Supplementary Information

Precisely Controlled Supramolecular Ionic Conduction Paths and Their Structure-Conductivity Relationships for Lithium Ion Transport

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Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C18 H36 F12 Li2 N6 O8 S4	
Formula weight	834.64	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4167(11) Å	α= 83.969(3)°.
	b = 10.2057(14) Å	β= 78.625(2)°.
	c = 11.0501(15) Å	γ= 79.928(3)°.
Volume	913.7(2) Å^3	
Z	1	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	0.367 mm^{-1}	
F(000)	428	
Crystal size	0.3 x 0.2 x 0.2 mm^3	
Theta range for data collection	1.88 to 28.34°.	
Index ranges	-10<=h<=11, -13<=k<=13, -14<=l<=13	
Reflections collected	6890	
Independent reflections	4489 [R(int) = 0.0181]	
Completeness to theta = 28.34°	98.5 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4489 / 0 / 230	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R_1 = 0.0401, wR_2 = 0.1046	
R indices (all data)	R_1 = 0.0447, wR_2 = 0.1084	
Largest diff. peak and hole	0.602 and -0.243 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	C18 H36 F12 Li2 N6 O8 S4	
Formula weight	834.64	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2(1)/n	
Unit cell dimensions	a = 12.4175(14) Å	α= 90°.
	b = 9.8024(11) Å	β= 105.303(3)°.
	c = 15.7042(16) Å	γ= 90°.
Volume	1843.8(3) Å^3	
Z	2	
Density (calculated)	1.503 Mg/m^3	
Absorption coefficient	0.364 mm^{-1}	
F(000)	856	
Crystal size	0.3 x 0.3 x 0.3 mm^3	
Theta range for data collection	1.87 to 28.33°.	
Index ranges	-14<=h<=16, -13<=k<=10, -19<=l<=20	
Reflections collected	13525	
Independent reflections	4575 [R(int) = 0.0684]	
Completeness to theta = 28.33°	99.6 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4575 / 0 / 231	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R_1 = 0.0876, wR_2 = 0.1839	
R indices (all data)	R_1 = 0.1295, wR_2 = 0.2038	
Largest diff. peak and hole	0.908 and -0.431 e.Å^{-3}	

Table S3. Crystal data and structure refinement for **3**.

Empirical formula	C24 H48 F12 Li2 N6 O8 S4	
Formula weight	918.80	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2(1)/n	
Unit cell dimensions	a = 11.964(3) Å	α= 90°.
	b = 10.381(3) Å	β= 100.531(4)°.
	c = 16.974(4) Å	γ = 90°.
Volume	2072.6(9) Å^3	
Z	2	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	0.331 mm^{-1}	
F(000)	952	
Crystal size	0.50 x 0.40 x 0.40 mm^3	
Theta range for data collection	1.93 to 27.50°.	
Index ranges	-15<=*h*<=15, -13<=*k*<=13, -15<=*l*<=22	
Reflections collected	14123	
Independent reflections	4757 [*R*(int) = 0.0237]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8789 and 0.8518	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4757 / 0 / 257	
Goodness-of-fit on F^2	1.016	
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0324, wR_2 = 0.0877	
R indices (all data)	R_1 = 0.0362, wR_2 = 0.0910	
Largest diff. peak and hole	0.553 and -0.290 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **5**.

Empirical formula	C14 H32 F6 Li2 N4 O6 S2	
Formula weight	544.44	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*P*ccn	
Unit cell dimensions	a = 12.2852(14) Å	α= 90°.
	b = 13.5924(16) Å	β= 90°.
	c = 16.4701(19) Å	γ= 90°.
Volume	2750.3(6) Å^3	
Z	4	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.266 mm^{-1}	
F(000)	1136	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.23 to 27.50°.	
Index ranges	-15<=h<=15, -17<=k<=16, -21<=l<=18	
Reflections collected	17947	
Independent reflections	3158 [R(int) = 0.0362]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9486 and 0.9486	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3158 / 0 / 158	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R_1 = 0.0732, wR_2 = 0.2063	
R indices (all data)	R_1 = 0.0889, wR_2 = 0.2276	
Largest diff. peak and hole	0.605 and -0.347 e.Å^{-3}	

