Supplemental materials

Supplemental method 1.

Lithium cation transference numbers (t_+) were calculated using d.c. polarization method combined with a.c. impedance method introduced by Bruce and Vincent. Samples of electrolyte were sandwiched between two lithium metal electrodes in Swagelok-type cell. Impedance spectroscopy measurements were performed on VMP3 multichannel potentiostat with a.c. signal of 5 mV in 500 kHz to 100 mHz range with 10 points per decade. Impedance spectra were analyzed with the Equivalent-circuit 4.55 program and each spectrum was fitted with an equivalent circuit which allowed to separate resistance contributions between different phenomena. This circuit consisted of two parts connected in series: 1. electrolyte resistance (R_e) and 2. parallel combination of interfacial resistance (R_i) and constant phase element connected with it. Polarization measurements were also executed on the VMP3 multichannel potentiostat. Polarization with 20 mV potential difference was applied on each sample until current reached steady-state (defined as a state where current difference in the last 10 minutes was lower than 1% relatively). All measurements took place at the temperature of 20°C, apart from EMImTDI samples which were thermostated in cryostat-thermostat system (the one described before in this paper) before experiment for 90 minutes in 70°C (to assure liquid state of the sample). The t_+ for every concentration of each salt was measured on three samples for higher consistency of data. Then the lithium cation transference number was calculated as:

$$t_+ = (I_s (\Delta V - R_0 I_0)) / (I_0 (\Delta V - R_s I_s))$$

where:

ΔV - d.c. voltage applied;

R_0 - initial interfacial layer resistance;

R_s - steady-state interfacial layer resistance;

I_0 - initial current;

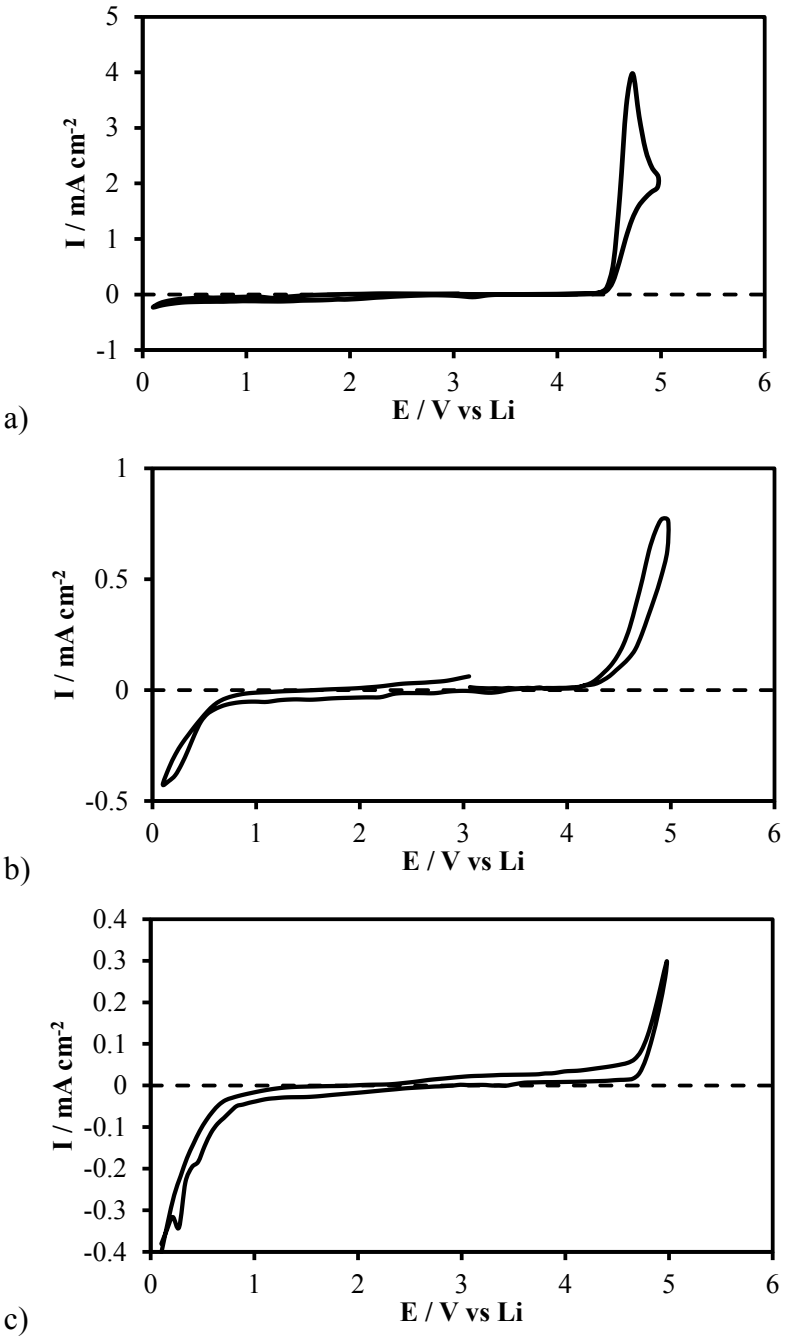
I_s - steady-state current.

Resulting individual t_+ values were calculated with error always smaller than 5%. Standard deviation of results at each concentration was always smaller than 10%.

