Electronic Supplementary Material (ESI) for RSC Advances.

SUPPLEMENTARY INFORMATION

EXCESS CHEMICAL POTENTIAL OF THIOPHENE IN [C_4MIM] [BF_4, Cl, Br, CH_3COO] IONIC LIQUIDS, DETERMINED BY MOLECULAR SIMULATIONS

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1. Structural analysis of thiophene in Ionic liquids, performed with the TRAVIS software.[1, 2]

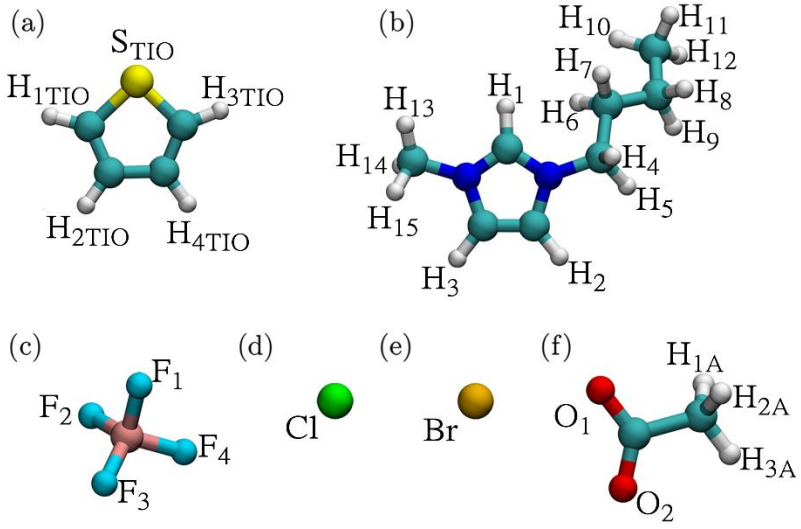

Figure S1. Atomic labels for **(a)** Thiophene, **(b)** 1-butyl-3-methylimidazolium ($[C_4mim]^+$) cation, **(c)** tetrafluoroborate ($[BF_4]^-$) anion, **(d)** chloride ($[Cl]^-$) anion, **(e)** bromide ($[Br]^-$) anion, and **(f)** acetate ($[CH_3COO]^-$) anion.

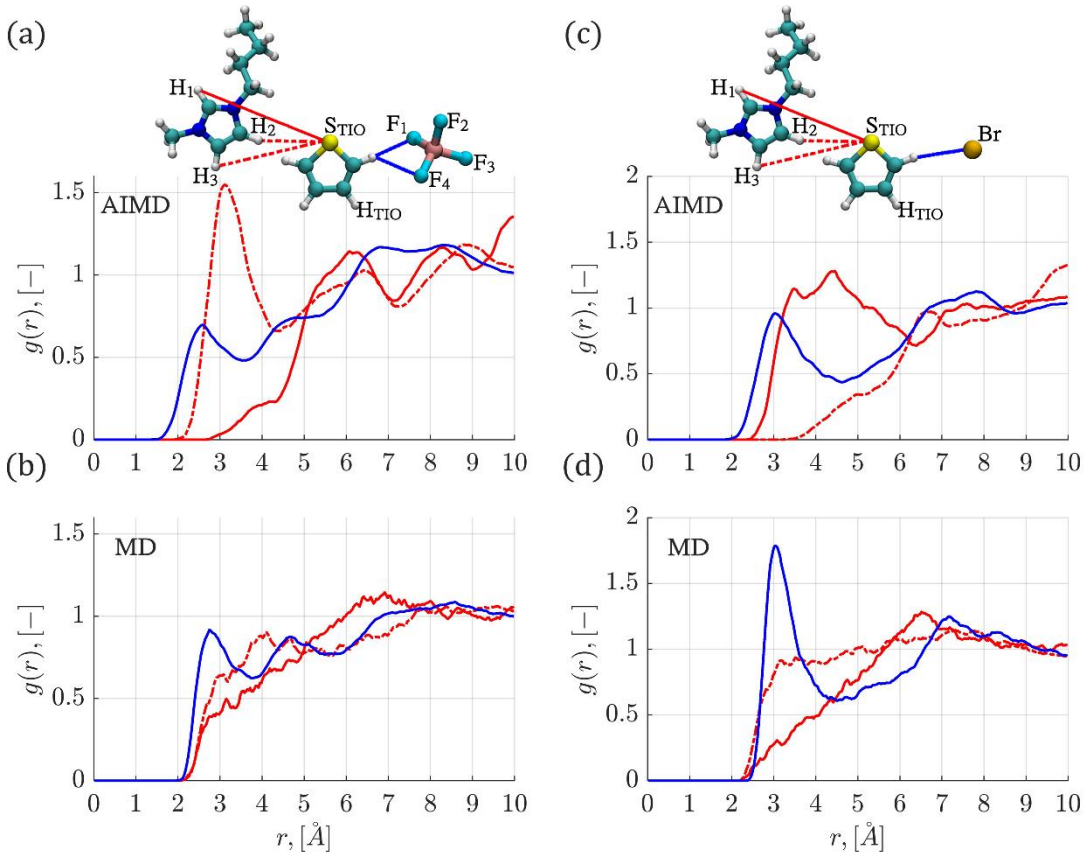

Figure S2. Radial distribution functions involving thiophene atoms paired with atoms from the IL ions, **(a)** AIMD simulations in the [C_4mim][BF_4] IL, **(b)** MD simulations in the [C_4mim][BF_4] IL, **(c)** AIMD simulations in the [C_4mim][Br] IL, **(d)** MD simulations in the [C_4mim][Br] IL; the solid blue line corresponds to the S_{TIO}-anion interaction, the solid red line refers to the S_{TIO}-H_1 interaction, and the dashed red line refers to the S_{TIO}-$H_{2,3}$ interaction.

