Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION:

The interaction of ethylammonium tetrafluoroborate [$EtNH_3^+$][BF_4^-] ionic liquid on the Li(001) surface: towards understanding early SEI formation on Li metal

[a]Jonathan Clarke-Hannaford, *[b]Michael Breedon, [b]Adam S. Best, *[a]Michelle J.S Spencer

[a]*School of Science, RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia*
[b]*CSIRO Manufacturing, Private Bag 10, Clayton South, Victoria 3169, Australia*
*Author to whom correspondence should be addressed
Corresponding Author E-mail: michelle.spencer@rmit.edu.au; michael.breedon@csiro.au

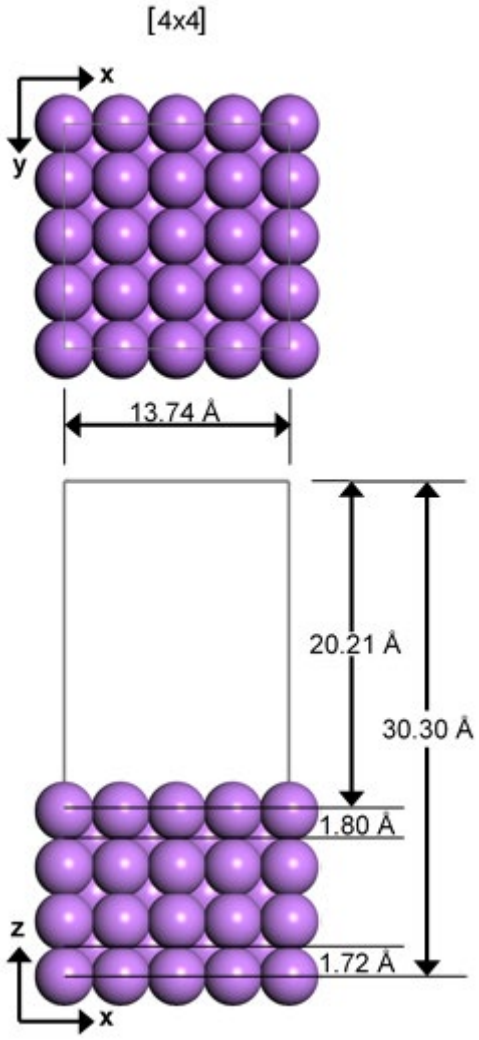


Figure S1. Supercells of the Li(001)-[4x4] surface showing top (above) and side (below) views.

Table S1. Geometric details and binding energy for the optimised $EtNH_3^+$, BF_4^- ions and the $[EtNH_3^+][BF_4^-]$ ion pair compared to previous theoretical results [1-3] and experimental findings [4]. ⟨H⟩ represents the average of all H atoms bonded to the element -X. Distances are in angstroms and angles are in degrees. Binding energy is shown in eV.

Measurement	**Index**	**Isolated Ion**	**[2]**	**[3]**	**[4]**	**Pair**	**[1]**
Distance							
d(C-C)	C1-C2	1.51	1.52	N/A	N/A	1.52	N/A
d(C-N)	C2-N	1.53	1.52			1.50	
d(C-H)	C1-⟨H⟩	1.10	1.09			1.10	
	C2-⟨H⟩	1.10	1.09			1.10	
d(N-H)	N-H1	1.03	1.03			1.03	
	N-H2	1.03	1.03			1.06	1.04
	N-H3	1.03	1.03			1.06	
d(B-F)	B-F1	1.43	N/A	1.42	1.43±0.05	1.46	N/A
	B-F2	1.43		1.42	1.43±0.05	1.41	
	B-F3	1.43		1.42	1.43±0.05	1.37	
	B-F4	1.43		1.42	1.43±0.05	1.46	
d(BF-HN)	F1-H3		N/A	N/A	N/A	1.69	
	F2-H5					2.36	
	F4-H2					1.71	1.66
d(B-N)			N/A	N/A	N/A	2.98	N/A
Angle							
≤C-C-N	C1-C2-N	110.77	110.20	N/A	N/A	111.23	N/A
≤C-C-H	C1-C2-⟨H⟩	110.89	110.50			111.37	
	C2-C1-⟨H⟩						
≤C-N-H	C2-N-⟨H⟩	111.18	111.00			112.31	
Binding energy							
$[EtNH_3^+][BF_4^-]$						4.79	4.61

[2] MP2/6-311G for isolated the $EtNH_3^+$ ion **[3]** PAW-PW91-GGA for the isolated BF_4^- ion