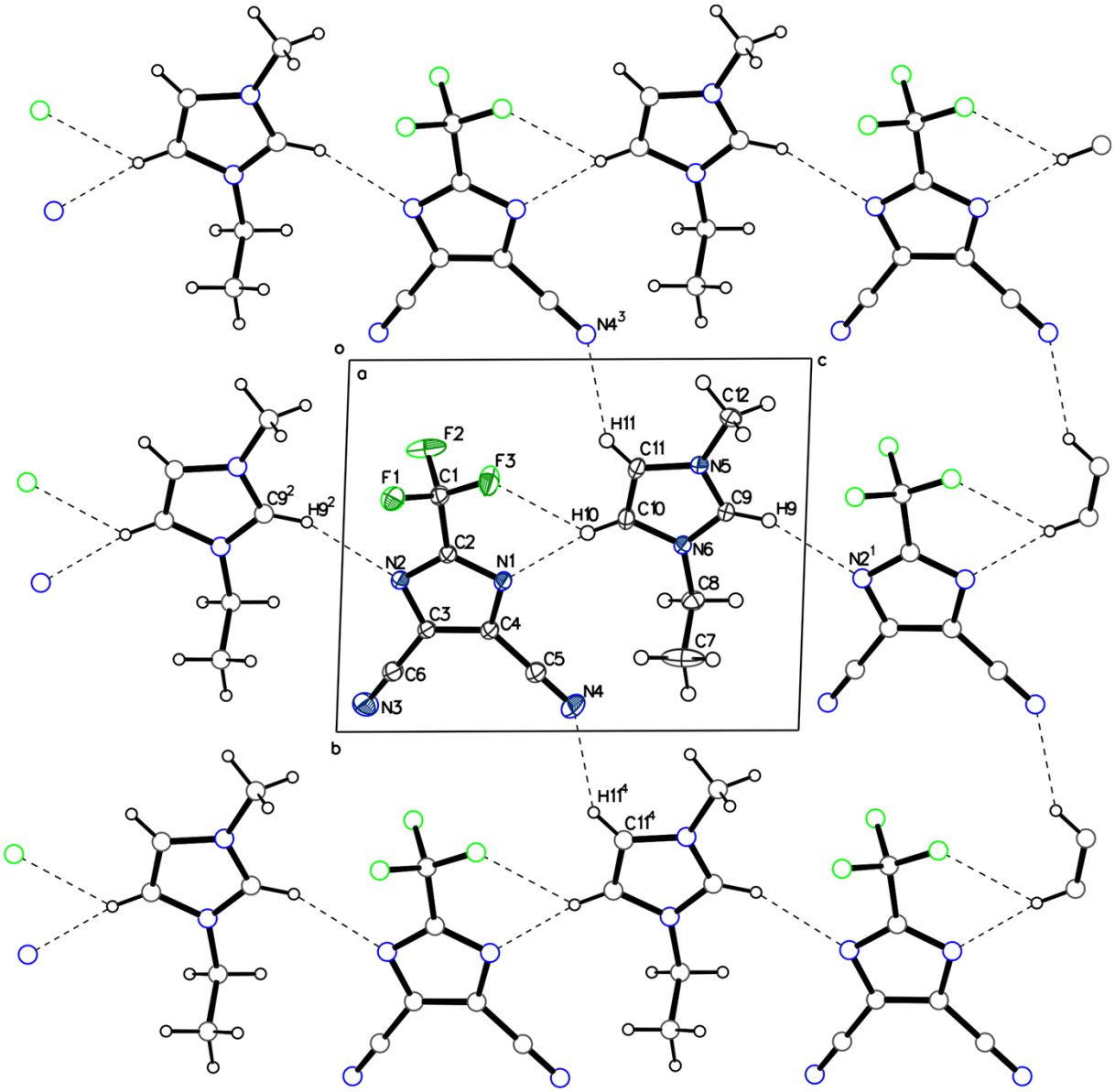
Structure abbreviations: 1 – EMImTDI, 2 – LiTDI-PMImTDI, 3 – LiTDI-BMImTDI

Supplemental method 2.

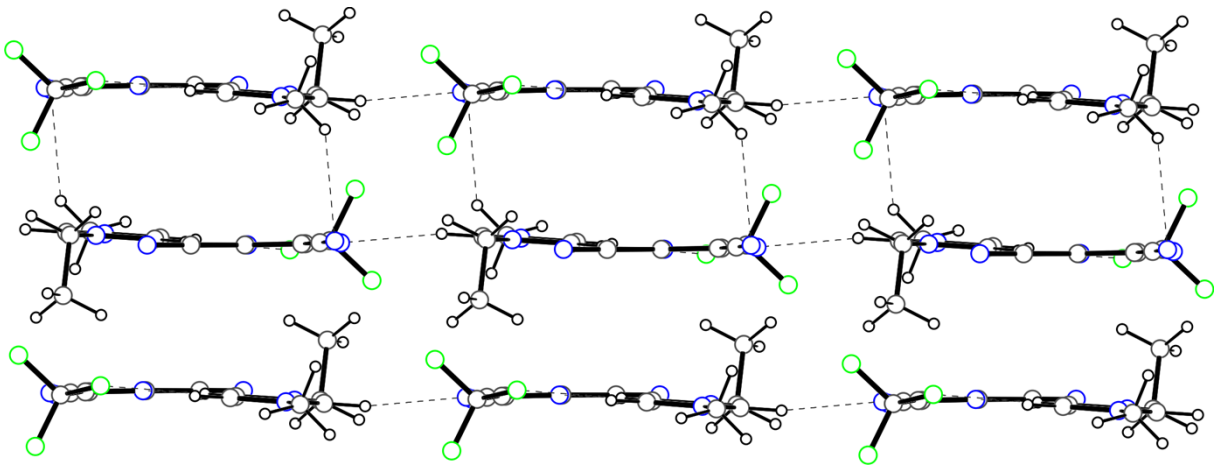
Cyclic voltametry (CV) was used to investigate electrochemical stability window. Samples of ionic liquids were sandwiched between lithium metal electrodes used as both counter and reference electrode and platinum electrode as a working electrode (Pt electrode surface was 0.1 cm^2). CV was performed every time with 1 mV s^{-1} scan rate at ambient temperature for PMImTDI and BMImTDI and at 70°C in case of EMImTDI (due to its high melting point).