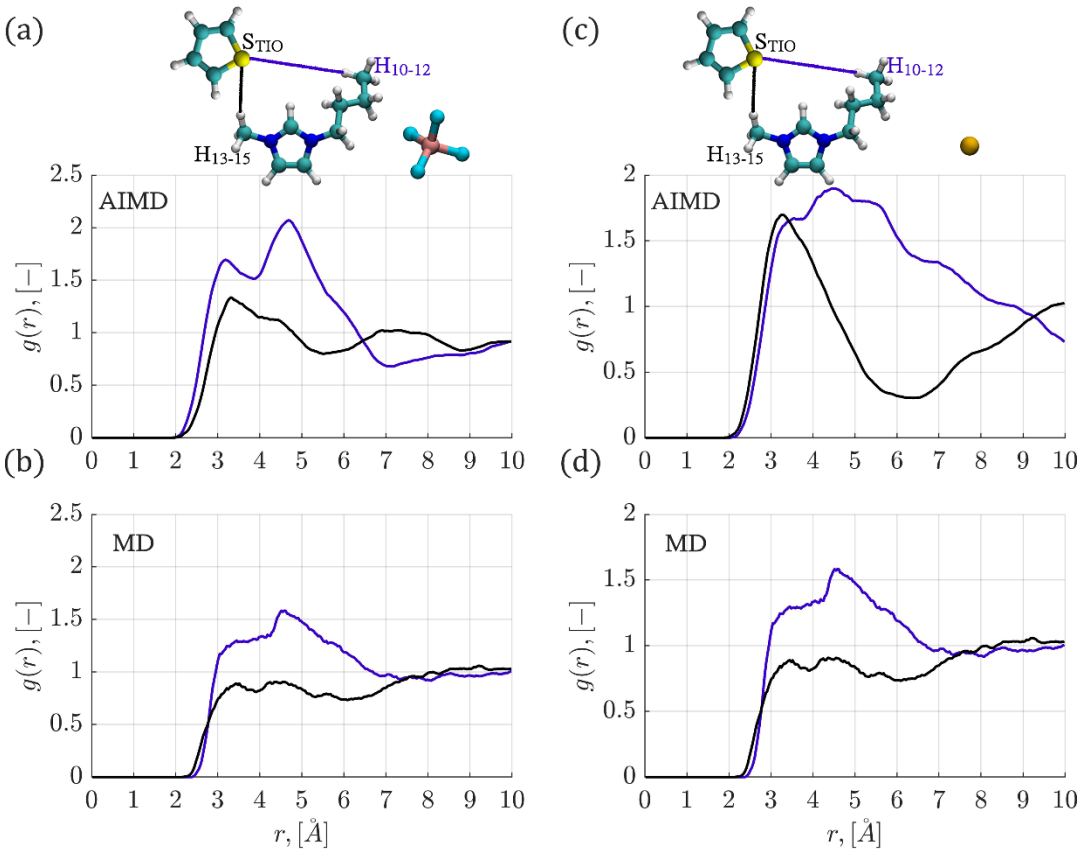

Figure S3. Radial distribution functions between imidazolium side chain-hydrogen atoms (H_{10-15}) paired with the thiophene sulfur atom (S_{TIO}), **(a)** AIMD simulations in the [C_4mim][BF_4] IL, **(b)** MD simulations in the [C_4mim][BF_4] IL, **(c)** AIMD simulations in the [C_4mim][Br] IL and **(d)** MD simulations in the [C_4mim][Br] IL; the blue line corresponds to the S_{TIO}-H_{10-12} interactions, and the black line represents the S_{TIO}-H_{13-15} interactions.

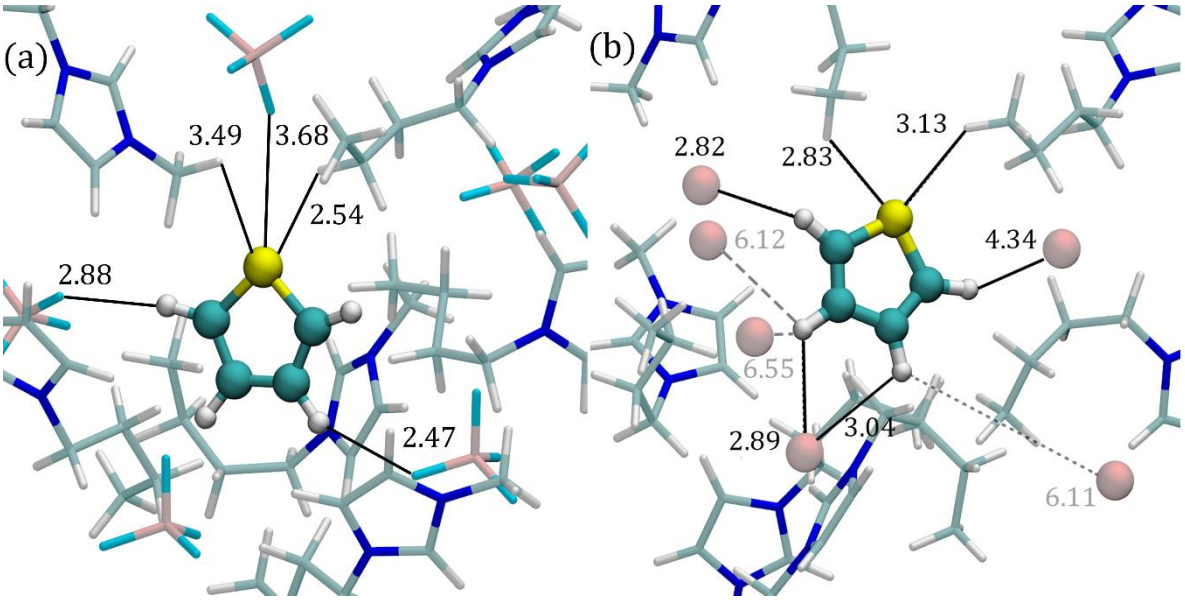

Figure S4. Close molecular environment for the thiophene molecule within the ILs extracted from AIMD simulations. **(a)** [C_4mim][BF_4] IL and **(b)** [C_4mim][Br] IL. The molecular representations were created with the VMD program;[3] and all distances are measured in angstroms.

