

Electronic Supplementary Information for

Microscopic properties of ionic liquid / organic semiconductor interfaces revealed by molecular dynamics simulations

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Fig. S1: Full-range number density profiles of ions.

Fig. S2: First-layer snapshots taken from the MD simulations.

Fig. S3: Orientations of ions as a function of the distance from the surface.

Fig. S4: Dihedral distribution function maps of ions as a function of the distance from the surface.

Fig. S5: Representative cation and anion structures at the interfaces.

Fig. S6: XY contour maps of the TFSI anions during a 5-ns simulation.

Fig. S7: XZ contour maps of the BMIM cations and TFSI anions during a 5-ns simulation.

Fig. S8: Details of TASD analyses: construction of a surface distribution image.

Fig. S9: Details of TASD analyses: construction of a TASD image and differential TASD image.

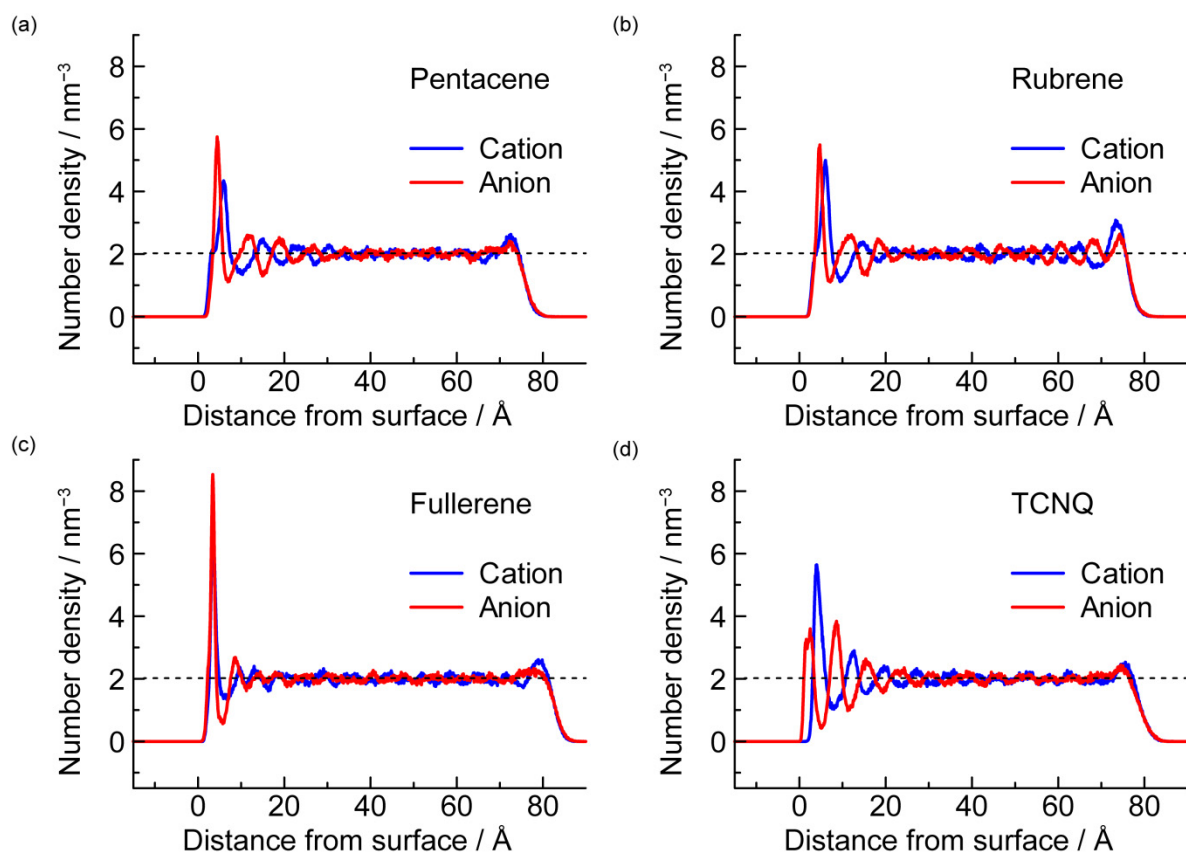


Fig. S1 Full-range number density profiles of the BMIM cation and the TFSI anion at (a) pentacene, (b) rubrene, (c) fullerene, and (d) TCNQ interfaces obtained by a MD simulation at 400 K. Horizontal dotted lines indicate the number density determined by the simulation of bulk BMIM-TFSI.

