Supporting Information

Reactive Interactions between the Ionic Liquid BMP-TFSI and a Na surface

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Table S1. Lattice parameters of the bcc and hcp crystal structure of Na, adsorption properties of (decomposed) BMP-TFSI on Na surfaces for different PAW potentials of Na including either one valence electron (Na_s1p0) or 7 valence electrons (Na_p6s1)

	bcc-Na		hcp-Na	
	Na_s1p0	Na_p6s1	Na_s1p0	Na_p6s1
a / Å	4.286	4.286	3.829	3.829
c / Å	-	-	6.209	6.209
	bcc-Na(100)		hcp-Na(0001)	
E_{ad} (BMP-TFSI) /eV	-1.23	-1.18	-1.28	-1.22
d (N_{BMP} – top most Na atoms) / Å				
d (N_{TFSI} – top most Na atoms) / Å				
E_{ad} (BMP-NSO_2CF_3-SO_2CF_3) /eV	-4.70	-4.59		-4.60

Table S2. Comparison of adsorption energies (in eV) of BMP-TFSI on Na surfaces for different k-points sets.

	bcc-Na(100)		hcp-Na(0001) *4 atomic layers*		hcp-Na(0001) *3 atomic layers*	
	Na_s1p0	Na_p6s1	Na_s1p0	Na_p6s1	Na_s1p0	Na_p6s1
1x1x1	-1.25	-1.2	-1.50	-1.46	-1.55	
2x2x1	-1.27		-1.31		-1.25	
m-2x2x1	-1.23	-1.18	-1.28	-1.22		-1.24

Table S3. Comparison of N 1s core level binding energy (in eV) of the N atom of TFSI in an adsorption structure of intact BMP-TFSI on different Na surfaces for different k-points sets, different numbers of atomic layers of the surface slab and different PAW potentials

	m-2x2x1		2x2x1	1x1x1
	Na_p6s1	Na_s1p0	Na_s1p0	Na_s1p0
bcc-Na(100) *5 atomic layers*	400.5			
hcp-Na(0001) *4 atomic layers*	400.5	400.5	400.5	400.3
hcp-Na(0001) *3 atomic layers*	400.5		400.5	

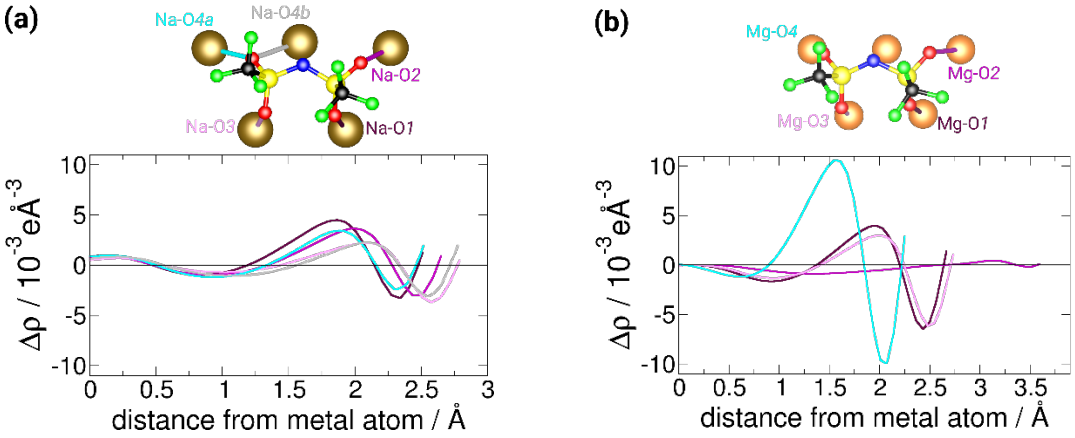

Figure S1. Charge density difference due to adsorption of BMP-TFSI on (a) Na(0001) and (b) Mg(0001) along the metal atom – oxygen atom bond.

