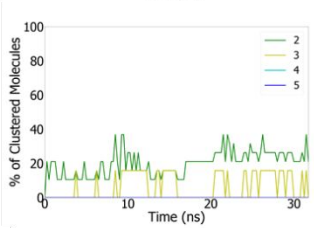
% of Clustered Molecules
Time (ns)
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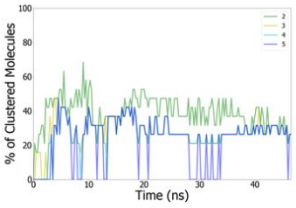
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Time (ns)

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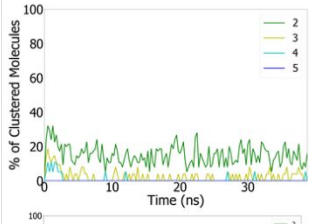
% of Clustered Molecules
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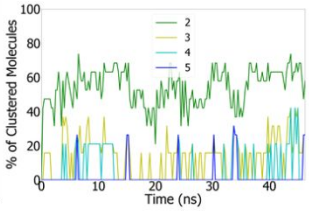
% of Clustered Molecules
Time (ns)
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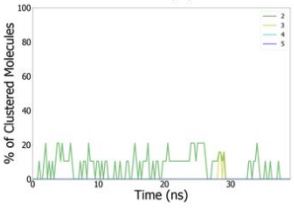
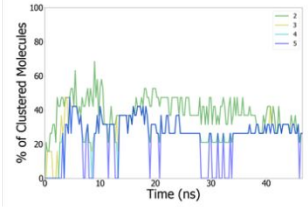
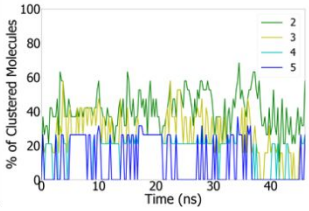
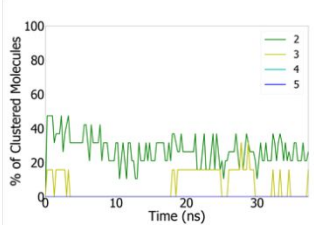

% of Clustered Molecules
Time (ns)


% of Clustered Molecules
Time (ns)

7


% of Clustered Molecules
Time (ns)
2
3
4
5

8


% of Clustered Molecules
Time (ns)
2
3
4
5

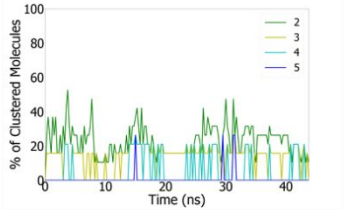

% of Clustered Molecules
Time (ns)
2
3
4
5

Figure S15: Polysulfide-Polysulfide clustering analysis for Polysulfides of chain length 2-8 in low (Left) and high (right) BTFE concentrations .

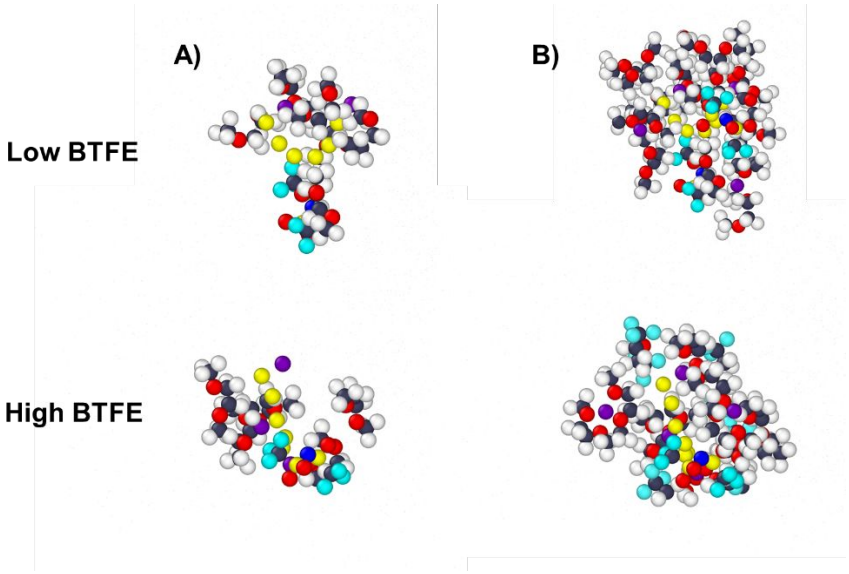


Figure S16 : Snapshots of Li_2S_6 in DME with high and low BTFE concentration A) 10 nearest neighbors B) 20 nearest neighbors. Red = Oxygen, White=Hydrogen, Black= Carbon, Purple = Lithium, Turquoise = Fluorine, Blue= Nitrogen, Yellow = Sulfur.