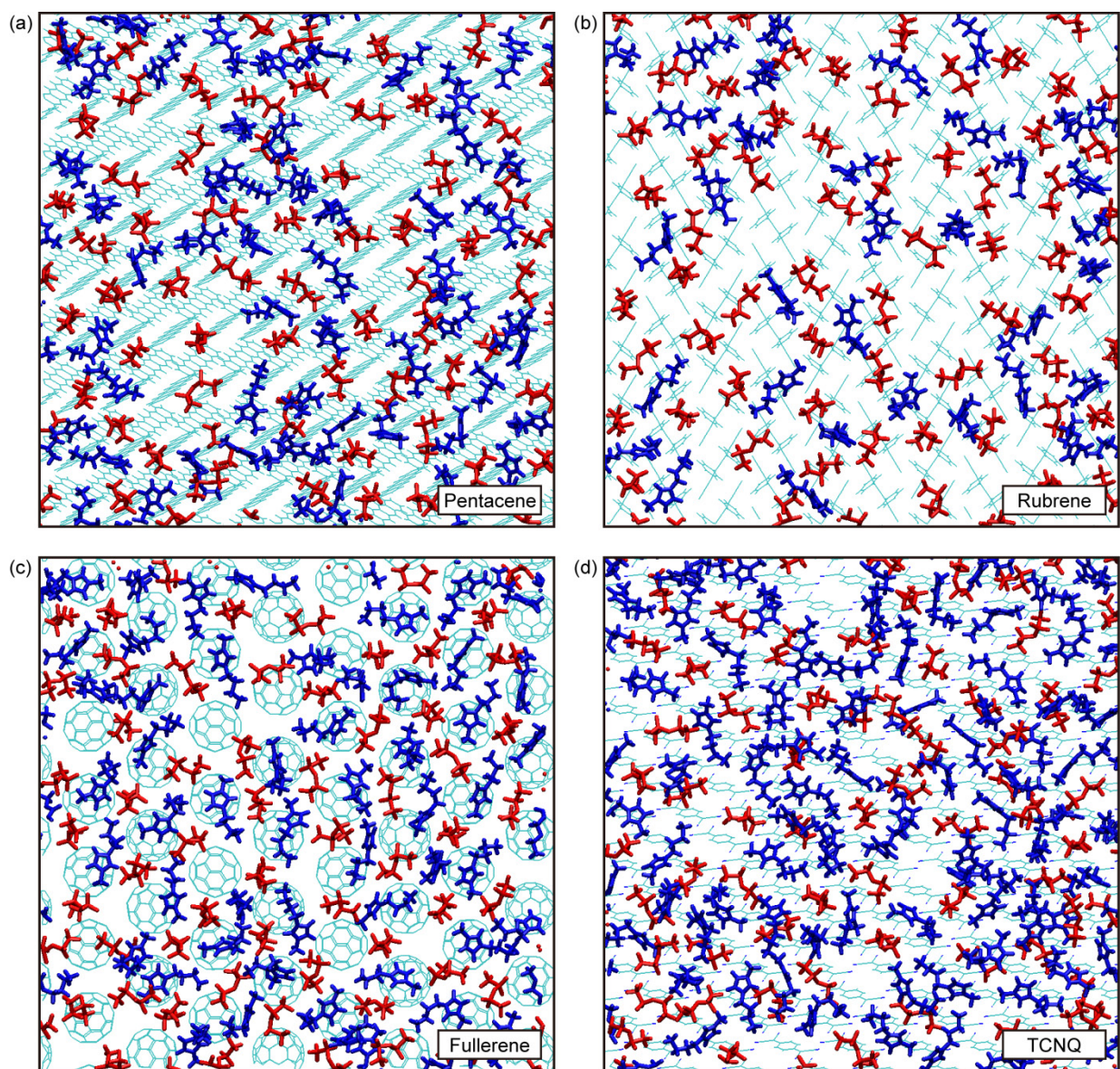


Fig. S2 First-layer snapshots taken from the MD simulation of (a) pentacene, (b) rubrene, (c) fullerene, and (d) TCNQ interfaces. Blue and red ions are BMIM cations and TFSI anions, respectively, within 6 Å of the surface. Only the uppermost molecular layer of the substrates is presented for clarity.