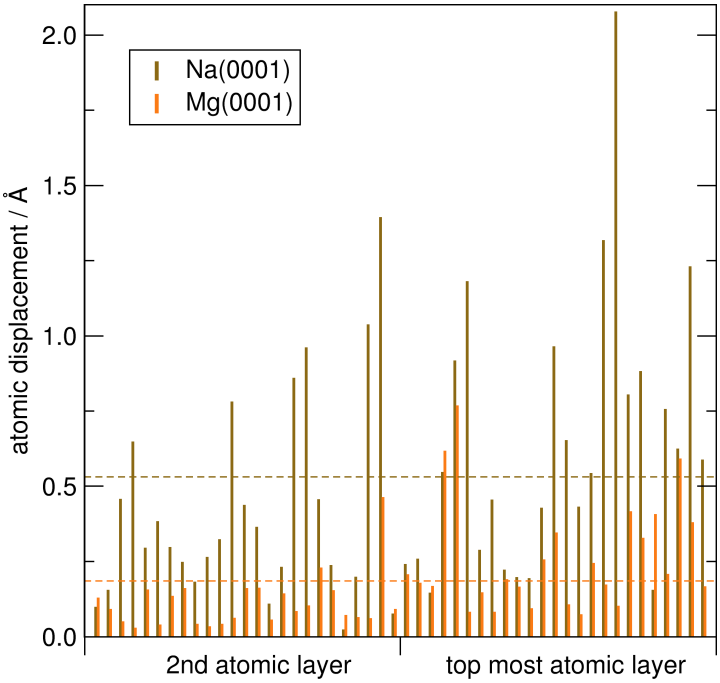

Figure S2. Displacement of Na or Mg atoms in the decomposition structures shown in Figure 3 from their respective positions in the bare (0001) surfaces. The dashed lines denote the respective average values.

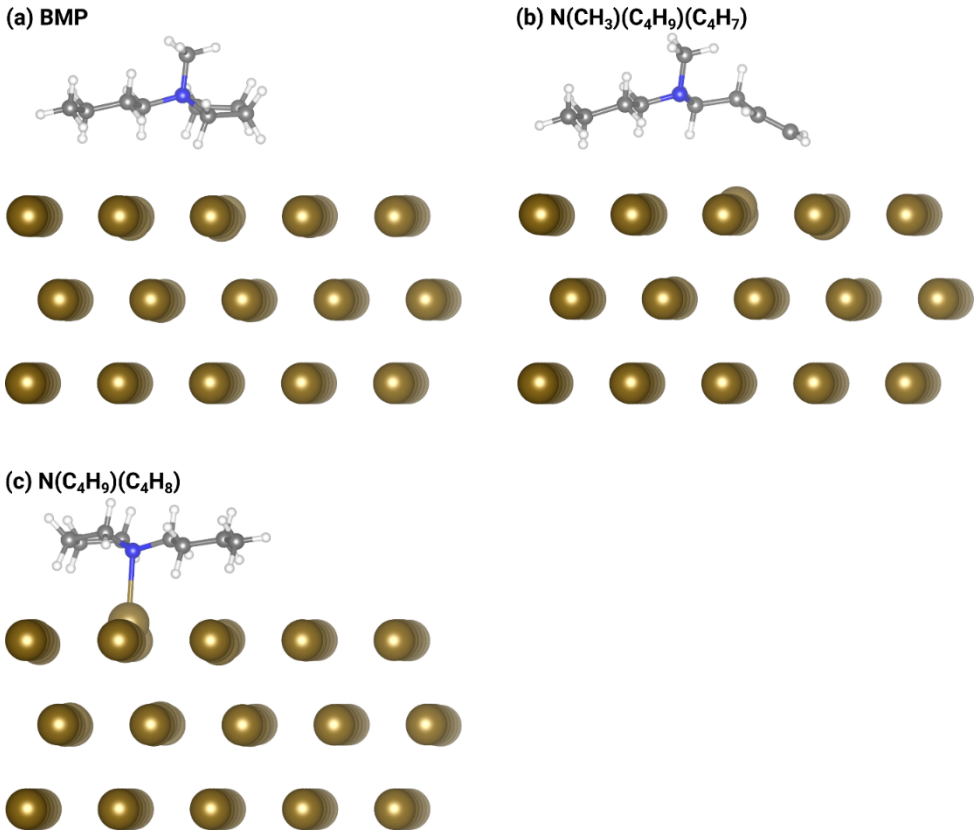

Figure S3. Structural models of the adsorption complexes of BMP and BMP based fragments on Na(0001).