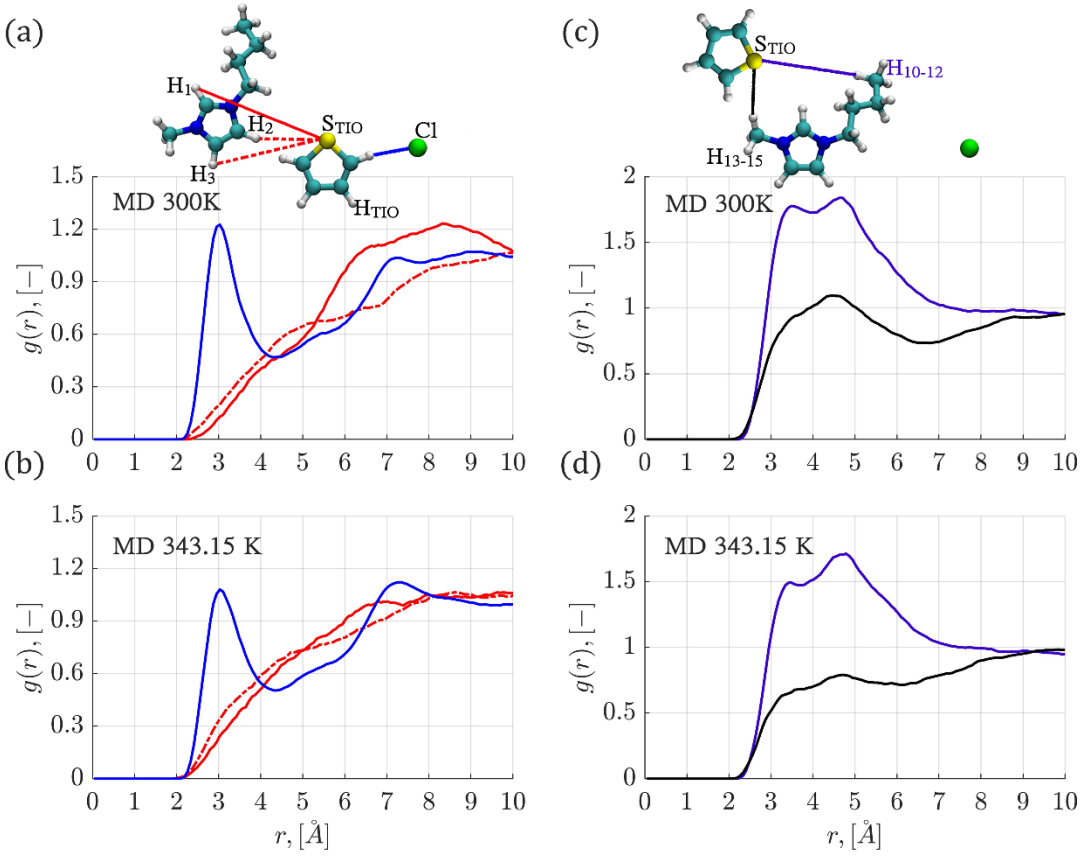

Figure S5. RDFs for the Thiophene-[C4mim][Cl] system, obtained at 300 K and 343.15 K.

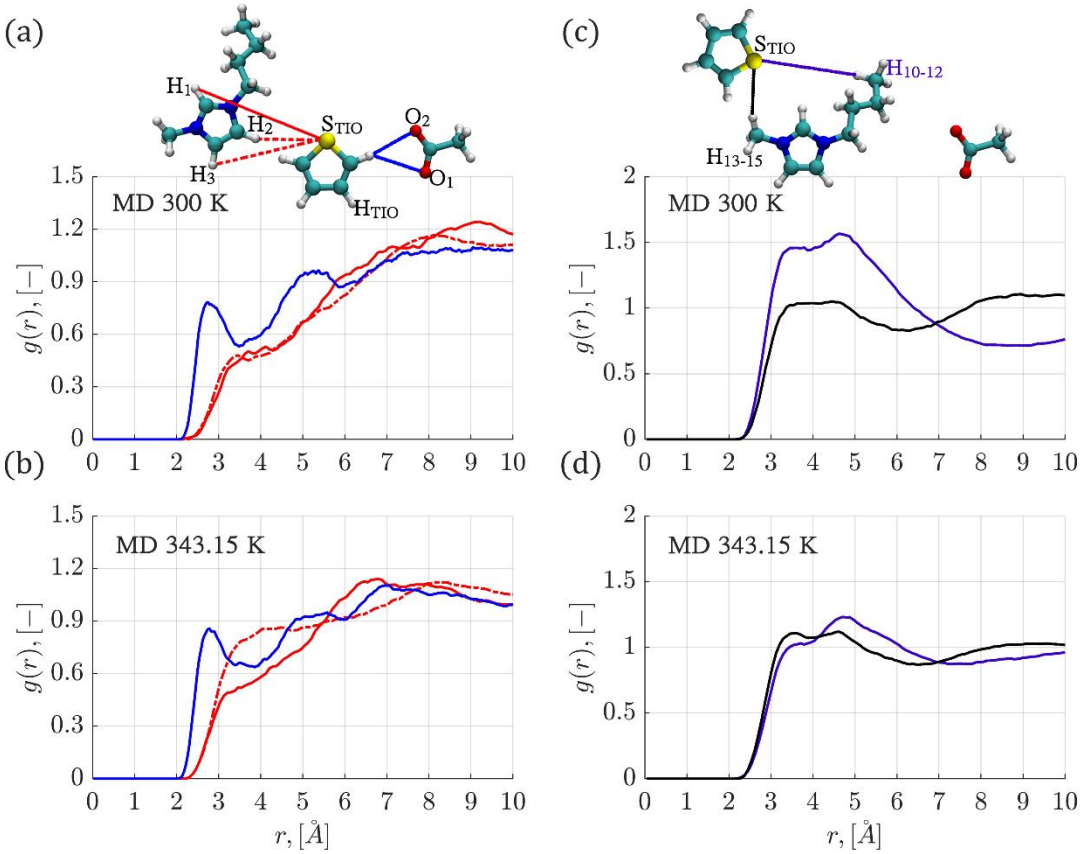

Figure S6. RDFs for the Thiophene-[C_4mim][CH_3COO] system, obtained at 300 K and 343.15 K.

