Electronic Supporting Information: Optimizing Cation-π Force-fields for Molecular Dynamics Studies of Competitive Solvation in Conjugated Organosulfur Polymers for Lithium-Sulfur Batteries

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Table. S1: By selecting different grid points for fitting benzene's energy surface, we analyzed their effects on the molecule's open parameters. Two different setups were considered - setup-A, which consists of 9 points, and setup-B, which consists of 25 points. As we have only the "CA" type of carbon atom in the benzene molecule, the open parameters are fixed to $C^4_{\mathrm{CA-Li^+}}$ and $\sigma_{\mathrm{CA-Li^+}}$. Further, we found that as the number of grid points increases, the outcome of the objective function, which signifies the error of the fit, L_2 (see Eq. 5 in the manuscript), also increases. For further details, please refer to the section 3.1.1 of the manuscript.

Parameters	Setup-A	Setup-B
$C^4_{\mathrm{CA-Li^+}}$	104.69	107.38
$\sigma_{\mathrm{CA-Li^+}}$	2.69	2.68
L_2	0.0043	0.0086

Table. S2: By selecting different grid points for fitting thiophene's energy surface, we analyzed their effects on the molecule's open parameters. Two different setups were considered, same as benzene. For thiophene, unlike benzene, there are three different atom types - two for carbon atoms ("CW" and "CS") and one for sulfur atom ("S"). Therefore, we have a total of six open parameters as mentioned in the table. Further, like benzene, we found that as the number of grid points increases, the outcome of the objective function, which signifies the error of the fit, L_2 (see Eq. 5 in the manuscript), also increases. For further details, please refer to the section 3.1.1 of the manuscript and the Fig. S3.

Parameters	Setup-A	Setup-B
$C^4_{\mathrm{CW-Li^+}}$	161.81	162.16
$\sigma_{\mathrm{CW-Li^+}}$	2.71	2.71
$C^4_{\mathrm{CS-Li^+}}$	161.81	162.16
$\sigma_{\mathrm{CS-Li^+}}$	2.71	2.71
$C^4_{\mathrm{S-Li^+}}$	190.24	190.15
$\sigma_{\mathrm{S-Li^+}}$	2.76	2.78
L_2	0.004	0.010

Table. S3: By selecting different grid points for fitting benzenethiol's energy surface, we analyzed their effects on the molecule's open parameters. Two different setups were considered, same as benzene. For benzenethiol, like benzene, there is only one atom type - "CA" for carbon. Therefore, we have a total of two open parameters as mentioned in the table. Further, like benzene, we found that as the number of grid points increases, the outcome of the objective function, which signifies the error of the fit, L_2 (see Eq. 5 in the manuscript), also increases. For further details, please refer to the section 3.1.1 of the manuscript and the Fig. S2.

Parameters	Setup-A	Setup-B
$C^4_{\mathrm{CA-Li^+}}$	139.92	140.60
$\sigma_{\mathrm{CA-Li^+}}$	2.70	2.70
L_2	0.001	0.013