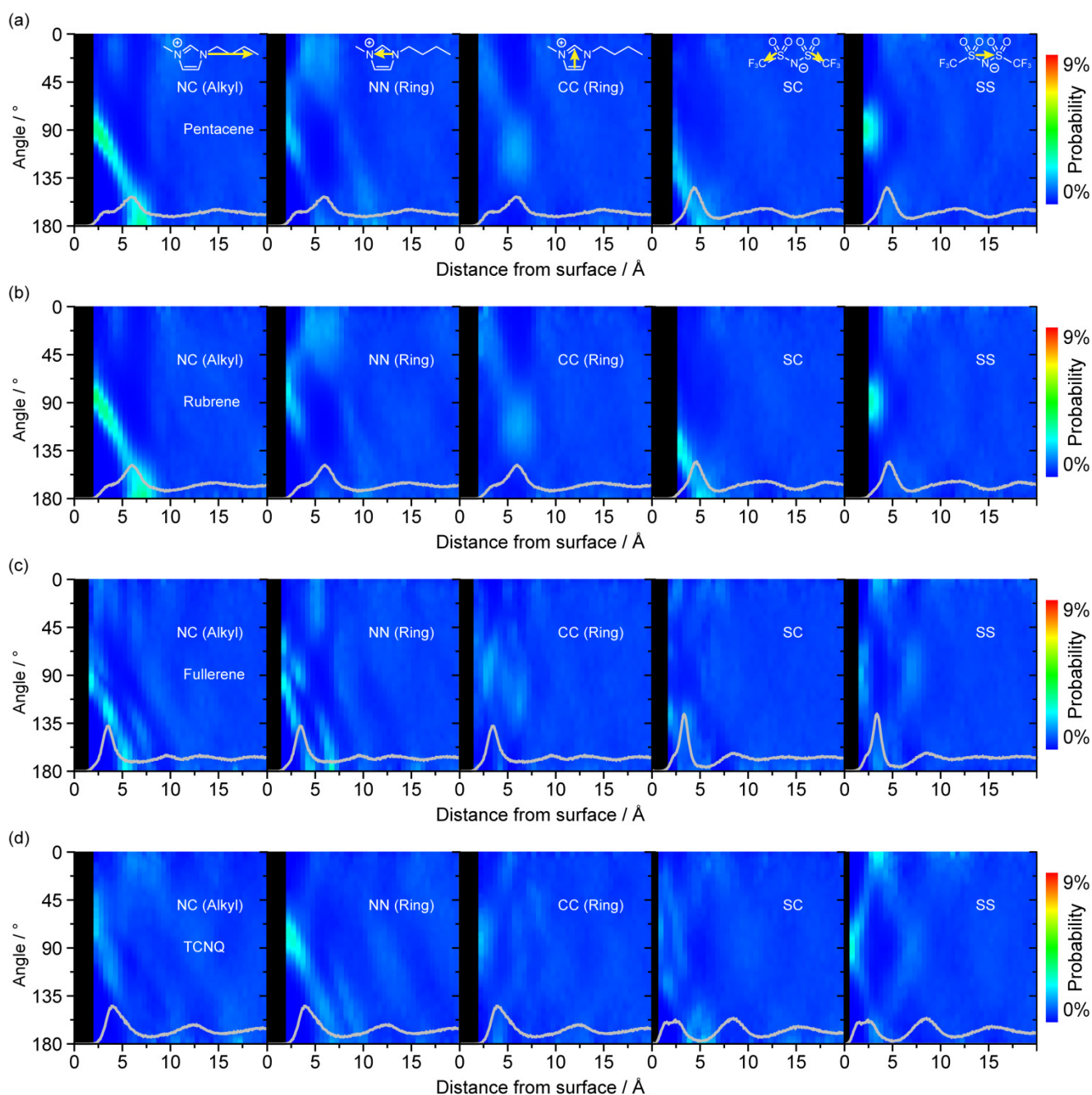


Fig. S3 Orientations of BMIM cations and TFSI anions as a function of distance from the surface at (a) pentacene, (b) rubrene, (c) fullerene, and (d) TCNQ interfaces. The vertical axis is the angle between the surface normal and the vector defined in (a). The bin sizes for the lateral and vertical axes are 0.5 Å and 10°, respectively. The number density profiles of cations and anions in arbitrary units are superimposed on each panel for comparison (grey lines). Black areas indicate that the number density of ions is less than 10% of the bulk number density.

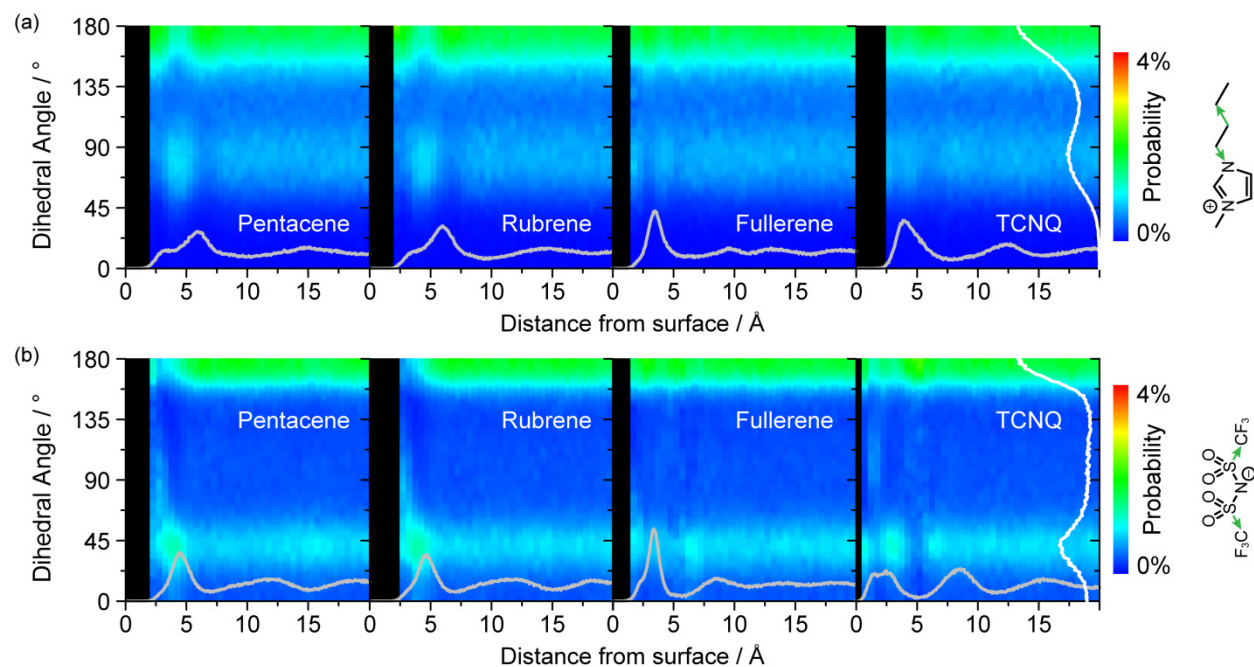


Fig. S4 Dihedral distribution function maps of (a) the BMIM cation and (b) the TFSI anion at organic semiconductor interfaces as a function of the distance from the surface. The vectors that define the dihedral angle are depicted in each panel. The bin sizes for the lateral and vertical axes are 0.5 \AA and 10° , respectively. The number density profiles of cations and anions, in arbitrary units, are superimposed in each panel (grey lines). Dihedral distribution functions of the bulk ionic liquid, in arbitrary units, are superimposed in TCNQ panels (white lines). Black areas indicate that the number density of ions is less than 10% of the bulk number density.