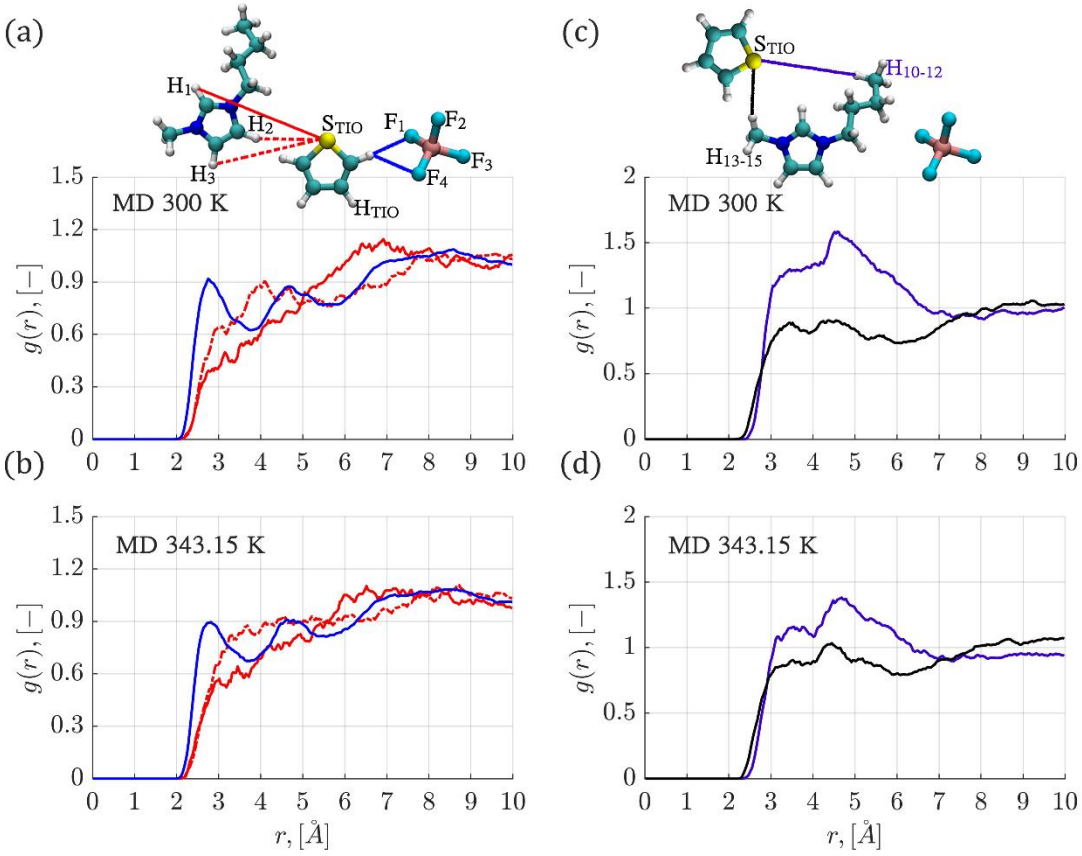

Figure S7. RDFs for the Thiophene-[C_4mim][BF_4] system, obtained at 300 K and 343.15 K.