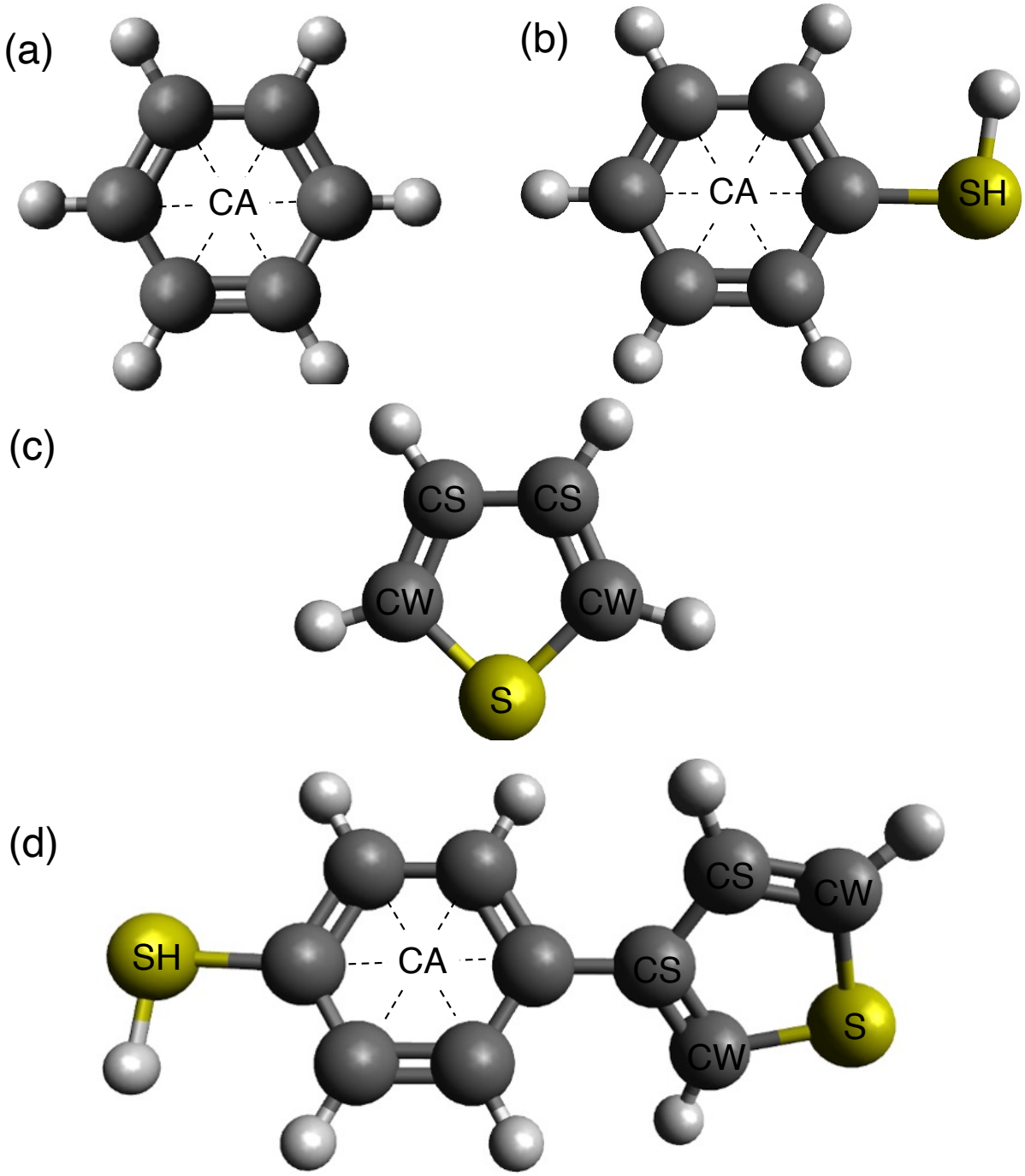

Fig. S1: Atom types: (a) In benzene, all carbon atoms are classified as the "CA" type. (b) In benzenethiol, the carbon atoms are classified as the "CA" type, and the sulfur atom as the "SH" type. (c) In thiophene, the carbon atoms bonded to sulfur are classified as the "CW" type, and the carbon atoms adjacent to "CW" are classified as the "CS" type. (d) TBT follows the same atom types as those mentioned for benzenethiol and thiophene.