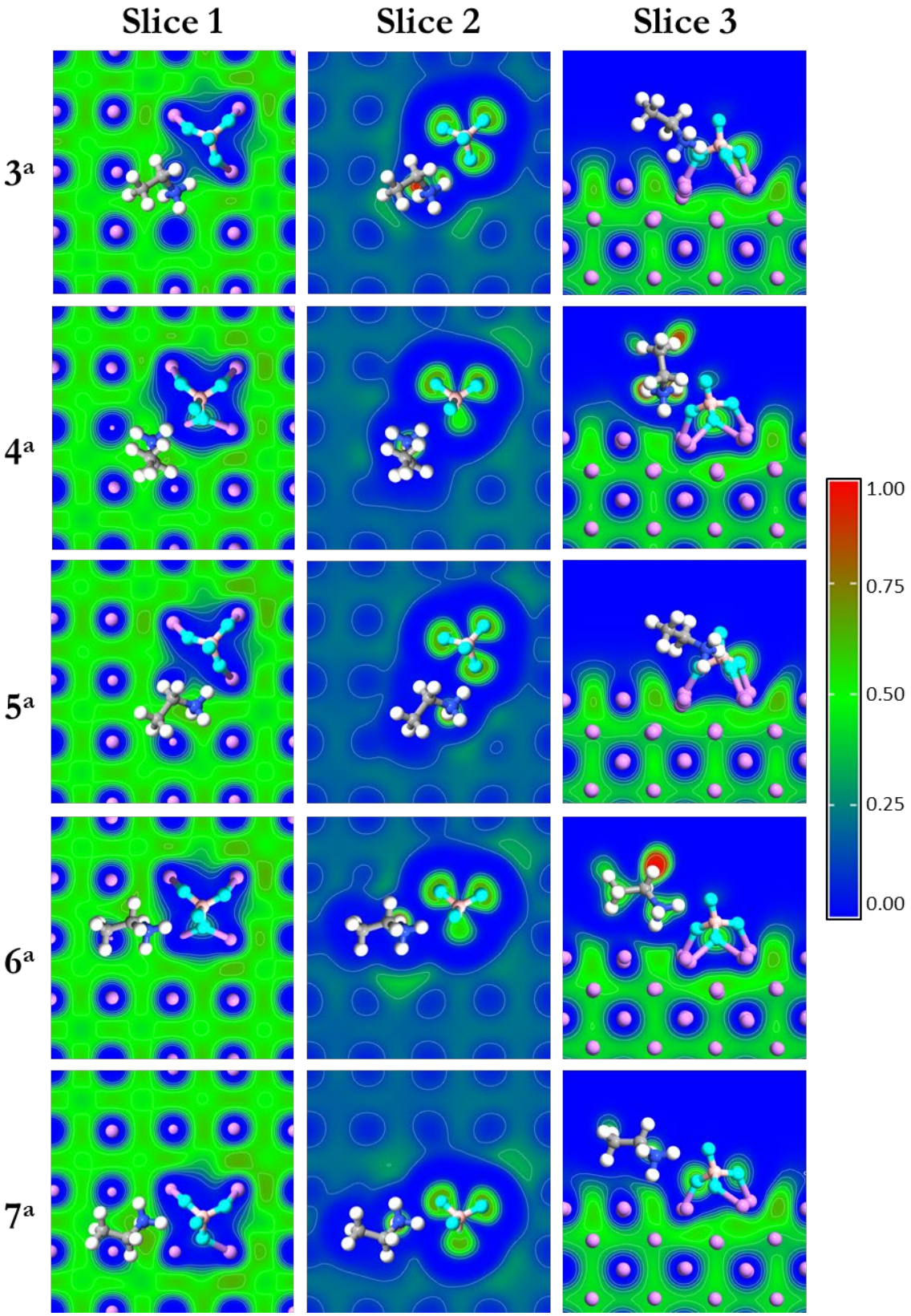
[4] Exp. for BF_4^- **[1]** MP2/TZVPP for $[EtNH_3^+][BF_4^-]$ pair

Table S2. Calculated partial charges for the individual ions and ion pair using Bader analysis. ***Δq*** is the change gained or loss for each atom of the ions once they become an ion pair.