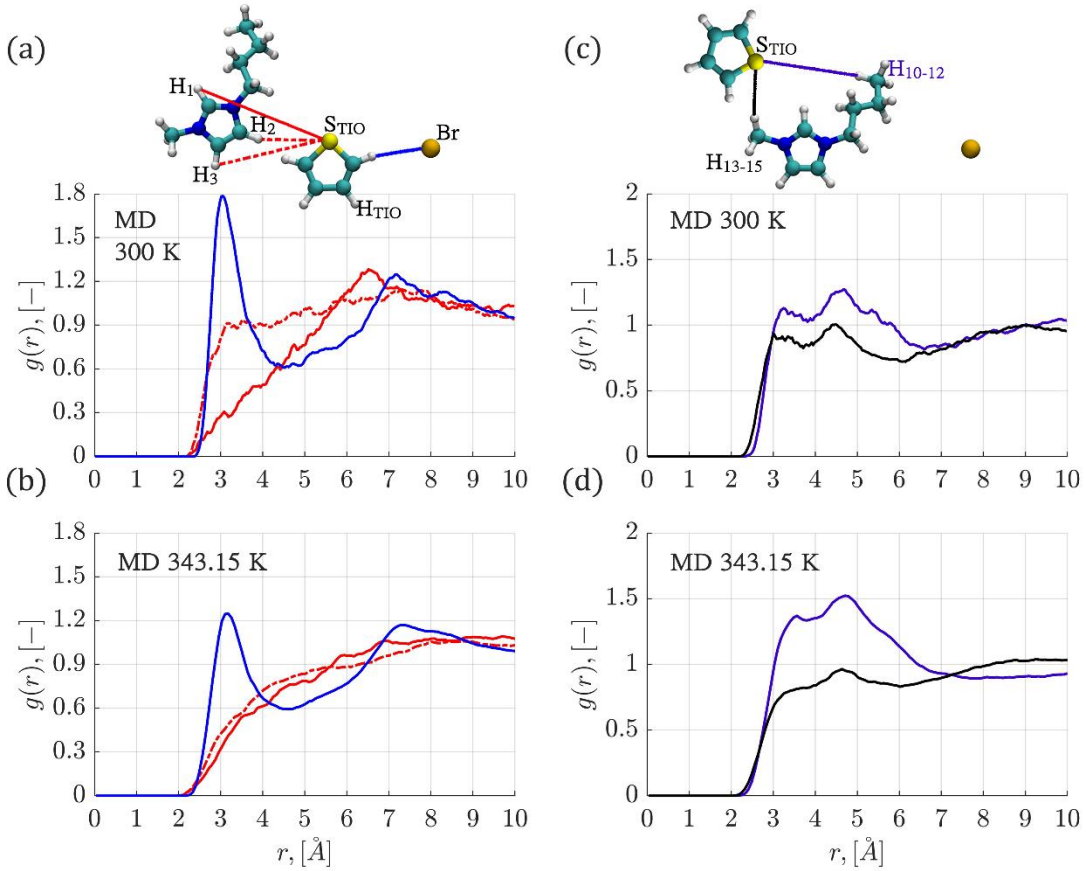

Figure S8. RDFs for the Thiophene-[C_4mim][Br] system, obtained at 300 K and 343.15 K.

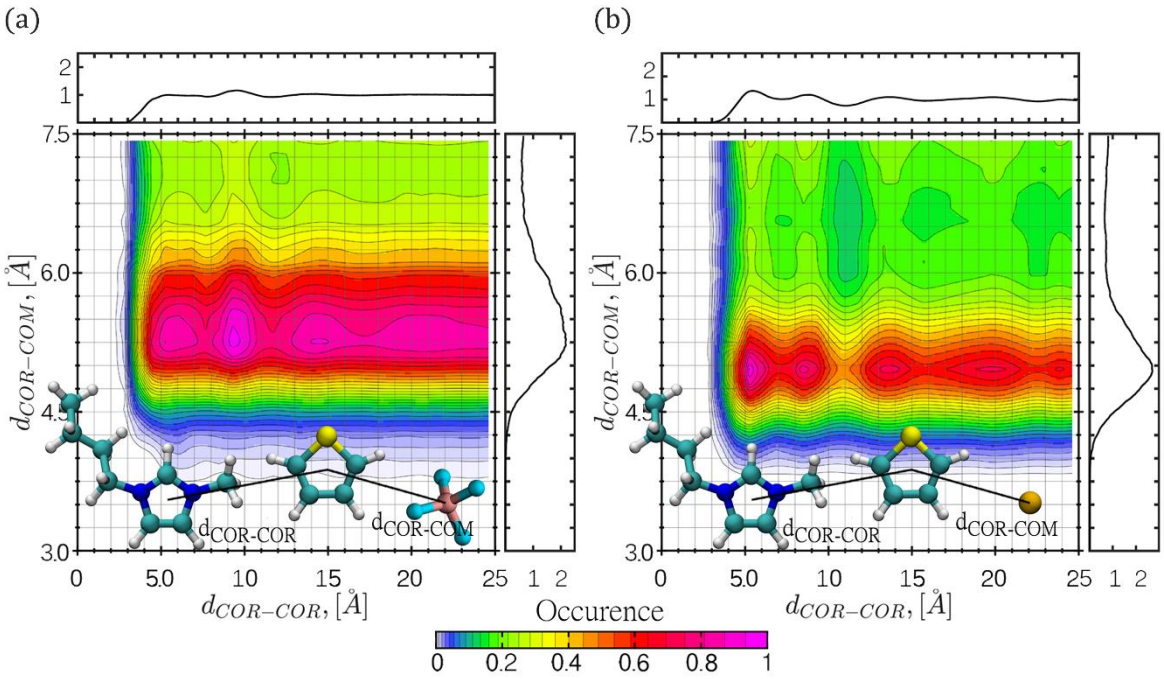

Figure S9. Combined distribution functions (CDFs) for two distances, the first distance involves thiophene-cation interactions and the second distance comprises thiophene-anion interactions **(a)** [C_4mim][BF_4] IL and **(b)** [C_4mim][Br] IL; the corresponding RDFs are also displayed at the top and right side of each figure. The number of occurrences was normalized.