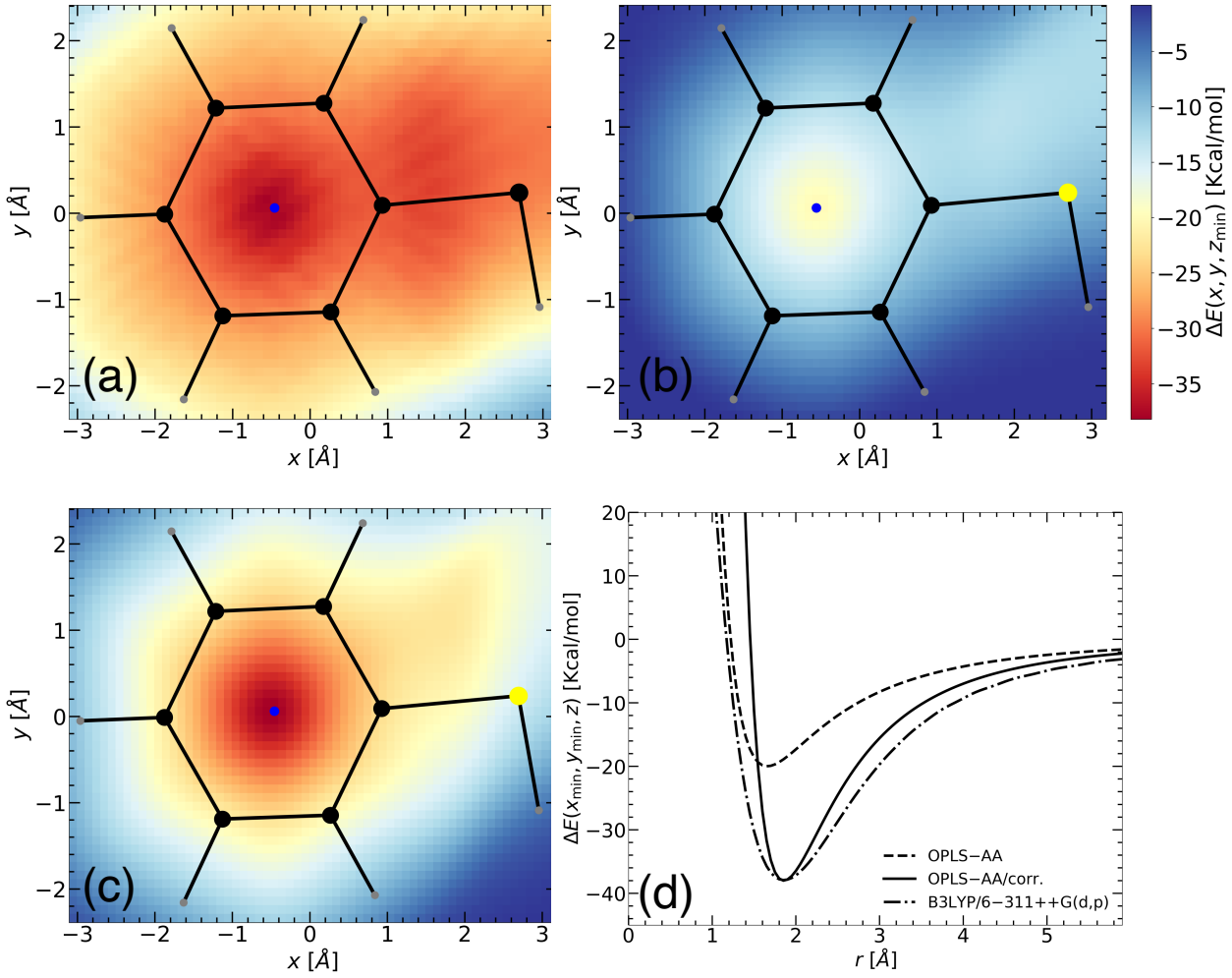

Fig. S2: Two-dimensional representation of the binding energy landscape between a thiophene molecule and a Li^+ ion complex from (a) DFT, (b) MS profile without corrections, and (c) MS profile with corrections. The x and y axes correspond to spatial positions, while the intensity of the plot (represented by a mesh) illustrates the binding energy, $\Delta E(x, y, z_{\min})$ (in kcal/mol) between the two entities. The binding energy was calculated at various positions, with the z-coordinate allowed to minimize for each point, resulting in this energy landscape. The blue point represents the location of the minimum energy. (d) Binding energy curves, $\Delta E(x_{\min}, y_{\min}, z)$, for separation of the thiophene-Li^+ complex shown with B3LYP/6−311++G(d,p) (dash-dot line) functional, OPLS−AA (dashed line), and OPLS−AA with corrections (OPLS−AA/corr.) (solid black line).

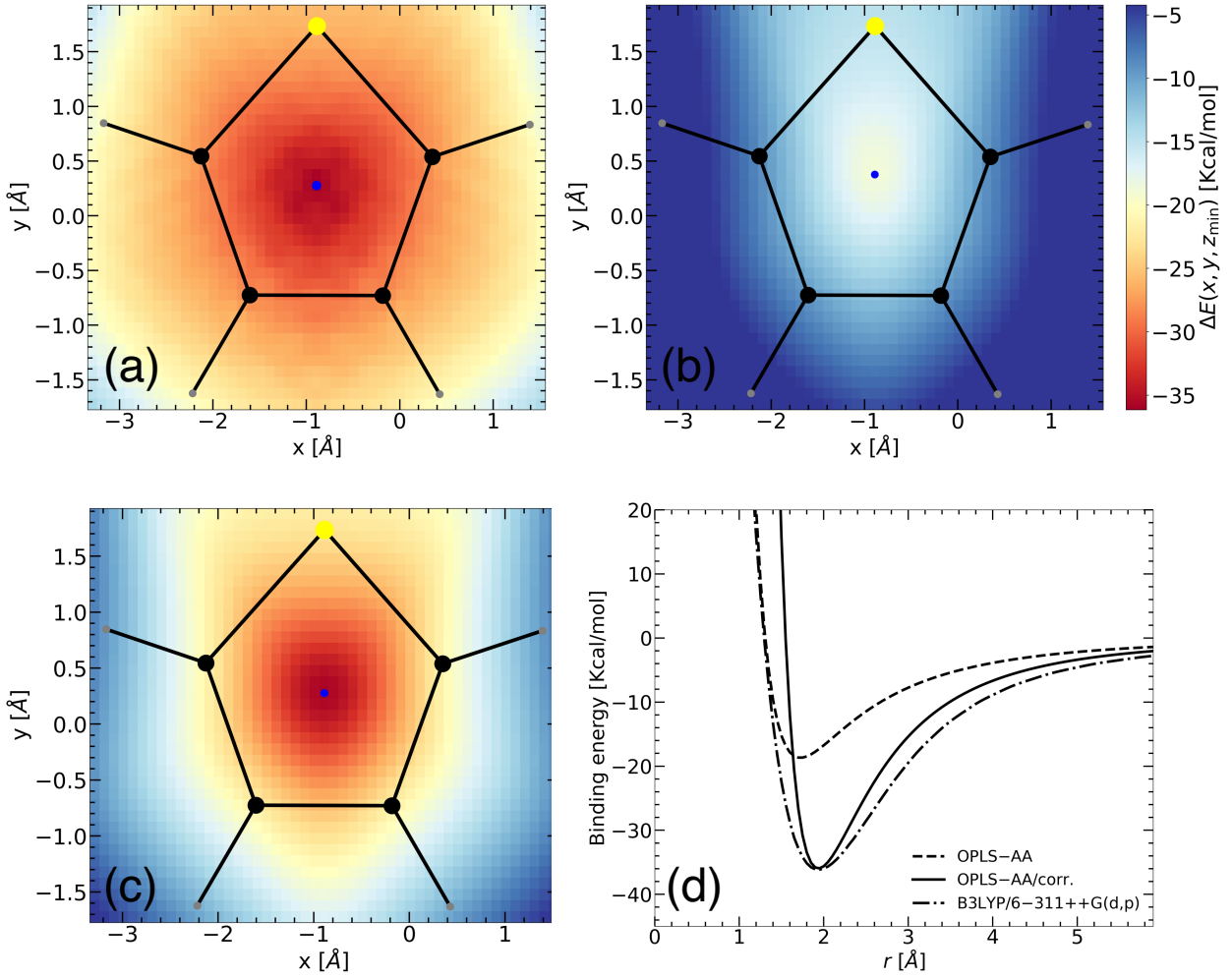

Fig. S3: Two-dimensional representation of the binding energy landscape between a benzenethiol molecule and a Li^+ ion complex from (a) DFT, (b) MS profile without corrections, and (c) MS profile with corrections. The x and y axes correspond to spatial positions, while the intensity of the plot (represented by a mesh) illustrates the binding energy, $\Delta E(x, y, z_{\min})$ (in kcal/mol) between the two entities. The binding energy was calculated at various positions, with the z-coordinate allowed to minimize for each point, resulting in this energy landscape. The blue point represents the location of the minimum energy. (d) Binding energy curves, $\Delta E(x_{\min}, y_{\min}, z)$, for separation of the benzenethiol-Li^+ complex shown with B3LYP/6−311++G(d,p) (dash-dot line) functional, OPLS−AA (dashed line), and OPLS−AA with corrections (OPLS−AA/corr.) (solid black line).