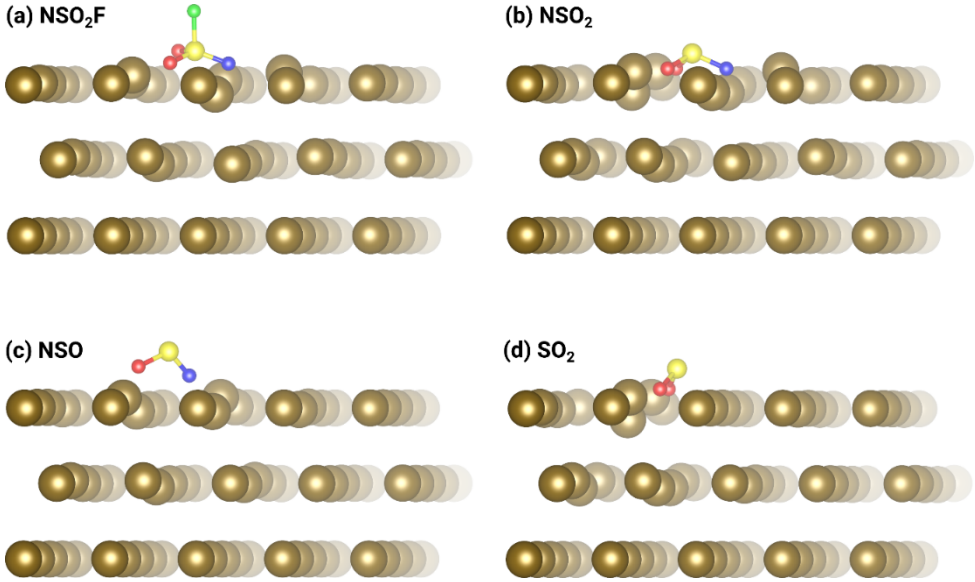

Figure S4. Structural models of the adsorption complexes of TFSI based fragments on Na(0001).