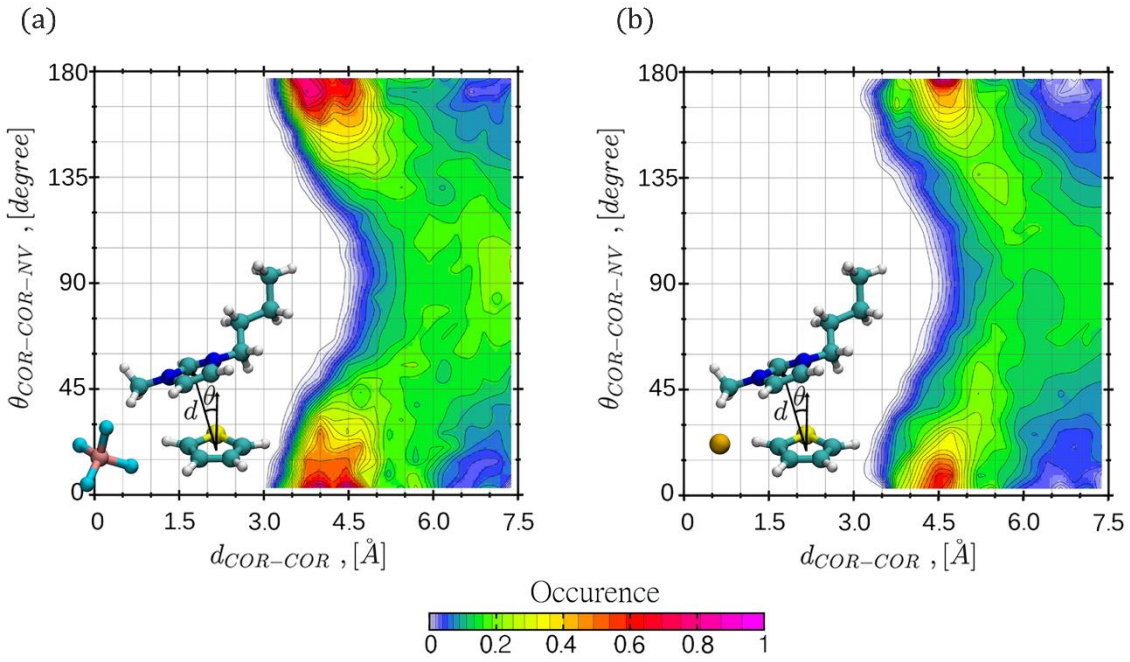

Figure S10. Combined distribution functions (CDF) for the center-of-ring (COR) angle θ and distance d between thiophene and the IL cations for **(a)** [C_4mim][BF_4] IL and **(b)** [C_4mim][Br] IL. The number of occurrences was normalized.

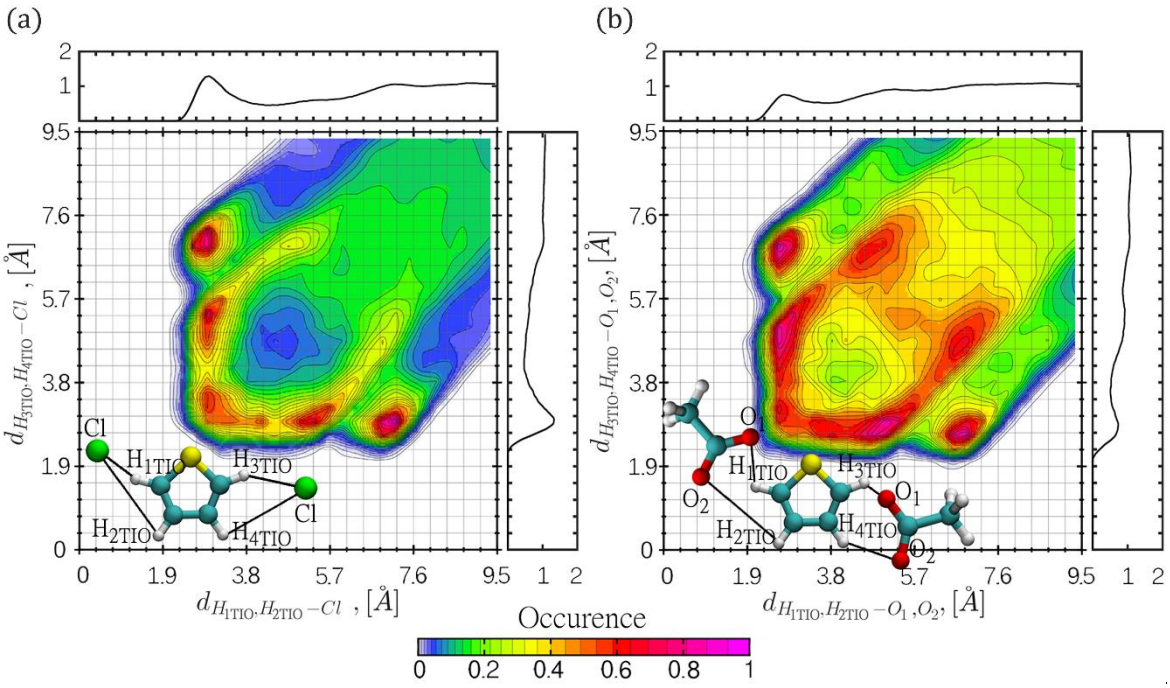

Figure S11. Combined distribution functions (CDFs) between hydrogen ($H_{1\text{-}4TIO}$) atoms from thiophene paired with negative atoms within the IL anion **(a)** [C_4mim][Cl] IL and **(b)** [C_4mim][CH_3COO] IL. The corresponding RDFs are also displayed at the top and right sides in each figure. The number of occurrences was normalized.