Supplemental Figure 1. Cyclic voltammetry plots for a) EMImTDI; b) PMImTDI; c) BMImTDI;

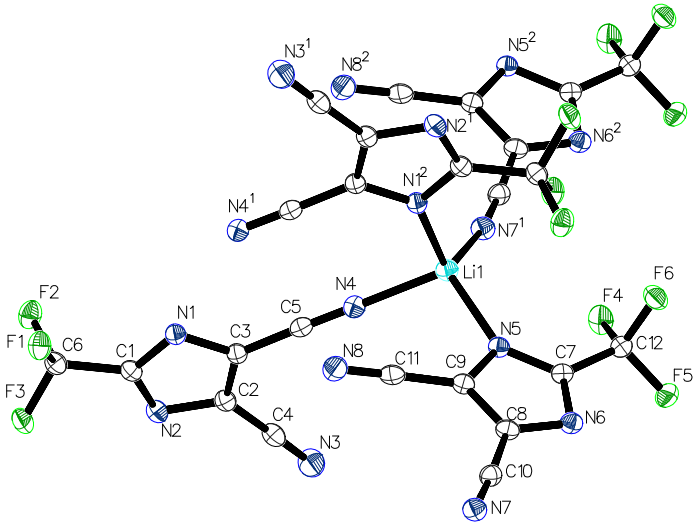


Supplemental Figure 2. Hydrogen bonded 2D layers observed in the crystal structure of EMImTDI (**1**). Symmetry codes: ([1]) $+x,+y,1+z$; ([2]) $+x,+y,-1+z$; ([3]) $1+x,-1+y,+z$; ([4]) $-1+x,1+y,+z$.

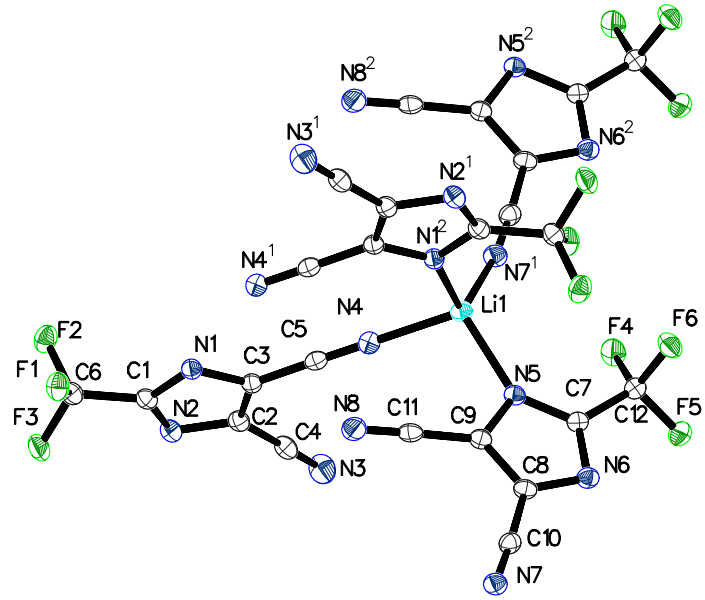


Supplemental Figure 3. Side view of the 2D layers stacked into 3D crystal structure in **1**.

a)



b)



Supplemental Figure 4. Coordination environment around Li^+ cations in the a) LiTDI-PMImTDI (**2**) and b) LiTDI-BMImTDI (**3**) crystal structures. Thermal ellipsoids at 50% probability level. Selected bond lengths (Å) for **2**: Li1—N4 2.044 (2), Li1—N5 2.062 (2), Li1—$N1^2$ 2.129 (2), Li1—$N7^1$ 2.044 (2); **3**: Li1—N4 2.058 (2), Li1—N5 2.081 (2), Li1—$N1^2$ 2.123 (2), Li1—$N7^1$ 2.081 (2). Symmetry codes: (^{1}) 1+*x*,+*y*,+*z*; (^{2}) 1−*x*, 1−*y*, 1−*z*.

Supplemental Table 1. Crystal data for the single crystal X-ray structures of **1–3**.

Compound	**1**	**2**	**3**
Chemical formula	$C_{12}H_{11}F_3N_6$	$C_{19}H_{13}F_6LiN_{10}$	$C_{20}H_{15}F_6LiN_{10}$
M /g·mol^{-1}	296.27	502.33	516.36
Crystal size /mm^3	0.95×0.8×0.35	0.4×0.35×0.15	0.63×0.51×0.35
T /K	100.0(2)	100.0(2)	100.0(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P***Error!**	*P***Error!**	*P***Error!**
a /Å	8.63283(15)	8.28368(13)	8.42410(11)
b /Å	8.86281(12)	11.45842(18)	11.66815(17)
c /Å	10.25772(13)	12.57923(20)	12.85431(18)
α/°	87.4723(11)	74.9663(14)	73.0547(13)
β /°	78.8034(13)	77.5238(13)	74.4505(12)
γ/°	66.0794(15)	78.6965(13)	76.7560(12)
V /Å^3	703.24(2)	1113.43(3)	1148.67(3)
Z	2	2	2
D_{calc} /g·cm^{-3}	1.399	1.498	1.493
Radiation, λ/ Å	Mo K_α, 0.7107	Cu K_α, 1.5418	Cu K_α, 1.5418
μ /mm^{-1}	0.119	1.157	1.137
F(000)	304	508	524
2Θ Range /°	7.24–58.98	7.38–133.34	7.36–133.4
Reflections collected	111869	60286	80701
Independent refln.	3902	3923	4047
R_{int}	0.0237	0.0330	0.0330
Parameters/restraints	192/0	327/0	337/0
S (F^2)[a]	1.026	1.046	1.075
$R1$, w$R2$ ($I>2\sigma(I)$)[b]	0.0408, 0.1078	0.0275, 0.0704	0.0298, 0.0718
$R1$, w$R2$ (all data)	0.0421, 0.1090	0.0285, 0.0711	0.0303, 0.0721
$\Delta\rho_{min/max}$/eÅ^{-3}	+ 0.49/-0.38	+0.21/-0.27	+0.23/-0.21