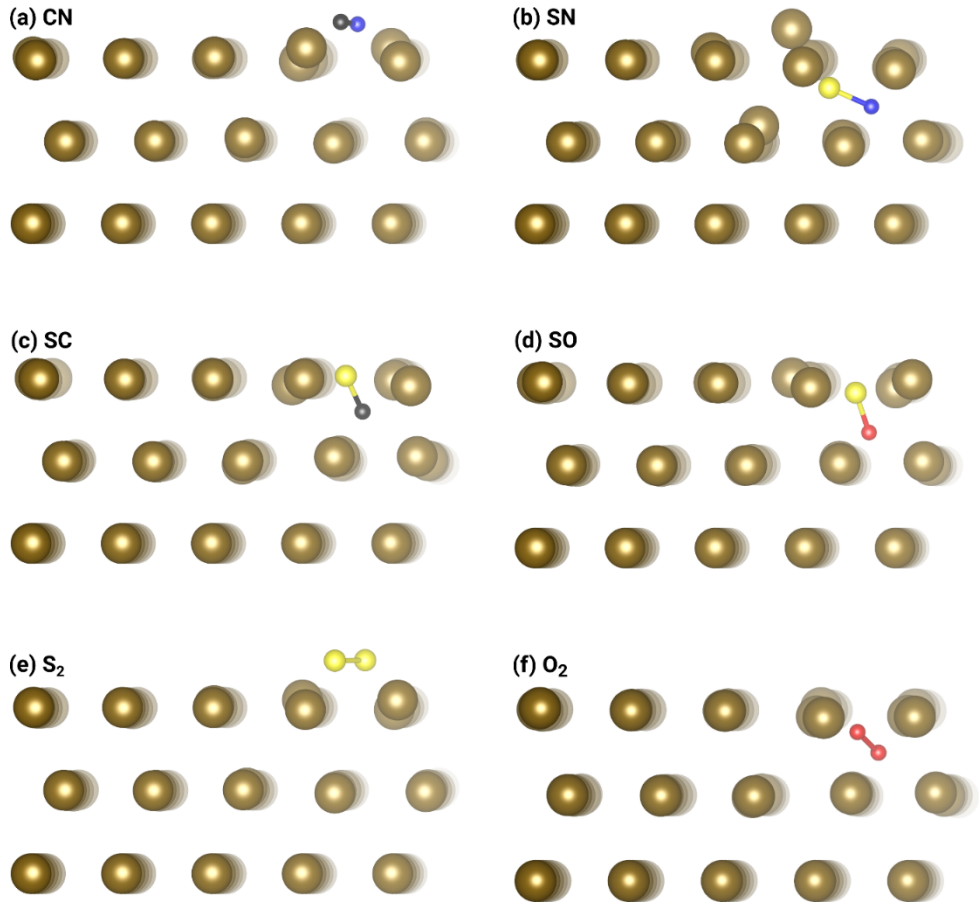

Figure S5. Structural models of the adsorption complexes of TFSI based diatomic fragments on Na(0001).

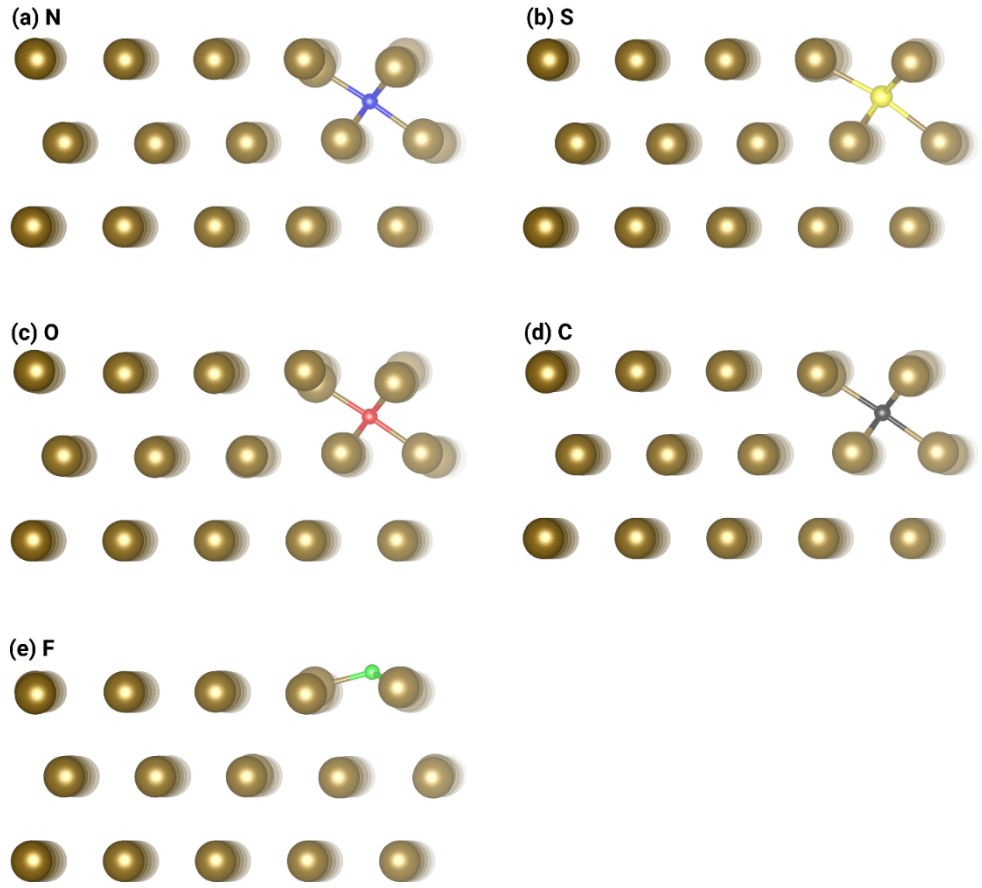

Figure S6. Structural models of the adsorption complexes of TFSI based atomic fragments on Na(0001).