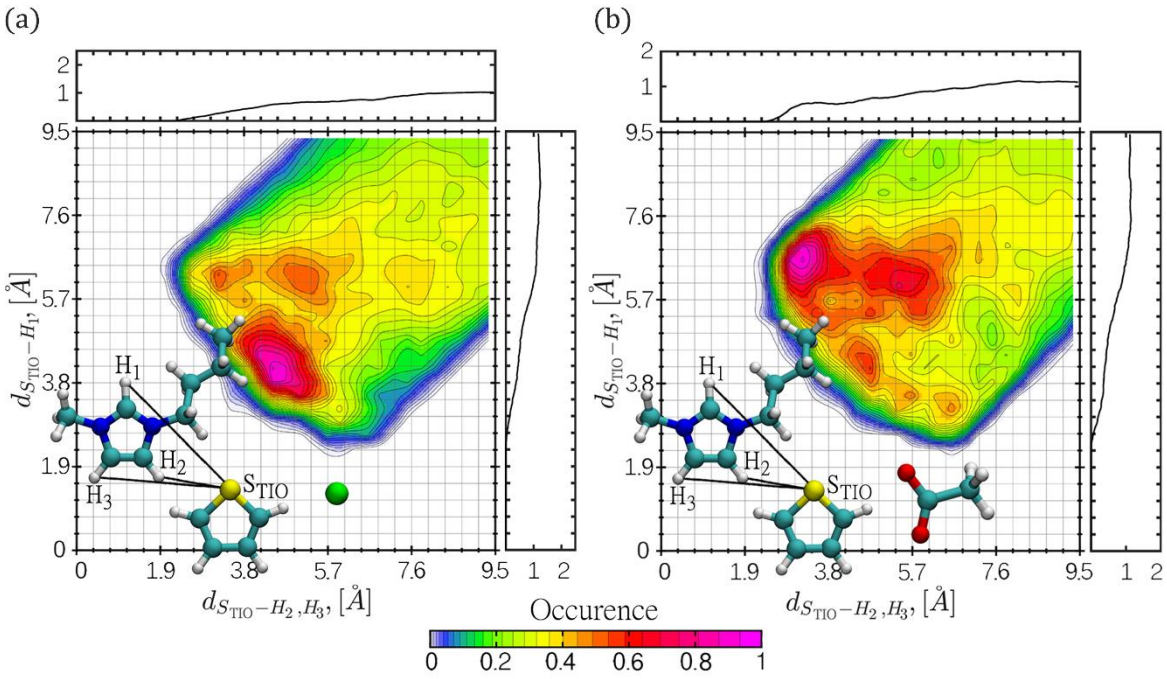

Figure S12. Combined distribution functions (CDFs) between the sulfur (S_{TIO}) atom from thiophene and hydrogen atoms within the imidazolium ring for **(a)** [C_4mim][Cl] IL and **(b)** [C_4mim][CH_3COO] IL. The corresponding RDFs are also displayed at the top and right side of each figure. The number of occurrences was normalized.

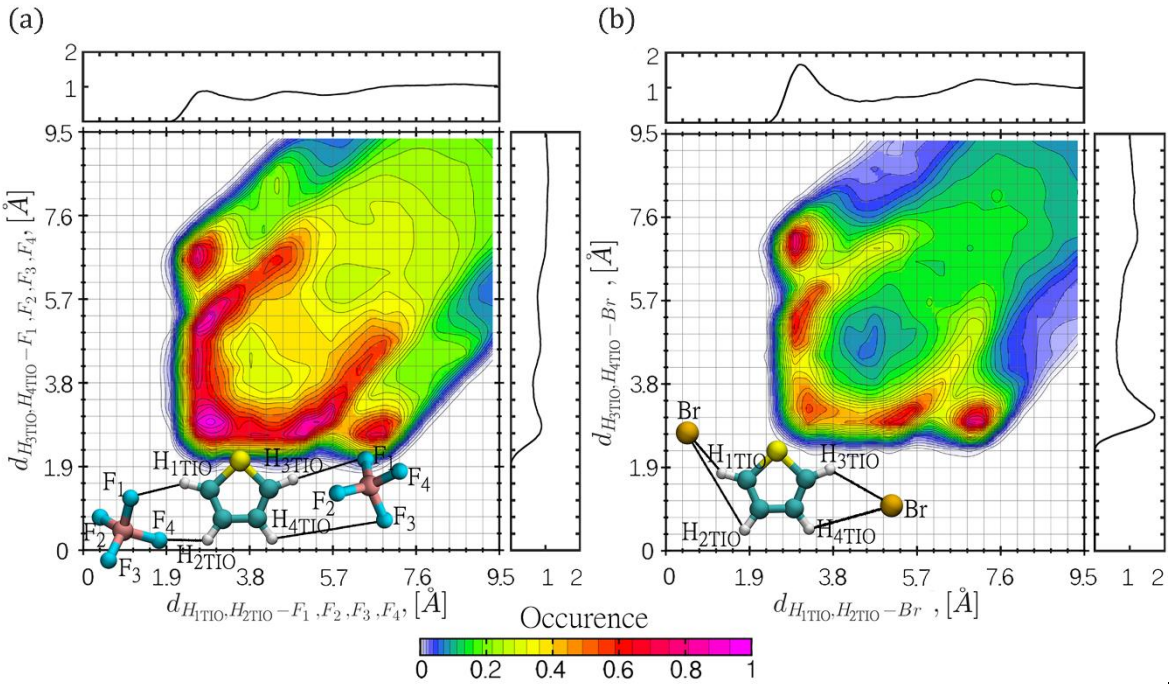

Figure S13. Combined distribution functions (CDFs) for the thiophene hydrogen ($H_{1\text{-}4TIO}$) atoms and negative atoms within the IL anion for **(a)** [C_4mim][BF_4] IL and **(b)** [C_4mim][Br] IL. The corresponding RDFs are also displayed at the top and right sides of each figure. The number of occurrences was normalized.