q	$EtNH_3^+$	BF_4^-	$[EtNH_3^+][BF_4^-]$	**Δ*q***
C1	-0.10		-0.08	0.02
C2	0.14		0.19	0.05
N	-1.16		-0.14	0.02
H1	0.53		0.46	-0.07
H2	0.54		0.54	0.00
H3	0.52		0.53	0.01
H4	0.12		0.06	-0.06
H5	0.13		0.17	0.04
H6	0.11		0.02	-0.09
H7	0.12		0.08	0.04
H8	0.06		0.06	0.00
B		2.40	2.39	-0.01
F1		-0.85	0.82	0.03
F2		-0.85	0.83	0.02
F3		-0.85	0.82	0.03
F4		-0.85	0.81	0.04

Table S3. Geometric measurements of the [$EtNH_3^+$][BF_4^-] pair adsorbed on the Li(001)-[4x4] surface. N_{Li}^c is the number of Li atoms bonded to F atoms (with Li-F distance <3 Å); Δz_{Li1-4} is the z-direction displacement for the Li atoms interacting with the F atoms; **d(Li-F_x)** gives the measured bond distance between any Li and F atoms that are <3 Å apart; **Li-⟨F⟩** gives the average value for **d(Li-F_x)**; **d(N-B)** is the distance between the B and N atoms after adsorption on the surface; **Δ N-B** is the change in distance compared to the distance in the isolated pair.

System	**[$EtNH_3^+$][BF_4^-]/Li(001)-[4x4]**											