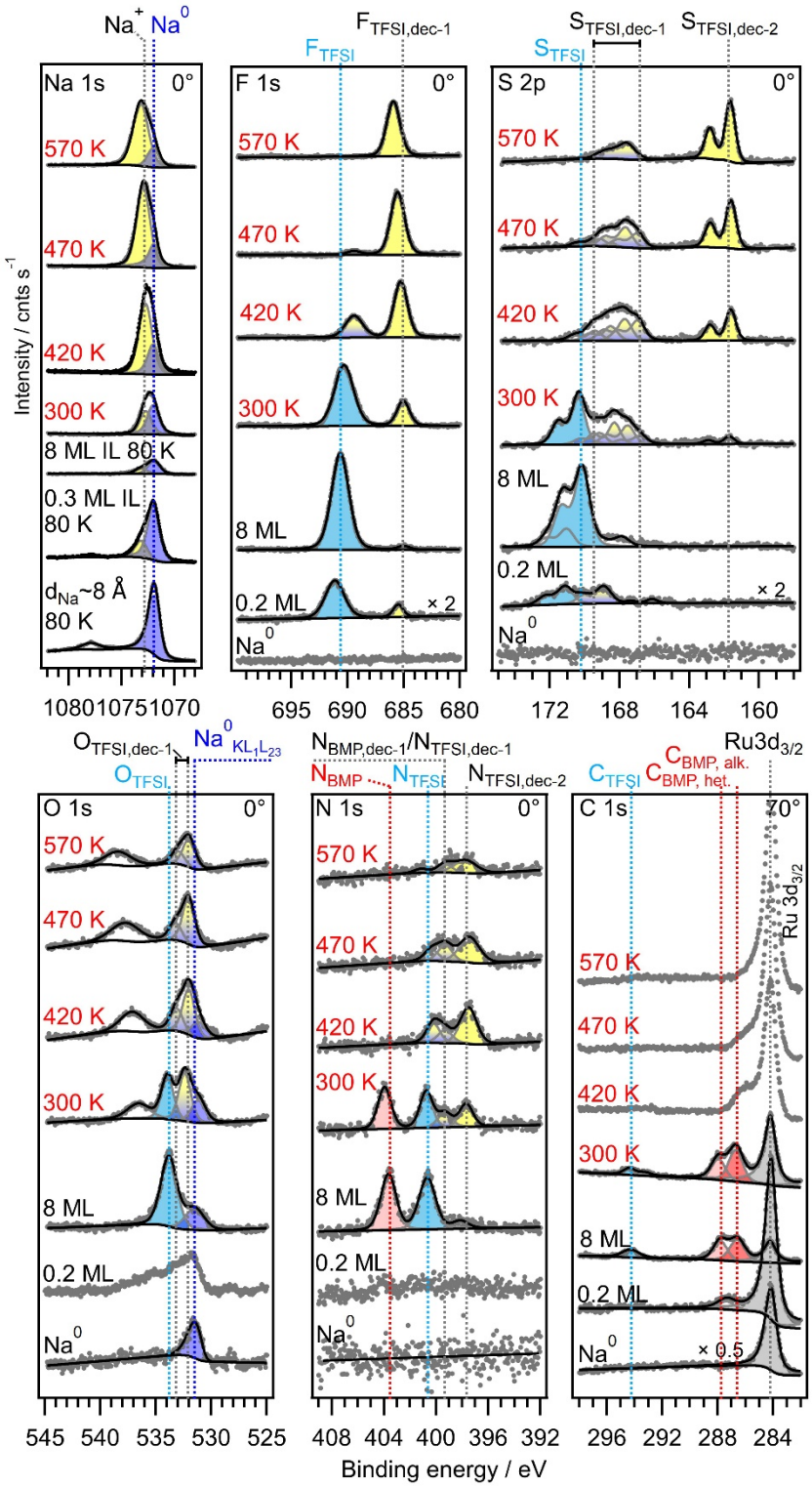

Figure S7. Stepwise IL deposition on a Na film at 80 K, up to 10 Ml, and thermal stability test. Calculated BEs on top of each panel.