Table. S4: By selecting different number of grid points and varying the number of open parameters for fitting "Free TBT monomer"'s energy surface, we analyzed their effects on the molecule's open parameters. Regarding the number of grid points, two different setups were considered: setup-A, which consists of 23 points - 9 points from each zone-1 and zone-3, and 5 points from zone-2, and setup-B, which consists of 59 points - 27 points from zone-1 and zone-3, and 5 points zone-2. The TBT molecule comprises a total of six different atom types" three for carbon atoms ("CA", "CW", and "CS"), two for sulfur atoms ("S" and "SH"), and one for hydrogen ("HA"). Out of these six, mainly four atoms types were considered for the fitting procedure - "CA", "CA", "CS", and "HA". A total of three different parameter sets were considered: Set-(i) "CA", "CW", and "CS" atom types, with "CW" and "CS" atom types treated as identical, Set-(ii) same as setup (i) expect "CW" and "CS" were treated as distinct atom types, and Set-(iii) "CA", "CW", and CS atom types "S" atom type were considered as open parameter. The selected parameters marked with an "*" were used for the simulation of TBT in the solution phase.

type (i)	atom (j)	C_4^{ij}	σ_{ij}	L_2
Setup-A : 4 parm. - Set(i)				
CA	Li^+	51.48	2.68	0.027
CW	Li^+	48.87	2.72	0.027
CS	Li^+	48.87	2.72	0.027
Setup-B : 4 parm. - Set(i)				
CA	Li^+	52.12	2.67	0.039
CW	Li^+	49.94	2.73	0.039
CS	Li^+	49.94	2.73	0.039
Setup-A : 6 parm. - Set(ii)				
CA	Li^+	50.91	2.68	0.027
CW	Li^+	45.26	2.72	0.027
CS	Li^+	52.77	2.72	0.027
Setup-B: 6 parm. - Set(ii)				
CA	Li^+	51.59	2.66	0.039
CW	Li^+	50.20	2.72	0.039
CS	Li^+	50.26	2.72	0.039
Setup-A: 6 parm.* - Set(iii)				
CA	Li^+	65.28	2.80	0.05
CW	Li^+	68.09	2.87	0.05
CS	Li^+	68.09	2.87	0.05
S	Li^+	78.28	2.76	0.05
Setup-B: 6 parm. - Set(iii)				
CA	Li^+	67.73	2.80	0.08
CW	Li^+	64.25	2.82	0.08
CS	Li^+	64.25	2.82	0.08
S	Li^+	76.82	2.80	0.08

Table. S5: By selecting different number of grid points and varying the number of open parameters for fitting "PTBT constituent monomer"'s energy surface, we analyzed their effects on the molecule's open parameters. Regarding the number of grid points, two different setups were considered: setup-A, which consists of 23 points - 9 points from each zone-1 and zone-3, and 5 points from zone-2, and setup-B, which consists of 59 points - 27 points from zone-1 and zone-3, and 5 points zone-2. The TBT molecule comprises a total of six different atom types" three for carbon atoms ("CA", "CW", and "CS"), two for sulfur atoms ("S" and "SH"), and one for hydrogen ("HA"). Out of these six, mainly four atoms types were considered for the fitting procedure - "CA", "CA", "CS", and "HA". A total of three different parameter sets were considered: Set-(i) "CA", "CW", and "CS" atom types, with "CW" and "CS" atom types treated as identical, Set-(ii) same as setup (i) expect "CW" and "CS" were treated as distinct atom types, and Set-(iii) "CA", "CW", and CS atom types "S" atom type were considered as open parameter. The selected parameters marked with an "*" were used for the simulation of TriTBT in the solution phase.

type (i)	atom (j)	C_4^{ij}	σ_{ij}	L_2
Setup-A: 4 parm. - Set(i)				
CA	Li^+	62.37	2.70	0.03
CW	Li^+	125.02	2.71	0.03
CS	Li^+	125.02	2.71	0.03
Setup-B: 4 parm. - Set(i)				
CA	Li^+	64.43	2.70	0.05
CW	Li^+	129.83	2.72	0.05
CS	Li^+	129.83	2.72	0.05
Setup-A: 6 parm. - Set(ii)				
CA	Li^+	60.78	2.67	0.03
CW	Li^+	110.17	2.74	0.03
CS	Li^+	158.52	2.74	0.03
Setup-B: 6 parm. - Set(ii)				
CA	Li^+	61.28	2.68	0.04
CW	Li^+	112.81	2.71	0.04
CS	Li^+	160.45	2.77	0.04
Setup-A: 6 parm.* - Set(iii)				
CA	Li^+	59.78	2.67	0.02
CW	Li^+	114.88	2.72	0.02
CS	Li^+	114.88	2.72	0.02
S	Li^+	110.26	2.65	0.02
Setup-A: 6 parm. - Set(iii)				
CA	Li^+	64.78	2.69	0.03
CW	Li^+	110.52	2.67	0.03
CS	Li^+	110.52	2.67	0.03
S	Li^+	111.08	2.67	0.03