Structure	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]	**7**[a]	**8**[a]	**9**[a]	**10**[a]	**11**[a]	**12**[a]
N_{Li}^c	3	4	3	4	3	4	4	3	3	2	2	3
Δz_{Li1}	0.48	0.42	0.39	0.55	0.41	0.45	0.45	0.51	0.43	0.35	0.42	0.29
Δz_{Li2}	0.36	0.28	0.30	0.08	0.36	0.15	0.16	0.43	0.25	0.41	0.37	0.26
Δz_{Li3}	0.28	-0.19	0.28	0.04	0.15	0.03	0.00	0.08	-0.04			0.18
Δz_{Li4}		-0.02		-0.36		-0.20	-0.01					
Δz_{Li5}	-0.71	-0.21	-0.55	-0.36	-0.29	-0.17		-0.52	-0.37	-0.45	-0.53	-0.50
d(Li_1-F)	1.91	2.05	1.91	2.03	1.92	2.08	2.15	1.88	1.92	1.82	1.83	2.01
d(Li_2-F)	1.88	2.05	1.88	2.02	1.88	2.04	2.15	1.87	1.89	1.81	1.81	1.96
d(Li_3-F)	1.86	1.91	1.86	1.96	1.87	1.94	1.94	1.86	1.86			1.88
d(Li_4-F)		1.90		1.88		1.88	1.88					
Li-⟨F⟩	1.88	1.98	1.88	1.97	1.89	1.98	2.03	1.87	1.89	1.82	1.82	1.95
d(Li_5-H)	2.72	2.89	2.72	2.66	3.00	2.89		2.80	2.78	2.87	2.81	2.67
d(N-B)	3.51	3.66	3.72	3.67	3.66	3.46	3.47	4.02	3.53	3.83	3.65	3.67
Δ N-B	0.53	0.68	0.74	0.69	0.68	0.48	0.49	1.04	0.55	0.85	0.67	0.69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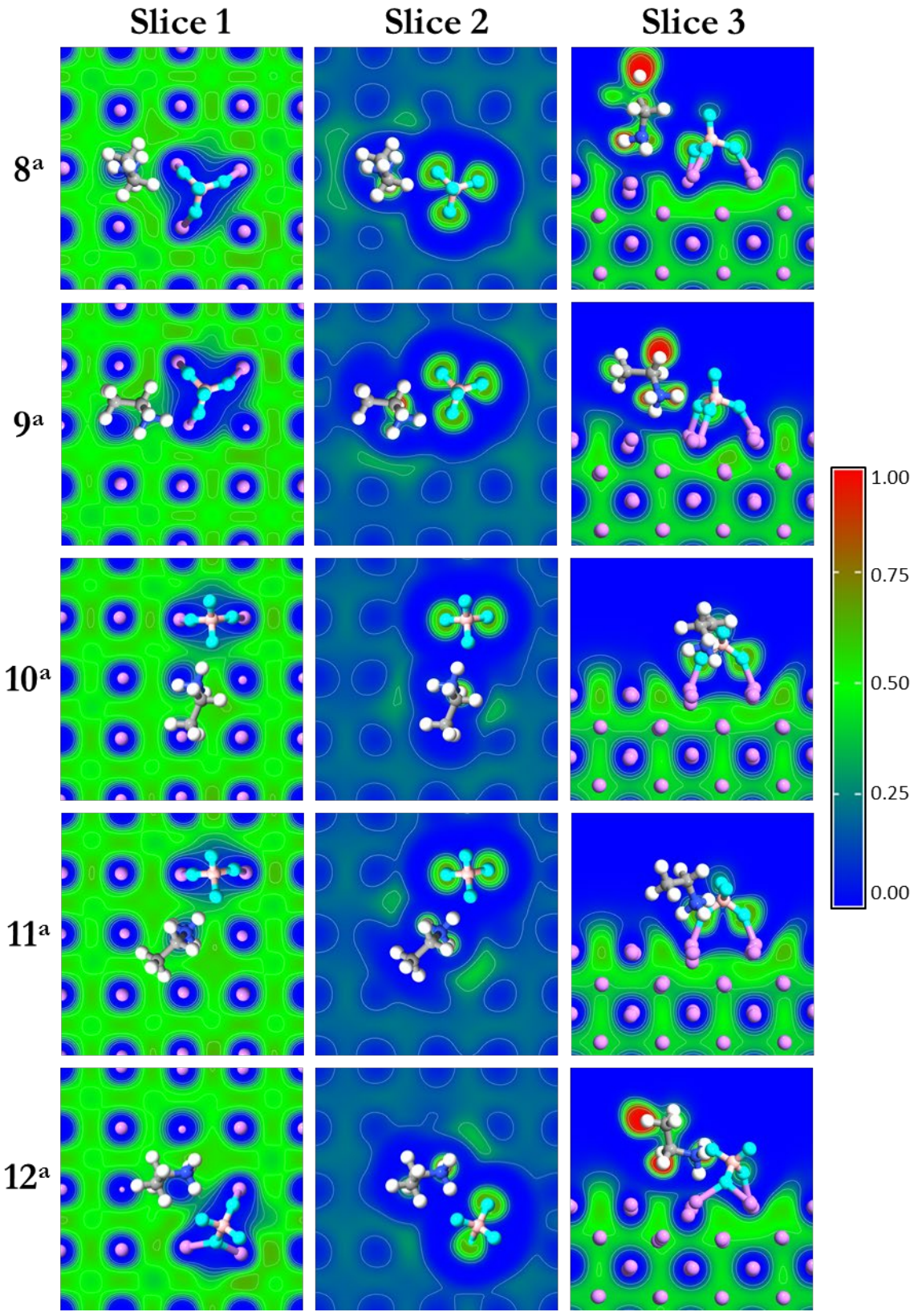