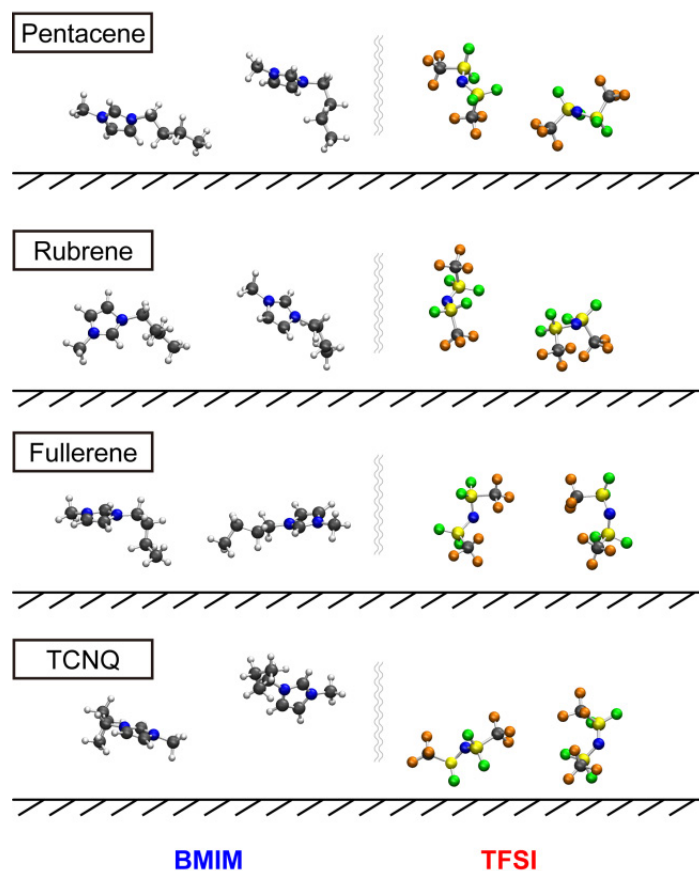


Fig. S5 The representative cation and anion structures at pentacene, rubrene, fullerene, and TCNQ interfaces taken from the MD simulation. The lateral solid lines in each panel represent $z = 0$. Gray, blue, white, yellow, green, and orange spheres represent the positions of carbon, nitrogen, hydrogen, sulfur, oxygen, and fluorine atoms, respectively.