[a] Goodness-of-fit $S=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ where n is the reflections number and p is the parameters number; [b] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Supplemental Table 2. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters (Å^2) for **1.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	U_{iso}*/U_{eq}
F1	1.00807 (8)	0.37302 (8)	0.10442 (7)	0.02864 (16)
F2	0.85451 (9)	0.23824 (8)	0.17311 (10)	0.0406 (2)
F3	0.96211 (10)	0.32512 (11)	0.31156 (7)	0.0443 (2)
N1	0.65639 (11)	0.59571 (10)	0.34911 (8)	0.01852 (17)
N2	0.65065 (10)	0.59185 (10)	0.12641 (8)	0.01673 (16)
N3	0.28515 (14)	0.92599 (13)	0.06099 (11)	0.0319 (2)
N4	0.29757 (15)	0.93283 (13)	0.51025 (11)	0.0357 (2)
N5	0.95824 (11)	0.28565 (10)	0.76541 (8)	0.01785 (17)
N6	0.73288 (10)	0.50029 (10)	0.73531 (8)	0.01619 (16)
C1	0.88791 (12)	0.36488 (12)	0.20573 (9)	0.01874 (18)
C2	0.72929 (12)	0.52254 (11)	0.22795 (9)	0.01588 (17)
C3	0.51160 (12)	0.72543 (11)	0.18812 (9)	0.01640 (17)
C4	0.51493 (12)	0.72750 (11)	0.32390 (9)	0.01785 (18)
C5	0.39462 (14)	0.84144 (13)	0.42698 (10)	0.0242 (2)
C6	0.38668 (13)	0.83742 (12)	0.11770 (10)	0.02120 (19)
C7	0.60445 (17)	0.80397 (15)	0.7444 (2)	0.0454 (4)
H7A	0.6681	0.8031	0.6541	0.068*
H7B	0.6726	0.8087	0.8090	0.068*
H7C	0.4940	0.9008	0.7587	0.068*
C8	0.57174 (12)	0.65015 (12)	0.76196 (11)	0.02127 (19)
H8A	0.5105	0.6499	0.8541	0.026*
H8B	0.4962	0.6496	0.7008	0.026*
C9	0.81844 (12)	0.41219 (11)	0.82682 (9)	0.01678 (18)
H9	0.7855	0.4355	0.9201	0.020*
C10	0.81968 (14)	0.42911 (13)	0.61128 (9)	0.0220 (2)
H10	0.7871	0.4671	0.5286	0.026*
C11	0.96128 (14)	0.29367 (13)	0.63012 (10)	0.0229 (2)
H11	1.0462	0.2188	0.5629	0.028*
C12	1.08760 (14)	0.15780 (12)	0.82997 (11)	0.0237 (2)
H12A	1.1569	0.0637	0.7673	0.035*
H12B	1.0290	0.1212	0.9084	0.035*
H12C	1.1631	0.2034	0.8572	0.035*

Supplemental Table 3. Bond Lengths for **1**.

	Length/Å		**Length/Å**
F1—C1	1.3404 (11)	N5—C12	1.4713 (12)
F2—C1	1.3372 (12)	N6—C8	1.4697 (12)
F3—C1	1.3289 (11)	N6—C9	1.3316 (11)
N1—C2	1.3408 (12)	N6—C10	1.3767 (12)
N1—C4	1.3645 (12)	C1—C2	1.4949 (13)
N2—C2	1.3427 (11)	C3—C4	1.3997 (12)
N2—C3	1.3645 (12)	C3—C6	1.4287 (13)
N3—C6	1.1500 (14)	C4—C5	1.4261 (13)
N4—C5	1.1490 (15)	C7—C8	1.4971 (16)
N5—C9	1.3343 (12)	C10—C11	1.3615 (14)
N5—C11	1.3821 (12)		

Supplemental Table 4. Bond Angles for **1**.

	Angle/°		**Angle/°**
C2—N1—C4	101.95 (8)	N1—C2—C1	121.90 (8)
C2—N2—C3	101.98 (8)	N2—C2—C1	120.34 (8)
C9—N5—C11	108.57 (8)	N2—C3—C4	109.13 (8)
C9—N5—C12	126.09 (8)	N2—C3—C6	122.15 (8)
C11—N5—C12	125.34 (8)	C4—C3—C6	128.71 (9)
C9—N6—C8	125.57 (8)	N1—C4—C3	109.25 (8)
C9—N6—C10	109.18 (8)	N1—C4—C5	121.85 (9)
C10—N6—C8	125.24 (8)	C3—C4—C5	128.90 (9)
F1—C1—C2	111.98 (8)	N4—C5—C4	179.78 (14)
F2—C1—F1	105.26 (8)	N3—C6—C3	179.05 (11)
F2—C1—C2	111.90 (8)	N6—C8—C7	111.92 (9)
F3—C1—F1	106.62 (8)	N6—C9—N5	108.46 (8)
F3—C1—F2	108.15 (9)	C11—C10—N6	106.69 (8)
F3—C1—C2	112.51 (8)	C10—C11—N5	107.10 (8)
N1—C2—N2	117.70 (8)		

Supplemental Table 5. Hydrogen-bond geometry (Å, °) for **1**.