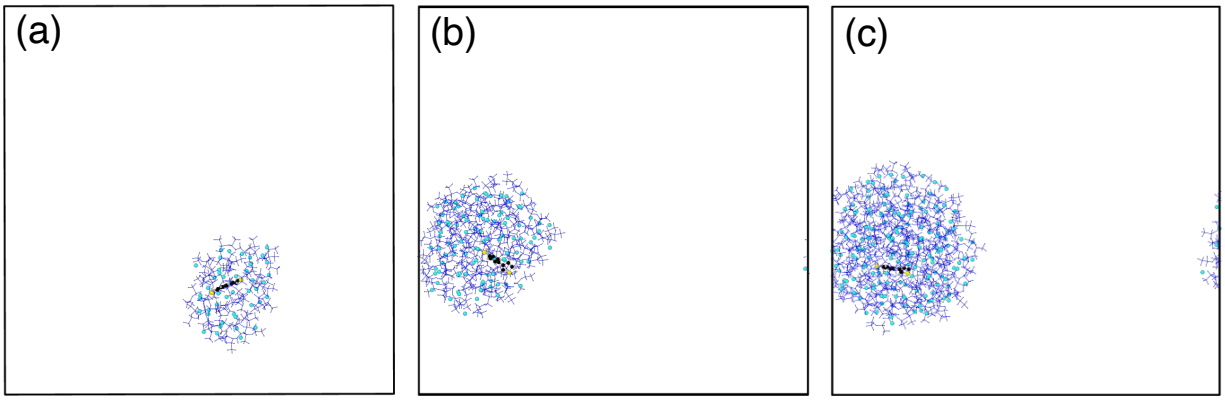

Fig. S4: Clustering of Li^+-$TFSI^+$ in the case of an implicit solvent for the salt concentration (a) C_{salt} = 0.1 M, (b) C_{salt} = 0.2 M, and (c) C_{salt} = 0.3 M.

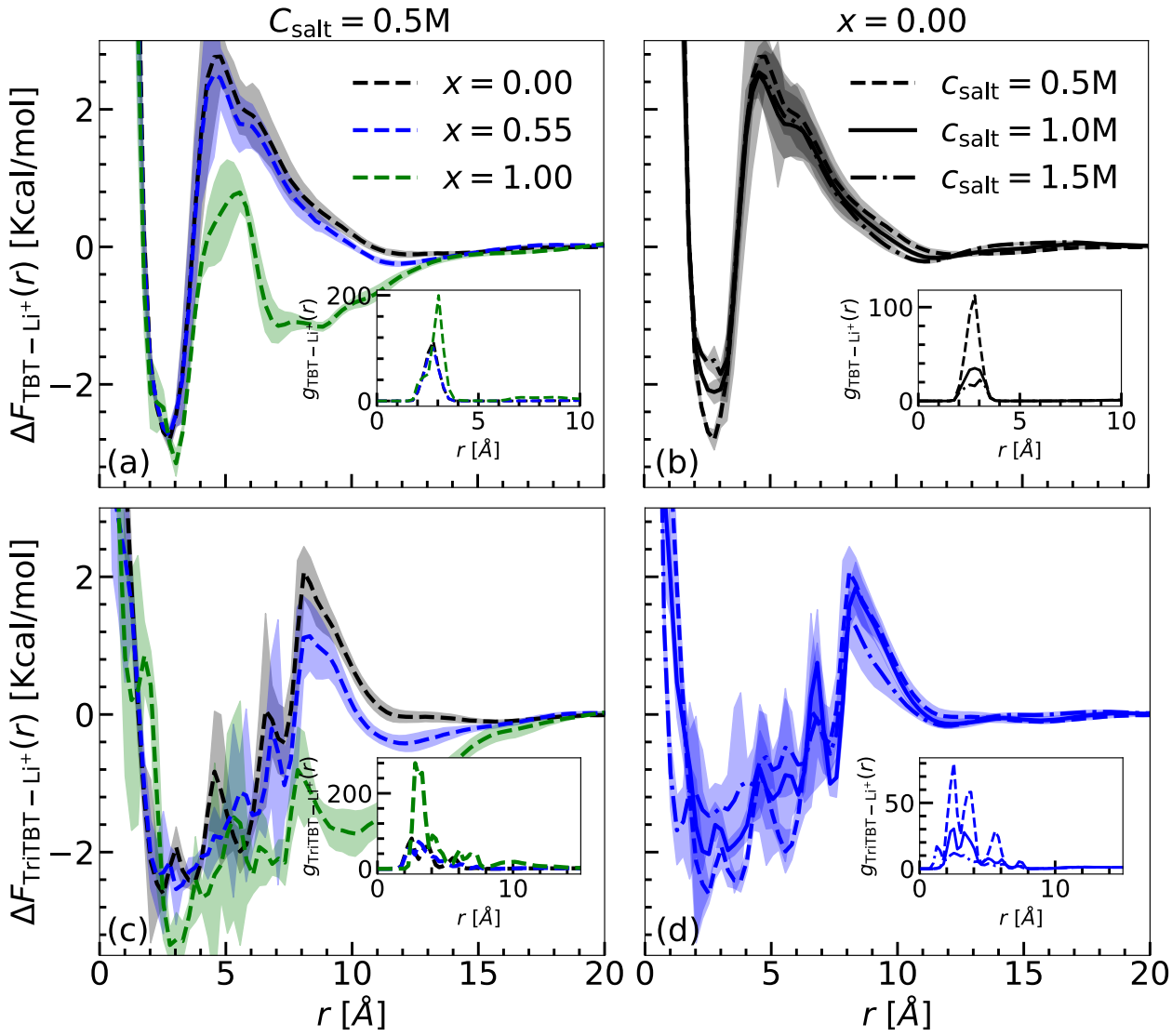

Fig. S5: Panels (a) and (c) display free energy profiles for TBT and TriTBT with varying solvent composition at a fixed salt concentration of $C_{salt} = 0.5$ M. Panels (b) and (d) show binding free energy profiles for TBT and TriTBT with varying salt concentrations at a fixed solvent composition, $x = 0.00$. The corresponding radial distribution functions (RDPs) concerning the COM of the oligomers are shown in the insets.