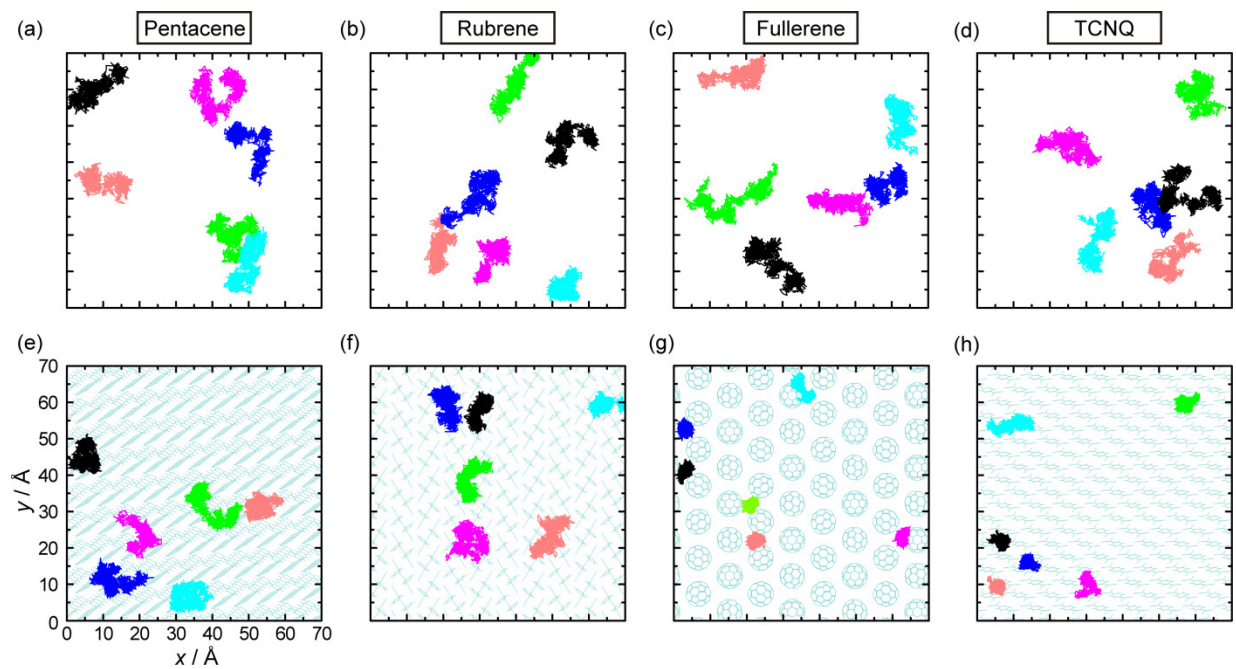


Fig. S6 XY contour maps ($7 \times 7 \text{ nm}^2$) for six TFSI anions during a 5-ns simulation (a)–(d) at the bulk region (the initial z -positions were $38 < z < 43 \text{ \AA}$) and (e)–(h) at the first layer ($z < 6 \text{ \AA}$); (a)(e) pentacene, (b)(f) rubrene, (c)(g) fullerene, and (d)(h) TCNQ interfaces. Different colors represent different ions. For (e)–(h), the substrate structures are superimposed.

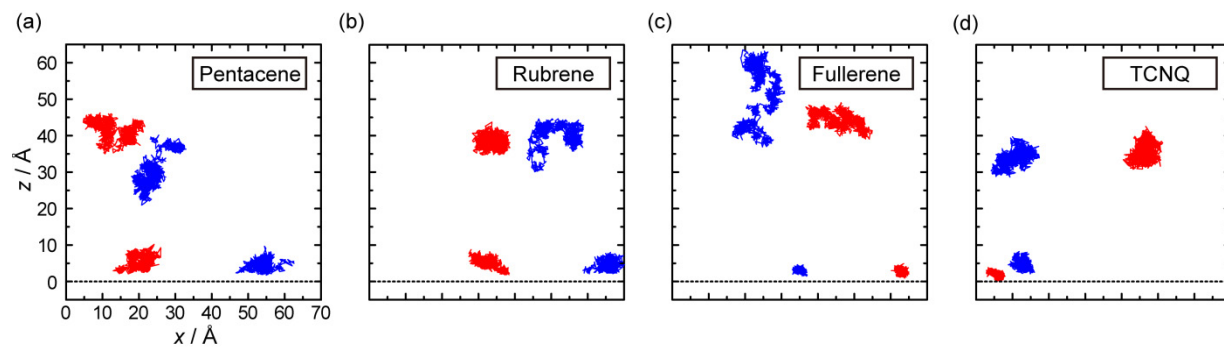


Fig. S7 XZ contour maps ($7 \times 7 \text{ nm}^2$) for two BMIM cations (blue) and two TFSI anions (red) during a 5-ns simulation at (a) pentacene, (b) rubrene, (c) fullerene, and (d) TCNQ interfaces. Ions at the bulk region and the first layer are categorized as in Fig. 5 and S6, and are randomly-chosen within each category.