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C9—H9···N2^{i}	0.95	2.40	3.3031 (12)	159
C10—H10···F3	0.95	2.49	3.1108 (12)	123
C10—H10···N1	0.95	2.35	3.2915 (13)	169
C11—H11···N4^{ii}	0.95	2.57	3.4058 (14)	146

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*+1, *y*−1, *z*.

Supplemental Table 6. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters (Å^2) for **2** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	U_{iso}*/U_{eq}
F1	0.40736 (9)	0.89843 (6)	0.18475 (6)	0.02429 (16)
F2	0.66713 (9)	0.89327 (6)	0.10942 (6)	0.02599 (17)
F3	0.48989 (10)	0.87050 (6)	0.01697 (6)	0.03043 (18)
F4	0.65509 (8)	−0.06232 (6)	0.63472 (6)	0.02724 (17)
F5	0.48903 (9)	−0.19193 (6)	0.65276 (6)	0.02606 (17)
F6	0.49314 (9)	−0.11681 (6)	0.79112 (6)	0.02623 (17)
N1	0.52839 (11)	0.65946 (8)	0.27473 (8)	0.0166 (2)
N2	0.62374 (12)	0.63134 (9)	0.09668 (8)	0.0189 (2)
N3	0.75780 (15)	0.32354 (10)	0.10121 (9)	0.0307 (3)
N4	0.58242 (12)	0.36817 (9)	0.45872 (8)	0.0184 (2)
N5	0.39573 (12)	0.13081 (9)	0.61261 (8)	0.0165 (2)
N6	0.21646 (12)	−0.00759 (9)	0.64164 (8)	0.0189 (2)
N7	−0.17611 (12)	0.16254 (9)	0.59196 (8)	0.0211 (2)
N8	0.17522 (13)	0.42562 (10)	0.52498 (10)	0.0262 (2)
N9	0.11943 (12)	0.41002 (10)	0.23050 (8)	0.0226 (2)
N10	0.08625 (12)	0.23771 (9)	0.20479 (8)	0.0217 (2)
C1	0.55822 (14)	0.70795 (10)	0.16430 (9)	0.0174 (2)
C2	0.63774 (14)	0.52122 (10)	0.17043 (10)	0.0175 (2)
C3	0.58038 (13)	0.53773 (10)	0.27888 (9)	0.0160 (2)
C4	0.70365 (15)	0.41064 (11)	0.13326 (10)	0.0211 (3)
C5	0.57879 (13)	0.44547 (10)	0.37993 (9)	0.0163 (2)
C6	0.52988 (15)	0.84265 (11)	0.11841 (9)	0.0196 (2)
C7	0.36886 (14)	0.01358 (10)	0.64221 (9)	0.0166 (2)
C8	0.13564 (14)	0.10741 (11)	0.60774 (9)	0.0178 (2)
C9	0.24409 (14)	0.19159 (10)	0.58999 (9)	0.0170 (2)
C10	−0.03691 (15)	0.13471 (10)	0.59769 (9)	0.0192 (2)
C11	0.20836 (14)	0.32135 (11)	0.55378 (10)	0.0193 (2)
C12	0.50124 (15)	−0.08936 (10)	0.68008 (10)	0.0190 (2)
C13	0.16604 (15)	0.33353 (11)	0.16199 (10)	0.0230 (3)
H13	0.2436	0.3457	0.0938	0.028*
C14	−0.01543 (15)	0.25266 (11)	0.30415 (10)	0.0218 (3)
H14	−0.0866	0.1977	0.3521	0.026*
C15	0.00537 (15)	0.36046 (12)	0.32044 (10)	0.0223 (3)
H15	−0.0483	0.3955	0.3821	0.027*
C16	0.10044 (17)	0.13407 (12)	0.15358 (11)	0.0280 (3)
H16A	0.1535	0.0600	0.1998	0.042*
H16B	0.1685	0.1505	0.0787	0.042*
H16C	−0.0112	0.1224	0.1479	0.042*

C17	0.16924 (16)	0.53147 (12)	0.20979 (11)	0.0265 (3)
H17A	0.2726	0.5362	0.1530	0.032*
H17B	0.1941	0.5429	0.2796	0.032*
C18	0.03351 (16)	0.63319 (12)	0.16934 (11)	0.0254 (3)
H18A	−0.0694	0.6298	0.2266	0.030*
H18B	0.0073	0.6215	0.1000	0.030*
C19	0.08938 (18)	0.75752 (12)	0.14676 (11)	0.0300 (3)
H19A	0.1241	0.7663	0.2136	0.045*
H19B	−0.0036	0.8220	0.1279	0.045*
H19C	0.1836	0.7643	0.0842	0.045*
Li1	0.5766 (2)	0.23544 (17)	0.60327 (16)	0.0186 (4)