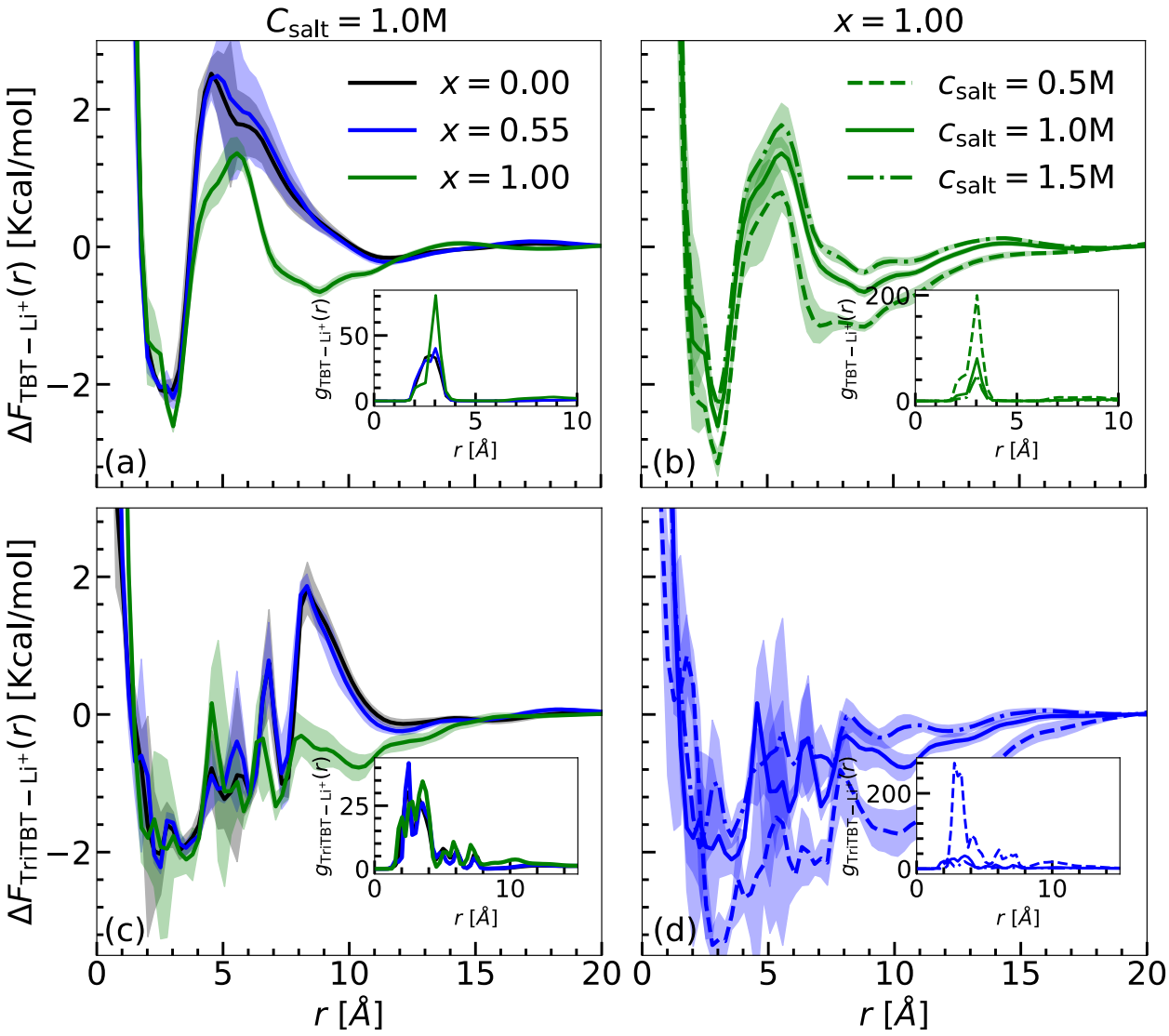

Fig. S6: Panels (a) and (c) display free energy profiles for TBT and TriTBT with varying solvent composition at a fixed salt concentration of C_{salt} = 1.0 M. Panels (b) and (d) show binding free energy profiles for TBT and TriTBT with varying salt concentrations at a fixed solvent composition, x = 1.00. The corresponding radial distribution functions (RDPs) concerning the COM of the oligomers are shown in the insets.