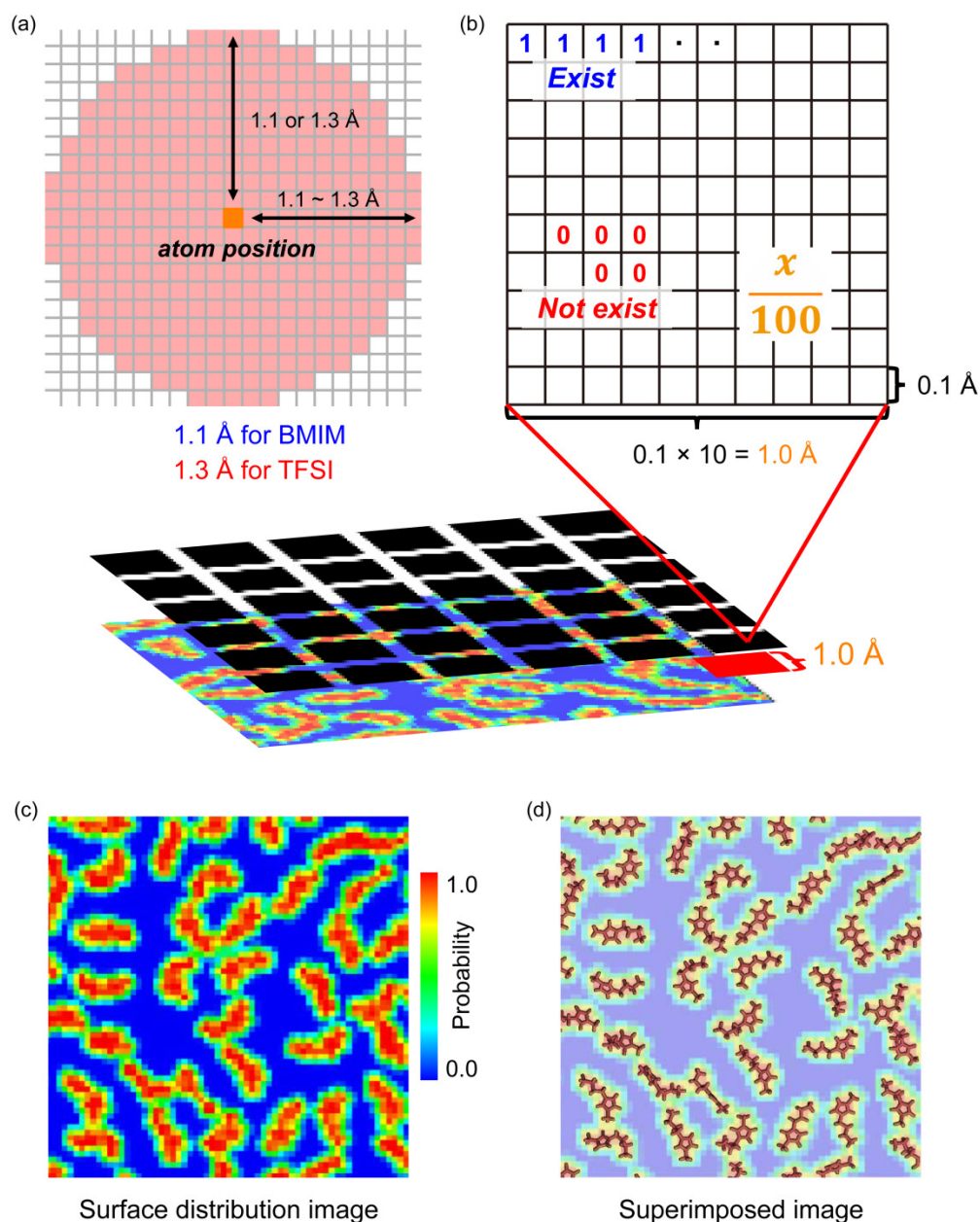


Fig. S8 Construction of a surface distribution (SD) image. (a) Individual atoms of the first-layer BMIM or TFSI ions, whose z -positions are less than 6 Å from the surface, occupy the surface area within 1.1 or 1.3 Å, respectively. (b) Occupancy of $0.1 \times 0.1 \text{ Å}^2$ areas (determined as shown in (a)) are digitized as 1 (exists) or 0 (does not exist). The probability of the surface occupancy of the matrix in a $1.0 \times 1.0 \text{ Å}^2$ area (see illustration at the bottom) is calculated by summing the stored digital data and dividing by 100. (c) An SD image is constructed as the contour map of the calculated probability values. (d) SD image with a superimposed MD snapshot shows the contribution of averaged van der Waals radii to our SD analysis.