Supplemental Table 7 Bond Lengths for **2**

	Length/Å		**Length/Å**
F1—C6	1.3384 (14)	N10—C16	1.4658 (16)
F2—C6	1.3457 (14)	C1—C6	1.4916 (16)
F3—C6	1.3303 (14)	C2—C3	1.3932 (16)
F4—C12	1.3397 (14)	C2—C4	1.4310 (16)
F5—C12	1.3345 (14)	C3—C5	1.4264 (16)
F6—C12	1.3396 (14)	C7—C12	1.4993 (16)
N1—C1	1.3434 (15)	C8—C9	1.3888 (16)
N1—C3	1.3676 (15)	C8—C10	1.4280 (16)
N1—Li1^{i}	2.129 (2)	C9—C11	1.4284 (16)
N2—C1	1.3378 (15)	C13—H13	0.9500
N2—C2	1.3595 (15)	C14—H14	0.9500
N3—C4	1.1467 (16)	C14—C15	1.3518 (18)
N4—C5	1.1466 (15)	C15—H15	0.9500
N4—Li1	2.044 (2)	C16—H16A	0.9800
N5—C7	1.3471 (15)	C16—H16B	0.9800
N5—C9	1.3611 (15)	C16—H16C	0.9800
N5—Li1	2.062 (2)	C17—H17A	0.9900
N6—C7	1.3332 (15)	C17—H17B	0.9900
N6—C8	1.3610 (15)	C17—C18	1.5190 (18)
N7—C10	1.1473 (16)	C18—H18A	0.9900
N7—Li1^{ii}	2.044 (2)	C18—H18B	0.9900
N8—C11	1.1506 (16)	C18—C19	1.5219 (18)
N9—C13	1.3325 (16)	C19—H19A	0.9800
N9—C15	1.3822 (16)	C19—H19B	0.9800
N9—C17	1.4714 (16)	C19—H19C	0.9800
N10—C13	1.3253 (17)	Li1—N1^{i}	2.129 (2)
N10—C14	1.3786 (15)	Li1—N7^{iii}	2.044 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*, *z*.

Supplemental Table 8 Bond Angles for **2**

	Angle/°		**Angle/°**
C1—N1—C3	101.87 (9)	F5—C12—F4	107.33 (9)
C1—N1—Li1^{i}	123.62 (9)	F5—C12—F6	106.42 (9)
C3—N1—Li1^{i}	134.50 (9)	F5—C12—C7	112.03 (10)
C1—N2—C2	102.12 (9)	F6—C12—F4	106.54 (9)
C5—N4—Li1	176.77 (11)	F6—C12—C7	112.50 (9)
C7—N5—C9	102.04 (9)	N9—C13—H13	125.7
C7—N5—Li1	140.77 (9)	N10—C13—N9	108.64 (10)
C9—N5—Li1	117.01 (9)	N10—C13—H13	125.7
C7—N6—C8	101.96 (9)	N10—C14—H14	126.5
C10—N7—Li1^{ii}	167.96 (11)	C15—C14—N10	106.95 (11)
C13—N9—C15	108.44 (10)	C15—C14—H14	126.5
C13—N9—C17	125.97 (10)	N9—C15—H15	126.5
C15—N9—C17	125.39 (10)	C14—C15—N9	107.05 (11)
C13—N10—C14	108.91 (10)	C14—C15—H15	126.5
C13—N10—C16	125.61 (10)	N10—C16—H16A	109.5
C14—N10—C16	125.46 (10)	N10—C16—H16B	109.5
N1—C1—C6	121.63 (10)	N10—C16—H16C	109.5
N2—C1—N1	117.50 (10)	H16A—C16—H16B	109.5
N2—C1—C6	120.75 (10)	H16A—C16—H16C	109.5
N2—C2—C3	109.48 (10)	H16B—C16—H16C	109.5
N2—C2—C4	121.29 (10)	N9—C17—H17A	109.2
C3—C2—C4	129.24 (11)	N9—C17—H17B	109.2
N1—C3—C2	109.02 (10)	N9—C17—C18	111.90 (10)
N1—C3—C5	124.09 (10)	H17A—C17—H17B	107.9
C2—C3—C5	126.86 (10)	C18—C17—H17A	109.2
N3—C4—C2	178.49 (13)	C18—C17—H17B	109.2
N4—C5—C3	177.11 (12)	C17—C18—H18A	109.5
F1—C6—F2	106.58 (9)	C17—C18—H18B	109.5
F1—C6—C1	111.42 (9)	C17—C18—C19	110.79 (11)
F2—C6—C1	111.72 (9)	H18A—C18—H18B	108.1
F3—C6—F1	108.06 (9)	C19—C18—H18A	109.5
F3—C6—F2	106.90 (9)	C19—C18—H18B	109.5
F3—C6—C1	111.88 (10)	C18—C19—H19A	109.5
N5—C7—C12	121.85 (10)	C18—C19—H19B	109.5
N6—C7—N5	117.35 (10)	C18—C19—H19C	109.5
N6—C7—C12	120.73 (10)	H19A—C19—H19B	109.5
N6—C8—C9	109.69 (10)	H19A—C19—H19C	109.5
N6—C8—C10	123.93 (10)	H19B—C19—H19C	109.5
C9—C8—C10	126.32 (11)	N4—Li1—N1^{i}	101.31 (9)
N5—C9—C8	108.96 (10)	N4—Li1—N5	108.89 (9)

N5—C9—C11	123.75 (10)	N5—Li1—N1^{i}	104.08 (9)
C8—C9—C11	127.29 (10)	N7^{iii}—Li1—N1^{i}	118.13 (10)
N7—C10—C8	176.03 (12)	N7^{iii}—Li1—N4	100.75 (9)
N8—C11—C9	178.20 (12)	N7^{iii}—Li1—N5	121.52 (10)
F4—C12—C7	111.65 (9)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*, *z*.

Supplemental Table 9. Hydrogen-bond geometry (Å, °) for **2**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C13—H13···N2^{iv}	0.95	2.38	3.3059 (15)	165
C16—H16*A*···F1^{v}	0.98	2.52	3.3315 (15)	140

Symmetry codes: (iv) −*x*+1, −*y*+1, −*z*; (v) *x*, *y*−1, *z*.