Table S1: Compositions of no polysulfide systems

	# of Molecules		
Systems	**DME**	**LiTFSI**	**BTFE**
0.5 M TFSI Low BTFE	642	37	27
1.0 M TFSI Low BTFE	606	75	25
0.5 M TFSI High BTFE	223	37	446
1.0 M TFSI High BTFE	210	75	421

Table S2: Compositions of Polysulfide Systems

	# of Molecules			
Systems	**DME**	**LiTFSI**	**BTFE**	**Li2PS**
1.0 M LiTFSI Low BTFE with PS	606	75	27	19
1.0 M LiTFSI High BTFE with PS	210	75	421	19

Table S3: Forcefield Data

DME

$atom:o1 $mol @atom:O -0.8

$atom:o2 $mol @atom:O -0.8

$atom:h1 $mol @atom:H -0.04

```
$atom:h2   $mol    @atom:H  -0.04
        $atom:h3   $mol    @atom:H -0.04
        $atom:h4   $mol    @atom:H -0.04
        $atom:h5   $mol    @atom:H -0.04
        $atom:h6   $mol    @atom:H -0.04
        $atom:h7   $mol    @atom:H -0.04
        $atom:c1   $mol    @atom:C 0.5
        $atom:c2   $mol    @atom:C 0.5
        $atom:c3   $mol    @atom:C 0.5
        $atom:c4   $mol    @atom:C 0.5
        $atom:h8   $mol    @atom:H -0.04
        $atom:h9   $mol    @atom:H -0.04
        $atom:h10   $mol    @atom:H -0.04

bond_coeff @bond:OC 320.000          1.410
        bond_coeff @bond:CC 268.000  1.529
        bond_coeff @bond:HC 340.000 1.09

        angle_coeff  @angle:CCH 37.500          110.700
        angle_coeff  @angle:OCC 50.000          109.500
        angle_coeff  @angle:HCO 35.000          109.500
        angle_coeff  @angle:HCH 33.000          107.800
        angle_coeff  @angle:COC  60.000         109.500

         dihedral_coeff @dihedral:HCOC 0.000   0.000    0.760    0.000
          dihedral_coeff @dihedral:CCOC 0.650  -0.250   0.670    0.000
          dihedral_coeff @dihedral:HCCH 0.000  0.000    0.300    0.000
          dihedral_coeff @dihedral:OCCH 0.000  0.000    0.468    0.000
          dihedral_coeff @dihedral:OCCO -0.5500.000    0.000    0.000
```

```
        pair_coeff   @atom:C @atom:C 0.066   3.5
        pair_coeff   @atom:H @atom:H 0.030  2.500
        pair_coeff   @atom:O @atom:O 0.170  3.000
TFSI
        #name  #atomtype       #charge
        $atom:s1   $mol    @atom:S 1.02
        $atom:s2   $mol    @atom:S 1.02
        $atom:o1   $mol    @atom:O -0.53
        $atom:o2   $mol    @atom:O -0.53
        $atom:o3   $mol    @atom:O -0.53
        $atom:o4   $mol    @atom:O -0.53
        $atom:n1   $mol    @atom:N -0.66
        $atom:c1   $mol    @atom:C 0.35
  $atom:f1   $mol    @atom:F -0.16
        $atom:f2   $mol    @atom:F -0.16
  $atom:f3   $mol    @atom:F -0.16
        $atom:c2   $mol    @atom:C 0.35
  $atom:f4   $mol    @atom:F -0.16
        $atom:f5   $mol    @atom:F -0.16
        $atom:f6   $mol    @atom:F -0.16

        bond_coeff @bond:CF 441.92   1.323
        bond_coeff @bond:CS  233.03  1.818
        bond_coeff @bond:OS 637.07   1.437
        bond_coeff @bond:SN 374.88   1.57

        angle_coeff @angle:NSO  94.29113.6
        angle_coeff @angle:NSC 91.3     103.5
```

```
        angle_coeff @angle:SCF 82.93    111.7
        angle_coeff @angle:SNS 80.19   125.6
        angle_coeff @angle:CSO 103.97102.6
        angle_coeff @angle:OSO 115.8  118.5
        angle_coeff @angle:FCF 93.33    107.1