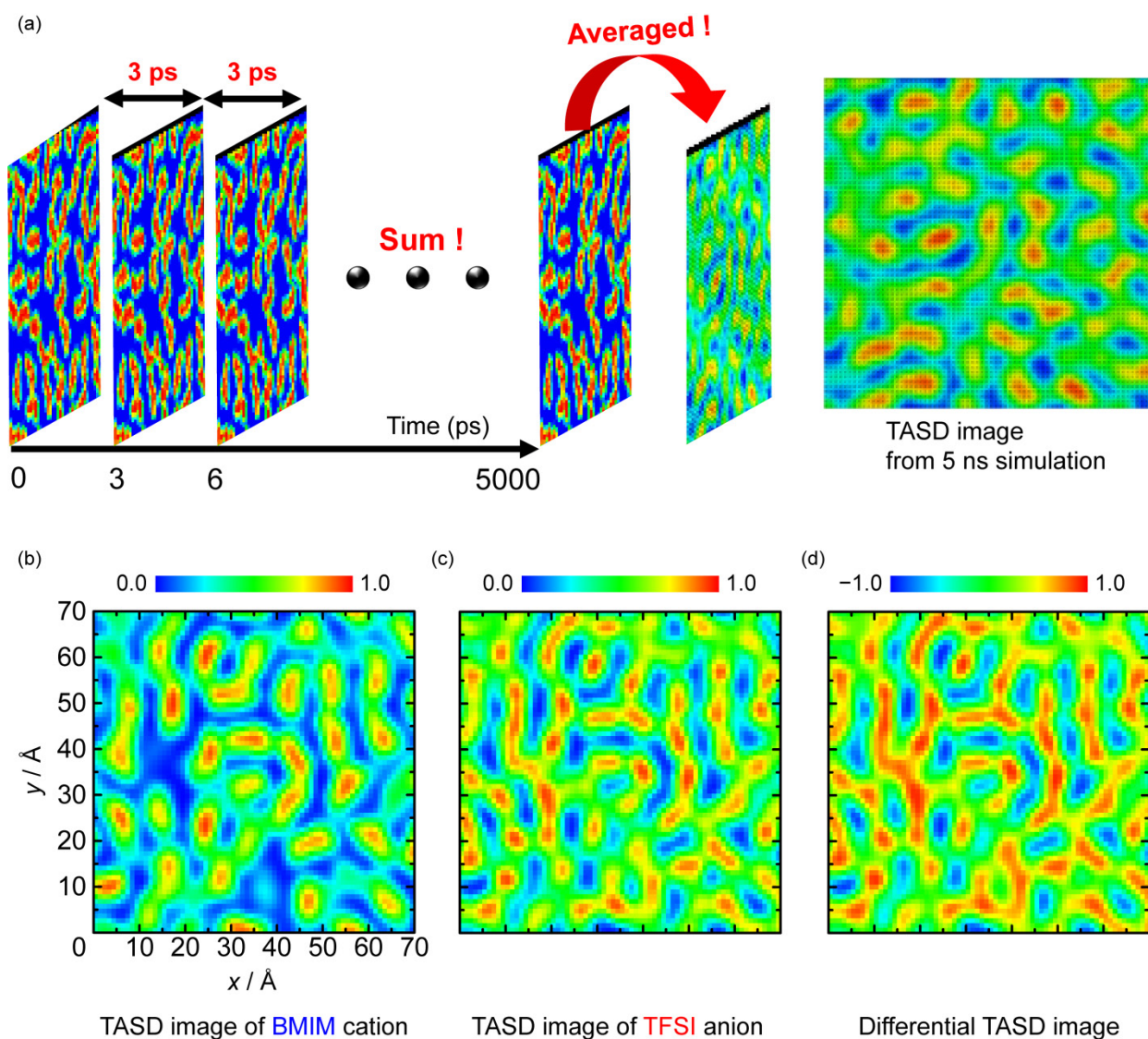


Fig. S9 Construction of a time-averaged SD (TASD) image and differential TASD image. (a) Individual SD images are constructed for each 3-ps step for 5 ns, and 1667 SD images are averaged to obtain a TASD image. TASD images of (b) the BMIM cation and (c) the TFSI anion, respectively. Averaging decreases the image contrast compared to the SD image shown in Fig. S8(c). (d) A differential TASD image from subtraction of the TASD (BMIM) image (b) from the TASD (TFSI) image (c). Blue and red represent the BMIM- and TFSI-rich regions, respectively, at the surface during a 5-ns simulation. Note that the theoretical TASD and differential TASD images of bulk BMIM-TFSI, constructed from an infinite simulation, should be monotonically green.