Supplemental Table 10. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters (Å^2) for **3** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	U_{iso}*/U_{eq}
F1	0.42315 (9)	0.89973 (7)	0.18574 (6)	0.02575 (18)
F2	0.68087 (9)	0.90079 (7)	0.10196 (6)	0.02746 (19)
F3	0.50854 (11)	0.87223 (7)	0.01907 (6)	0.02884 (19)
F4	0.64896 (10)	−0.05836 (7)	0.63479 (7)	0.0330 (2)
F5	0.48819 (10)	−0.18469 (7)	0.65073 (7)	0.0304 (2)
F6	0.47905 (10)	−0.11600 (7)	0.78996 (6)	0.0302 (2)
N1	0.54819 (13)	0.66286 (9)	0.27512 (8)	0.0184 (2)
N2	0.65447 (14)	0.63753 (10)	0.09800 (9)	0.0216 (2)
N3	0.77871 (18)	0.32851 (11)	0.10742 (10)	0.0350 (3)
N4	0.58428 (13)	0.36848 (9)	0.45798 (9)	0.0206 (2)
N5	0.38941 (13)	0.13512 (9)	0.61377 (8)	0.0188 (2)
N6	0.21376 (13)	0.00016 (10)	0.64178 (9)	0.0210 (2)
N7	−0.17683 (14)	0.16840 (10)	0.59712 (9)	0.0226 (2)
N8	0.17258 (14)	0.43108 (10)	0.52894 (10)	0.0266 (3)
N9	0.13556 (14)	0.38767 (10)	0.24351 (9)	0.0236 (2)
N10	0.08862 (14)	0.22548 (10)	0.21704 (9)	0.0216 (2)
C1	0.58467 (15)	0.71241 (11)	0.16497 (10)	0.0192 (3)
C2	0.66474 (16)	0.52710 (11)	0.17197 (10)	0.0203 (3)
C3	0.60076 (15)	0.54198 (11)	0.27969 (10)	0.0185 (3)
C4	0.72888 (18)	0.41650 (13)	0.13656 (11)	0.0252 (3)
C5	0.58937 (15)	0.44784 (11)	0.38034 (10)	0.0184 (3)
C6	0.54936 (16)	0.84641 (12)	0.11784 (10)	0.0210 (3)
C7	0.36394 (16)	0.01919 (11)	0.64220 (10)	0.0192 (3)

C8	0.13306 (16)	0.11551 (12)	0.60927 (10)	0.0197 (3)
C9	0.23926 (16)	0.19774 (11)	0.59203 (10)	0.0189 (3)
C10	−0.03833 (17)	0.14283 (11)	0.60126 (10)	0.0204 (3)
C11	0.20441 (15)	0.32717 (12)	0.55685 (11)	0.0205 (3)
C12	0.49497 (16)	−0.08500 (12)	0.67916 (11)	0.0218 (3)
C13	0.17804 (16)	0.31470 (12)	0.17481 (11)	0.0236 (3)
H13	0.2591	0.3248	0.1067	0.028*
C14	−0.01608 (16)	0.24208 (12)	0.31589 (11)	0.0226 (3)
H14	−0.0940	0.1916	0.3633	0.027*
C15	0.01298 (16)	0.34375 (12)	0.33272 (11)	0.0233 (3)
H15	−0.0406	0.3784	0.3942	0.028*
C16	0.10007 (18)	0.12542 (12)	0.16678 (11)	0.0269 (3)
H16A	0.1590	0.1457	0.0886	0.040*
H16B	−0.0125	0.1122	0.1711	0.040*
H16C	0.1614	0.0513	0.2070	0.040*
C17	0.20345 (18)	0.49933 (13)	0.22447 (12)	0.0290 (3)
H17A	0.3137	0.4943	0.1722	0.035*
H17B	0.2207	0.5051	0.2959	0.035*
C18	0.09033 (17)	0.61359 (12)	0.17728 (11)	0.0244 (3)
H18A	−0.0155	0.6248	0.2327	0.029*
H18B	0.0636	0.6057	0.1095	0.029*
C19	0.17767 (18)	0.72301 (12)	0.14874 (12)	0.0262 (3)
H19A	0.2065	0.7284	0.2168	0.031*
H19B	0.2833	0.7104	0.0935	0.031*
C20	0.07344 (19)	0.84240 (13)	0.10214 (12)	0.0305 (3)
H20A	0.0422	0.8374	0.0356	0.046*
H20B	0.1386	0.9082	0.0823	0.046*
H20C	−0.0277	0.8586	0.1584	0.046*
Li1	0.5702 (3)	0.23517 (19)	0.60449 (18)	0.0211 (4)