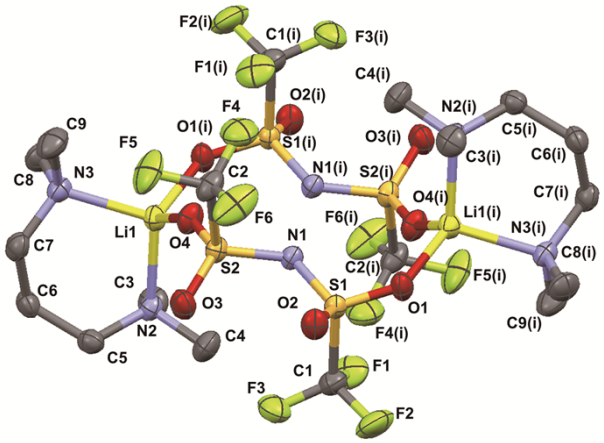

Fig. S1. Crystal structure of **1** with labels (Li: yellow, C: gray, N: blue, O: red, F: green, S: dark yellow. Thermal ellipsoid is 40 % probability. Hydrogen atoms are omitted for clarity.). The dimer in compound **1** lies about an inversion centre. The atoms in the asymmetric unit of the CIF are labelled as Li1 and any symmetry-related atoms are described as Li1(i) for clarity.

Table S5. Selected bond distances (Å) and angles (°) for **1**.

Li1-O1(i)	1.946(4)	Li1-O4	1.932(3)	Li1-N2	2.031(3)
Li1-N3	2.055(3)				

O1(i)-Li1-O4	110.51(14)	O1(i)-Li1-N2	111.37(14)	O1(i)-Li1-N3	108.73(14)
O4-Li1-N2	113.40(14)	O4-Li1-N3	109.29(14)	N2-Li1-N3	103.21(13)

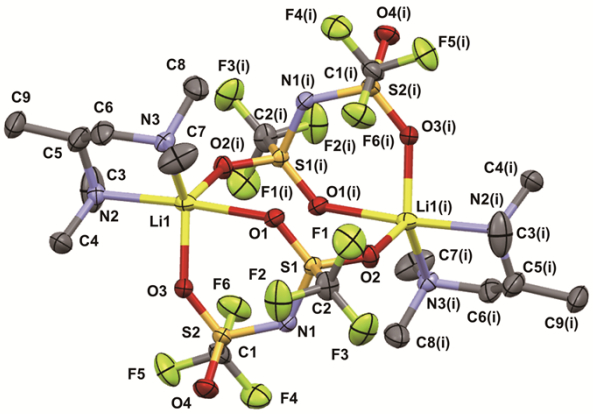

Fig. S2. Crystal structure of **2** with labels (Li: yellow, C: gray, N: blue, O: red, F: green, S: dark yellow. Thermal ellipsoid is 40 % probability. Hydrogen atoms are omitted for clarity.). The dimer in compound **2** lies about an inversion centre. The atoms in the asymmetric unit of the CIF are labelled as Li1 and any symmetry-related atoms are described as Li1(i) for clarity.

Table S6. Selected bond distances (Å) and angles (°) for **2**.

Li1-O1	2.257(8)	Li1-O2(i)	2.014(7)	Li1-O3	1.983(8)
Li1-N2	2.185(8)	Li1-N3	2.082(8)		

O1-Li1-O2(i)	88.2(3)	O1-Li1-O3	80.9(3)	O1-Li1-N2	174.2(4)
O1-Li1-N3	93.3(3)	O2(i)-Li1-O3	117.6(4)	O2(i)-Li1-N2	97.5(3)
O2(i)-Li1-N3	112.6(3)	O3-Li1-N2	95.2(3)	O3-Li1-N3	129.1(4)
N2-Li1-N3	85.8(3)				

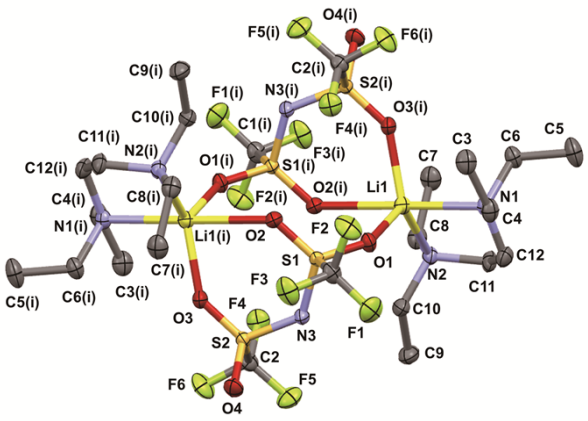

Fig. S3. Crystal structure of **3** with labels (Li: yellow, C: gray, N: blue, O: red, F: green, S: dark yellow. Thermal ellipsoid is 40 % probability. Hydrogen atoms are omitted for clarity.). The dimer in compound **3** lies about an inversion centre. The atoms in the asymmetric unit of the CIF are labelled as Li1 and any symmetry-related atoms are described as Li1(i) for clarity.