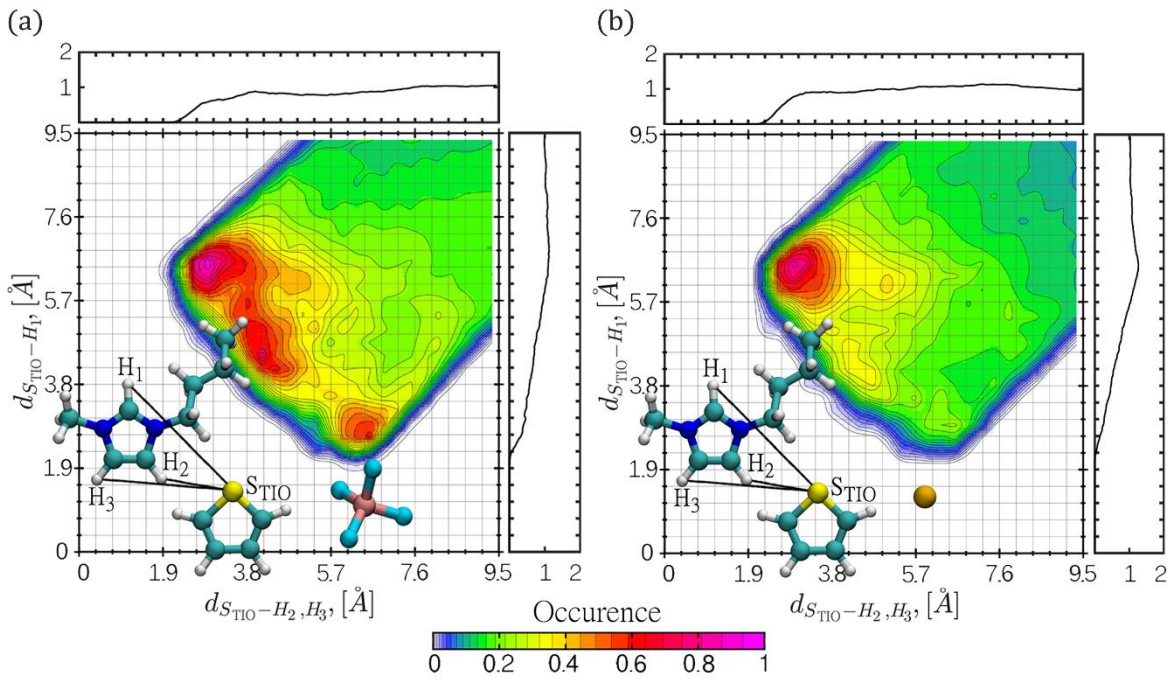

Figure S14. Combined distribution functions (CDFs) for thiophene sulfur (S_{TIO}) atom and top (H_1) and bottom ($H_{2,3}$) hydrogen atoms in imidazolium ring for **(a)** [C_4mim][BF_4] IL and **(b)** [C_4mim][Br] IL. The corresponding RDFs are also displayed at the top and right side of each figure. The number of occurrences was normalized.

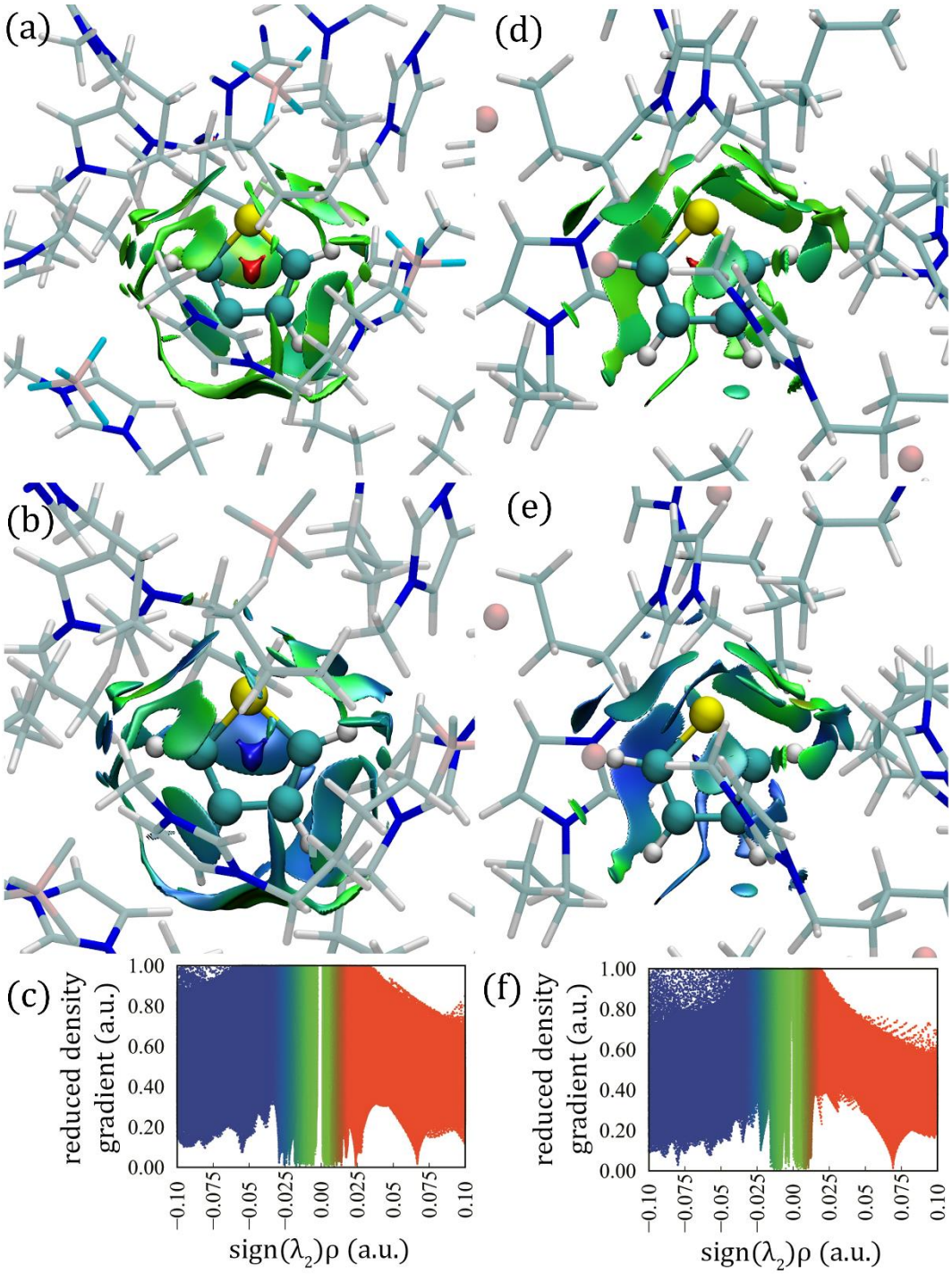

Figure S15. Averaged noncovalent interactions between the thiophene molecule and ILs, (a) aNCI surface, (b) TFI index, and (c) reduced electronic density gradient (s) vs density plot in the thiophene-[C_4mim][BF_4] system; (d) aNCI surface, (e) TFI index and (f) reduced electronic density gradient (s) vs density plot in the thiophene-[C_4mim][Br] system. The aNCI iso-surfaces correspond to s=0.4 a.u., and are colored on a BGR scale of -0.04< ρ < 0.04 a.u; TFI iso-surfaces are colored on a BGR scale within the 0 to 1.5 range.[4]

References.

1. M. Brehm, M. Thomas, S. Gehrke and B. Kirchner, *J. Chem. Phys.*, 2020, **152**, 164105.
2. M. Brehm and B. Kirchner, *J. Chem. Inf. Model.*, 2011, **51**, 2007-2023.
3. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33-38.
4. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.