Supplemental Table 11. Bond Lengths for **3**

	Length/Å		**Length/Å**
F1—C6	1.3398 (15)	C2—C3	1.3911 (18)
F2—C6	1.3405 (15)	C2—C4	1.4337 (19)
F3—C6	1.3359 (15)	C3—C5	1.4293 (17)
F4—C12	1.3378 (15)	C7—C12	1.5006 (18)
F5—C12	1.3339 (15)	C8—C9	1.3904 (18)
F6—C12	1.3404 (15)	C8—C10	1.4305 (18)
N1—C1	1.3434 (16)	C9—C11	1.4288 (18)
N1—C3	1.3670 (16)	C13—H13	0.9500
N1—Li1^{i}	2.123 (2)	C14—H14	0.9500
N2—C1	1.3348 (17)	C14—C15	1.3510 (19)
N2—C2	1.3604 (17)	C15—H15	0.9500
N3—C4	1.1459 (19)	C16—H16A	0.9800
N4—C5	1.1454 (17)	C16—H16B	0.9800
N4—Li1	2.058 (2)	C16—H16C	0.9800
N5—C7	1.3461 (16)	C17—H17A	0.9900
N5—C9	1.3635 (16)	C17—H17B	0.9900
N5—Li1	2.081 (2)	C17—C18	1.5198 (19)
N6—C7	1.3353 (17)	C18—H18A	0.9900
N6—C8	1.3614 (17)	C18—H18B	0.9900
N7—C10	1.1479 (17)	C18—C19	1.5227 (18)
N7—Li1^{ii}	2.081 (2)	C19—H19A	0.9900
N8—C11	1.1487 (17)	C19—H19B	0.9900
N9—C13	1.3274 (18)	C19—C20	1.518 (2)
N9—C15	1.3817 (17)	C20—H20A	0.9800
N9—C17	1.4714 (17)	C20—H20B	0.9800
N10—C13	1.3253 (18)	C20—H20C	0.9800
N10—C14	1.3764 (17)	Li1—N1^{i}	2.123 (2)
N10—C16	1.4643 (17)	Li1—N7^{iii}	2.081 (2)
C1—C6	1.4938 (17)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*, *z*.

Supplemental Table 12. Bond Angles for **3**

	Angle/°		**Angle/°**
C1—N1—C3	101.76 (10)	F5—C12—C7	112.07 (11)
C1—N1—Li1^{i}	123.70 (10)	F6—C12—C7	112.32 (11)
C3—N1—Li1^{i}	134.49 (10)	N9—C13—H13	125.7
C1—N2—C2	102.02 (10)	N10—C13—N9	108.65 (11)
C5—N4—Li1	175.76 (12)	N10—C13—H13	125.7
C7—N5—C9	102.04 (10)	N10—C14—H14	126.5
C7—N5—Li1	140.16 (10)	C15—C14—N10	107.00 (12)
C9—N5—Li1	117.66 (10)	C15—C14—H14	126.5
C7—N6—C8	101.92 (10)	N9—C15—H15	126.6
C10—N7—Li1^{ii}	170.59 (12)	C14—C15—N9	106.89 (12)
C13—N9—C15	108.60 (11)	C14—C15—H15	126.6
C13—N9—C17	125.23 (12)	N10—C16—H16A	109.5
C15—N9—C17	126.13 (12)	N10—C16—H16B	109.5
C13—N10—C14	108.86 (11)	N10—C16—H16C	109.5
C13—N10—C16	125.47 (11)	H16A—C16—H16B	109.5
C14—N10—C16	125.67 (11)	H16A—C16—H16C	109.5
N1—C1—C6	121.77 (11)	H16B—C16—H16C	109.5
N2—C1—N1	117.66 (11)	N9—C17—H17A	109.0
N2—C1—C6	120.57 (11)	N9—C17—H17B	109.0
N2—C2—C3	109.50 (11)	N9—C17—C18	113.03 (11)
N2—C2—C4	121.95 (11)	H17A—C17—H17B	107.8
C3—C2—C4	128.53 (12)	C18—C17—H17A	109.0
N1—C3—C2	109.06 (11)	C18—C17—H17B	109.0
N1—C3—C5	124.40 (11)	C17—C18—H18A	109.8
C2—C3—C5	126.54 (12)	C17—C18—H18B	109.8
N3—C4—C2	179.14 (15)	C17—C18—C19	109.58 (11)
N4—C5—C3	176.69 (13)	H18A—C18—H18B	108.2
F1—C6—F2	106.70 (10)	C19—C18—H18A	109.8
F1—C6—C1	111.33 (10)	C19—C18—H18B	109.8
F2—C6—C1	112.65 (10)	C18—C19—H19A	108.8
F3—C6—F1	107.88 (10)	C18—C19—H19B	108.8
F3—C6—F2	106.72 (10)	H19A—C19—H19B	107.7
F3—C6—C1	111.28 (10)	C20—C19—C18	113.63 (12)
N5—C7—C12	121.75 (11)	C20—C19—H19A	108.8
N6—C7—N5	117.42 (11)	C20—C19—H19B	108.8
N6—C7—C12	120.74 (11)	C19—C20—H20A	109.5
N6—C8—C9	109.71 (11)	C19—C20—H20B	109.5
N6—C8—C10	122.98 (11)	C19—C20—H20C	109.5
C9—C8—C10	127.23 (12)	H20A—C20—H20B	109.5
N5—C9—C8	108.90 (11)	H20A—C20—H20C	109.5

N5—C9—C11	123.33 (11)	H20B—C20—H20C	109.5
C8—C9—C11	127.77 (12)	N4—Li1—N1^{i}	101.94 (10)
N7—C10—C8	177.19 (14)	N4—Li1—N5	108.06 (10)
N8—C11—C9	178.42 (13)	N4—Li1—N7^{iii}	99.90 (10)
F4—C12—F6	106.55 (10)	N5—Li1—N1^{i}	102.85 (10)
F4—C12—C7	111.69 (10)	N7^{iii}—Li1—N1^{i}	115.68 (11)
F5—C12—F4	107.45 (11)	N7^{iii}—Li1—N5	125.79 (11)
F5—C12—F6	106.40 (10)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*, *z*.

Supplemental Table 13 Hydrogen-bond geometry (Å, °) for **3**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C13—H13···N2^{iv}	0.95	2.47	3.3417 (17)	153
C16—H16*C*···F1^{v}	0.98	2.50	3.3316 (16)	143

Symmetry codes: (iv) −*x*+1, −*y*+1, −*z*; (v) *x*, *y*−1, *z*.