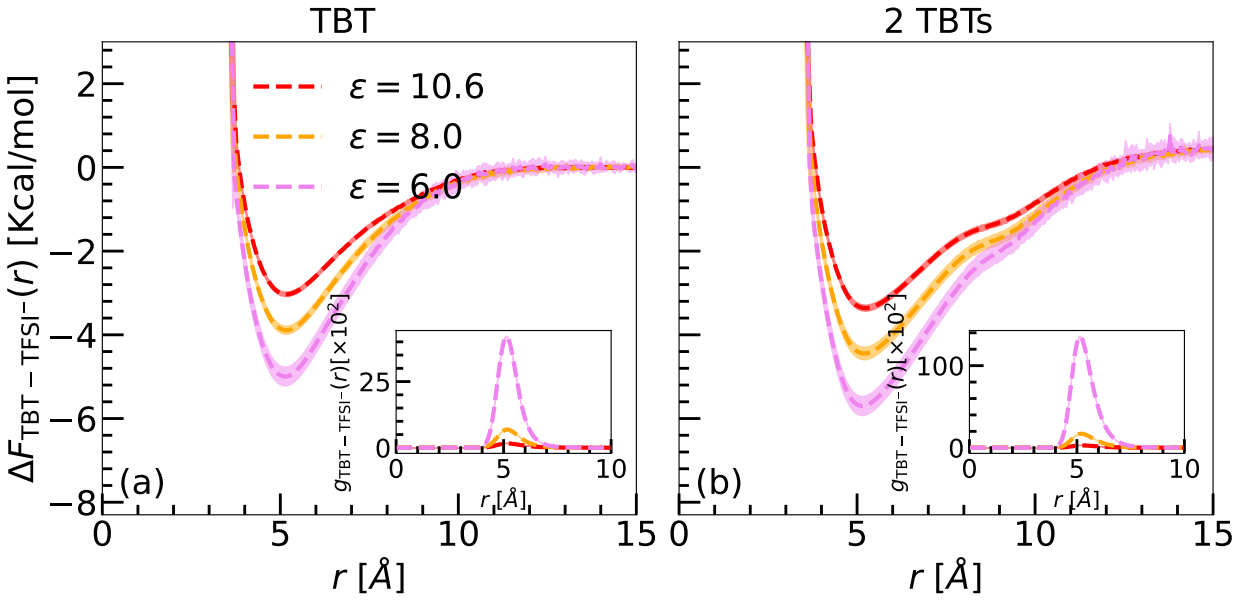

Fig. S7: Free energy profiles ($\Delta F_{\mathrm{TBT-TFSI^-}}$) as a function of distance for (a) Sys. I a/b/c (a single TBT monomer with one LiTFSI salt) and (b) Sys. II (2 TBTs with one LiTFSI salt) at three different dielectric constants. Each profile is block-averaged over 500 ns intervals, with three lines representing different dielectric constants: violet ($\epsilon = 6.0$), orange ($\epsilon = 8.0$), and red ($\epsilon = 10.6$). Shaded regions indicate the standard deviation from the block averages. The free energy profiles are calculated with the Boltzmann inversion. Insets display the corresponding $\mathrm{TFSI^-}$ RDPs relative to the center of mass of the TBT oligomers.