Figure S2. ELF plots for structures 2^a-12^a

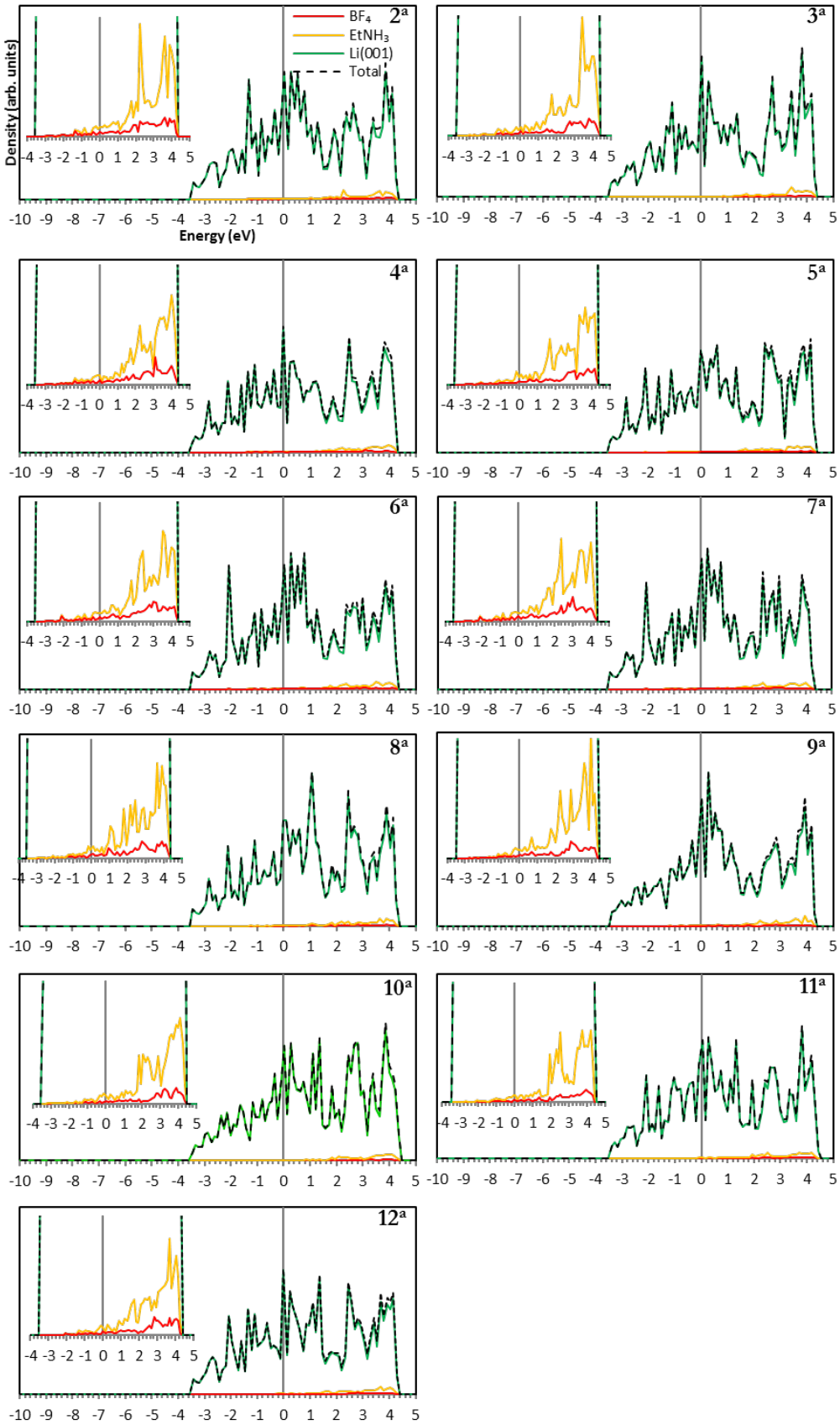

Figure S3. LDOS for structures **2ª-12ª**

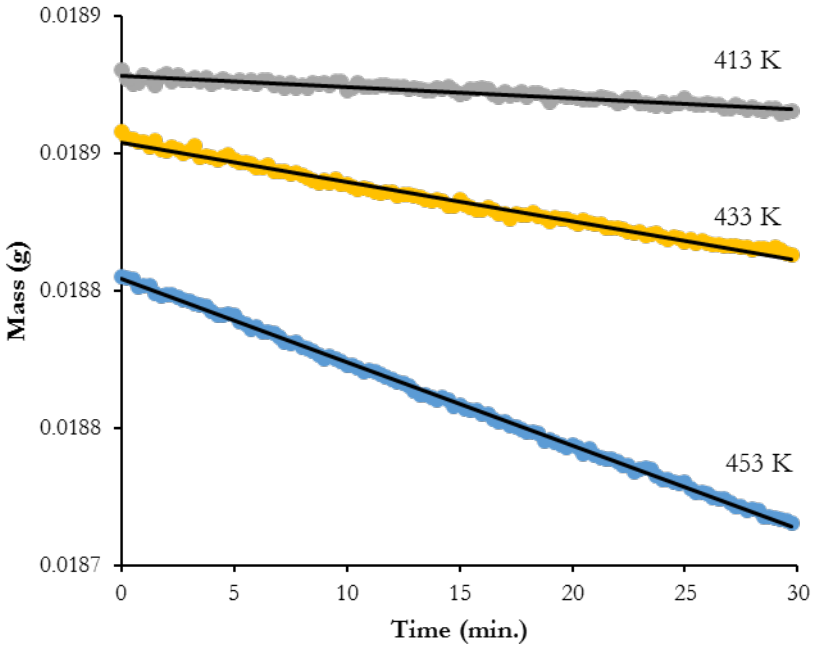

Figure S4. Plot of isothermal mass loss of $[EtNH_3^+][BF_4^-]$ determined using TGA.