        dihedral_coeff @dihedral:NSCF 0.00      0.00      0.316    0.00
        dihedral_coeff @dihedral:SNSO  0.00     0.00      -0.004   0.00
        dihedral_coeff @dihedral:SNSC  7.933    -2.49     -0.764   0.00
        dihedral_coeff @dihedral:OSCF  0.00     0.00      0.347    0.00

        pair_coeff   @atom:O @atom:O 0.17      2.96
        pair_coeff   @atom:F @atom:F 0.06      2.9
        pair_coeff   @atom:N @atom:N 0.17      3.25
        pair_coeff   @atom:C @atom:C 0.066     3.5
        pair_coeff   @atom:S @atom:S 0.25      3.55
BTFE
        #name  #atomtype        #charge
        $atom:c1   $mol    @atom:C -0.15
        $atom:c3   $mol    @atom:C 0.584
        $atom:h1   $mol    @atom:H 0.129
        $atom:h2   $mol    @atom:H 0.129
        $atom:o1   $mol    @atom:O -0.22
   $atom:c2   $mol    @atom:C -0.15
        $atom:h3   $mol    @atom:H 0.129
        $atom:h4   $mol    @atom:H 0.129
        $atom:c4   $mol    @atom:C 0.584
        $atom:f1   $mol    @atom:F -0.194
        $atom:f2   $mol   @atom:F -0.194
```

```
  $atom:f3   $mol    @atom:F  -0.194
  $atom:f4   $mol    @atom:F  -0.194
        $atom:f5   $mol    @atom:F -0.194
        $atom:f6   $mol    @atom:F -0.194

   bond_coeff @bond:CH 323.04421     1.096654
         bond_coeff @bond:CC 235.669631       1.402874
         bond_coeff @bond:OC 205.15523        1.51745
         bond_coeff @bond:FC 380.74815        1.340951

         angle_coeff  @angle:FCF  67.987106     113.070636
         angle_coeff  @angle:FCC 124.598134    107.907469
         angle_coeff  @angle:CCH 84.316518     108.410527
         angle_coeff  @angle:CCO 55.353132     107.77985
         angle_coeff  @angle:HCO 69.208343     111.884315
         angle_coeff  @angle:HCH 88.493357     112.092131
         angle_coeff  @angle:COC  50.95924     108.930635

         dihedral_coeff @dihedral:HCCF -6.665684       -0.507758       0.316201        0.107507
         dihedral_coeff @dihedral:HCOC 1.365705        0.431033        0.454297        -0.173709
         dihedral_coeff @dihedral:CCOC -1.353268       -0.517821       0.791454        0.11575
         dihedral_coeff @dihedral:OCCF 7.351752        0.388244        0.628858        0.086821

         pair_coeff   @atom:C @atom:C 0.066   3.5
         pair_coeff   @atom:H @atom:H 0.030  2.500
         pair_coeff   @atom:F @atom:F 0.061   2.94
         pair_coeff   @atom:O @atom:O 0.170  3.000
Li
        #name  #atomtype       #charge
```

```
        $atom:li1   $mol    @atom:Li 1.00
  pair_coeff   @atom:Li @atom:Li 0.018279 2.7
S6
        #name  #atomtype        #charge
        $atom:s1   $mol    @atom:S -1.0
        $atom:s2   $mol    @atom:S 0.05
        $atom:s3   $mol    @atom:S  0.05
        $atom:s4   $mol    @atom:S  -0.05
        $atom:s5   $mol    @atom:S  -0.05
        $atom:s6   $mol    @atom:S  -1.0
        bond_coeff @bond:SS 315.7483  2.133
        bond_coeff @bond:SSinternal 308.7203 2.117

        angle_coeff  @angle:SSS 112.74 147.120

        dihedral_coeff @dihedral:SSSS -2.902 -9.477 31.999 -17.666

        pair_coeff   @atom:S @atom:S 0.25 3.55
```