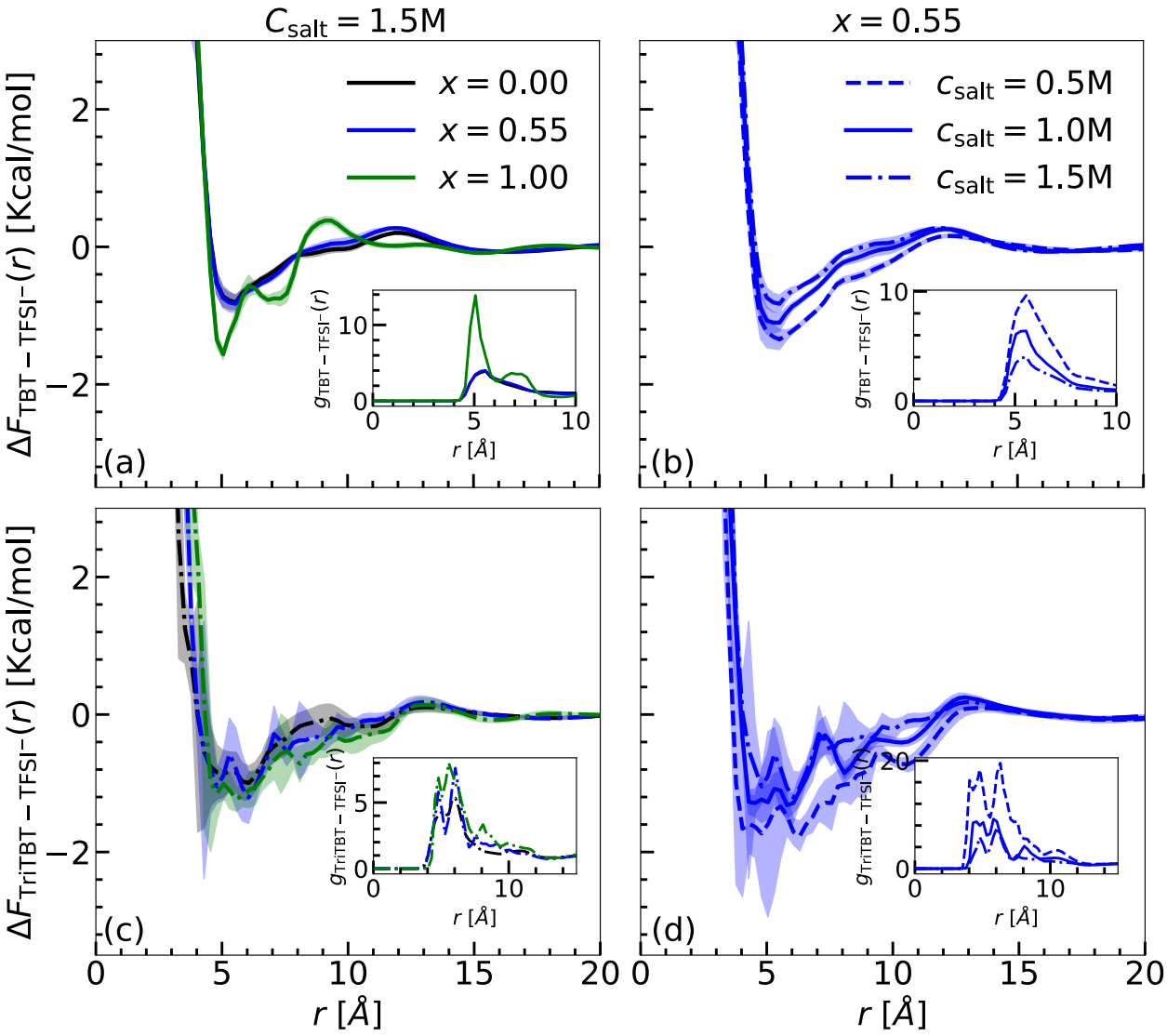

Fig. S8: Panels (a) and (c) display free energy profiles for TBT and TriTBT with varying solvent composition at a fixed salt concentration of C_{salt} = 1.5 M. Panels (b) and (d) show binding free energy profiles for TBT and TriTBT with varying salt concentrations at a fixed solvent composition, $x = 0.55$. The corresponding radial distribution functions (RDPs) concerning the COM of the oligomers are shown in the insets.

Computational time required for parameterization

The computational time for the parameterization of the potential is limited by the computational time for DFT calculations. For instance, in the case of "Free TBT monomer" complexed Li+, optimizing the structure and calculating the ground state energy over 4800 points took 158 seconds per point. Whereas, in the case of "PTBT constituent monomer" complexed with Li+, over 5836 points required 2186 seconds per point. This difference arises as the complexity of the latter has increased. Iterative fitting parameters required hundreds of iterations – ranging from 324 to 770 iterations at 20-43 seconds each.

Optimized Coordinates in .xyz Format

- **The following table contains the optimized coordinates in '.xyz' format for Benzene:**

Benzene

12

C −1.174819 1.223403 0.000000

C 0.221741 1.233615 −0.000000

C −1.864225 0.008815 0.000000

C −1.156975 −1.195462 −0.000000

C 0.929020 0.029305 −0.000000

C 0.239640 −1.185238 −0.000000

H 0.759991 2.181391 −0.000000

H 2.018937 0.037355 0.000000

H 0.791460 −2.125177 0.000000

H −1.694887 −2.143404 0.000000

H −2.954141 0.000639 0.000000

H −1.726642 2.163356 0.000000

- **The following table contains the optimized coordinates in '.xyz' format for Benzenethiol:**

Benzenethiol

13

C −1.217609 1.217417 0.000000

C 0.173607 1.271786 0.000000

C −1.878453 −0.010502 0.000000

C −1.131782 −1.187323 0.000000

C 0.921675 0.088785 −0.000000

C 0.261298 −1.143939 0.000000

H 0.676762 2.232634 −0.000000

S 2.702154 0.238004 −0.000000

H 0.827236 −2.069062 0.000000

H −1.632151 −2.149681 −0.000000

H −2.961658 −0.048793 −0.000000

H −1.785330 2.141608 0.000000

H 2.977950 −1.080834 0.000000

- **The following table contains the optimized coordinates in '.xyz' format for Thiophene:**

Thiophene

9

S −0.885944 1.746203 −0.000000

C −2.130702 0.540429 −0.000000

C 0.351837 0.533258 0.000000

C −1.607042 −0.721418 −0.000000

C −0.179051 −0.725584 0.000000

H 1.391390 0.823777 0.000000

H 0.423091 −1.624907 −0.000000

H −2.214382 −1.617249 0.000000

H −3.168597 0.836790 0.000000

- **The following table contains the optimized coordinates in '.xyz' format for "Free TBT monomer":**

Free TBT Monomer

21

S 12.771638 1.352331 −0.856770

H 14.814219 7.902784 −0.850214

C 13.816365 8.323482 −0.823644

C 11.625426 5.288436 −1.501909

C 13.677766 5.307448 −0.234962

C 12.675082 3.198188 −0.874829

H 14.465136 5.843890 0.284929

H 10.845063 3.354036 −2.020916

C 12.641043 6.026050 −0.862821

C 12.619238 7.504991 −0.846136

H 14.502240 3.383679 0.264276

C 11.636698 3.891690 −1.508006

C 13.697933 3.911691 −0.237453

H 10.830523 5.811662 −2.024055

C 13.580541 9.663567 −0.810503

C 11.473711 8.261214 −0.845714

S 11.814193 10.026208 −0.819816

H 14.285256 10.480312 −0.812382

H 10.447610 7.929010 −0.821215

H 11.535235 1.121681 −1.417893

- **The following table contains the optimized coordinates in '.xyz' format for "PTBT constituent monomer":**

PTBT Constituent Monomer

27

S 11.634096 1.382597 −0.147600

H 13.169226 7.809245 −1.330629

C 12.413623 8.253496 −0.693462

C 10.281623 5.244842 −0.167543

C 12.659779 5.281104 0.134659

C 11.511609 3.163138 −0.081749

H 13.585536 5.825853 0.284951

H 9.377056 3.311191 −0.368320

C 11.454985 5.990997 0.011055

C 11.452554 7.471086 0.040160

H 13.640350 3.375309 0.201381

C 10.303844 3.853240 −0.213911

C 12.693117 3.892481 0.091960

H 9.336195 5.757609 −0.302421

C 12.275697 9.601139 −0.552499

C 10.579949 8.255502 0.758224

S 10.939062 9.950747 0.518289

C 13.081465 10.695768 −1.184211

C 9.469926 7.859089 1.687561

H 10.312028 1.126457 −0.193076

H 13.847422 10.261538 −1.830888

H 12.461355 11.357681 −1.796680

H 13.585253 11.315038 −0.435122

H 9.625572 6.842357 2.053343

H 9.422374 8.524402 2.553805

H 8.490433 7.892005 1.197084