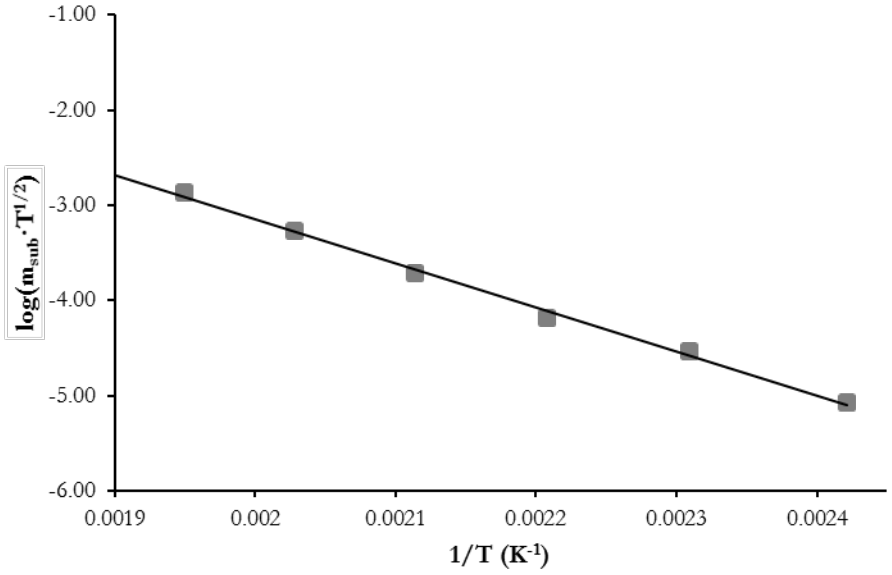

Figure S5. Plot of $\log(m_{sub} \cdot T^{1/2})$ versus 1/T and the determination of ΔH_{sub} (0.92 eV) for $[EtNH_3^+][BF_4^-]$, where m_{sub} is the rate of mass loss by sublimation.

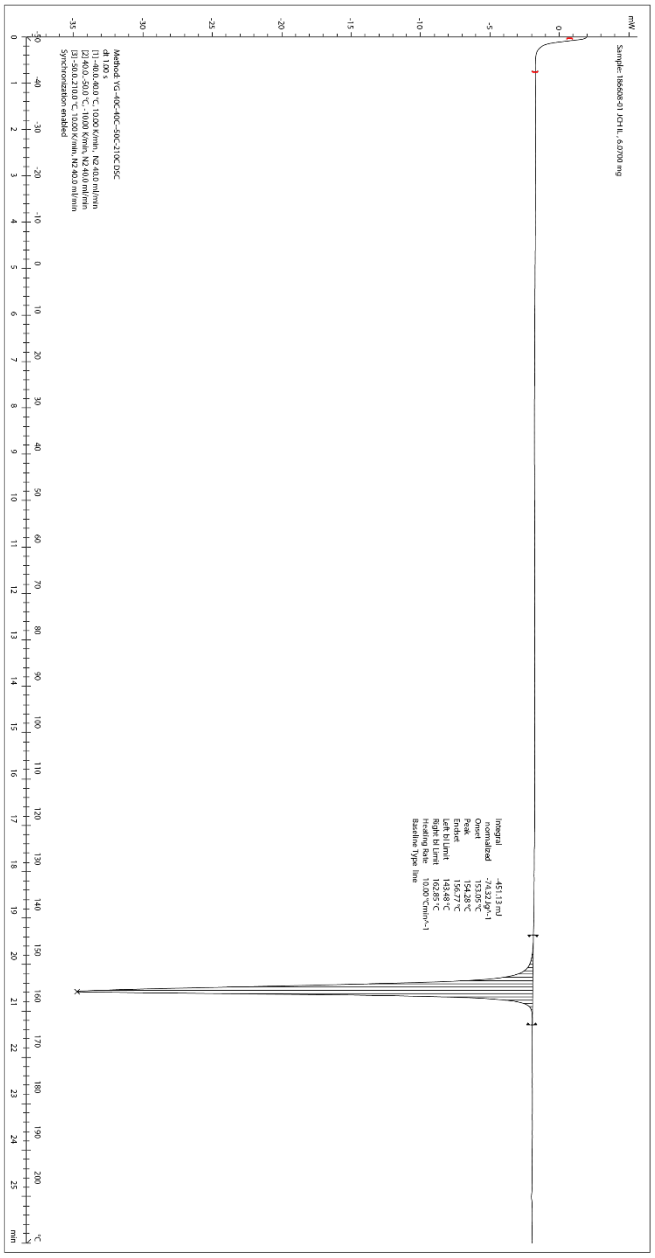

Figure S6. Differential scanning calorimeter thermogram of $[EtNH_3^+][BF_4^-]$ recorded at a heating rate of 10 $K \cdot min^{-1}$ after cooling from 313 K to 223 K.

References

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