Table S7. Selected bond distances (Å) and angles (°) for **3**.

Li1-O1	2.015(2)	Li1-O2(i)	2.337(3)	Li1-O3(i)	1.976(2)
Li1-N1	2.161(3)	Li1-N2	2.122(3)		

O1-Li1-O2(i)	85.21(9)	O1-Li1-O3(i)	112.54(11)	O1-Li1-N1	96.99(10)
O1-Li1-N2	117.26(11)	O2(i)-Li1-O3(i)	80.58(8)	O2(i)-Li1-N1	177.10(12)
O2(i)-Li1-N2	90.64(9)	O3(i)-Li1-N1	100.24(11)	O3(i)-Li1-N2	128.39(12)
N1-Li1-N2	86.68(9)				

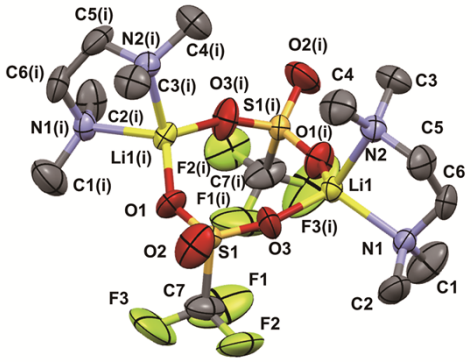

Fig. S4. Crystal structure of **5** with labels (Li: yellow, C: gray, N: blue, O: red, F: green, S: dark yellow. Thermal ellipsoid is 40 % probability. Hydrogen atoms are omitted for clarity.). The dimer in compound **5** lies about a twofold axis. The atoms in the asymmetric unit of the CIF are labelled as Li1 and any symmetry-related atoms are described as Li1(i) for clarity.

Table S8. Selected bond distances (Å) and angles (°) for **5**.

Li1-O1(i)	1.894(5)	Li1-O3	1.897(5)	Li1-N1	2.081(5)
Li1-N2	2.085(6)				

O1(i)-Li1-O3	117.9(3)	O1(i)-Li1-N1	113.2(3)	O1(i)-Li1-N2	111.4(2)
O3-Li1-N1	110.9(2)	O3-Li1-N2	110.8(3)	N1-Li1-N2	89.0(2)

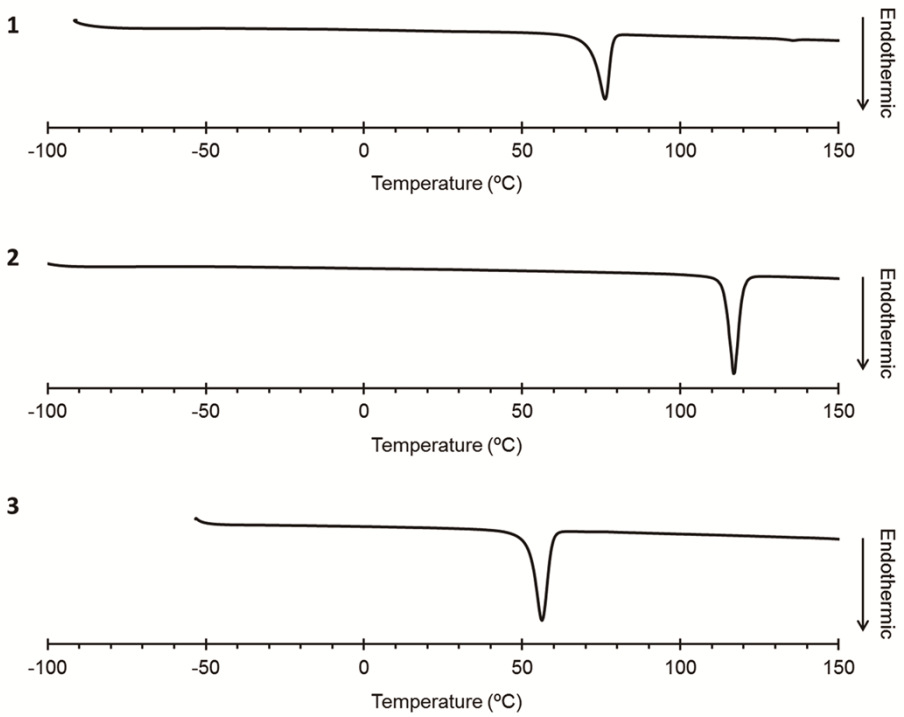

Fig. S5. DSC curves of **1**, **2** and **3**.

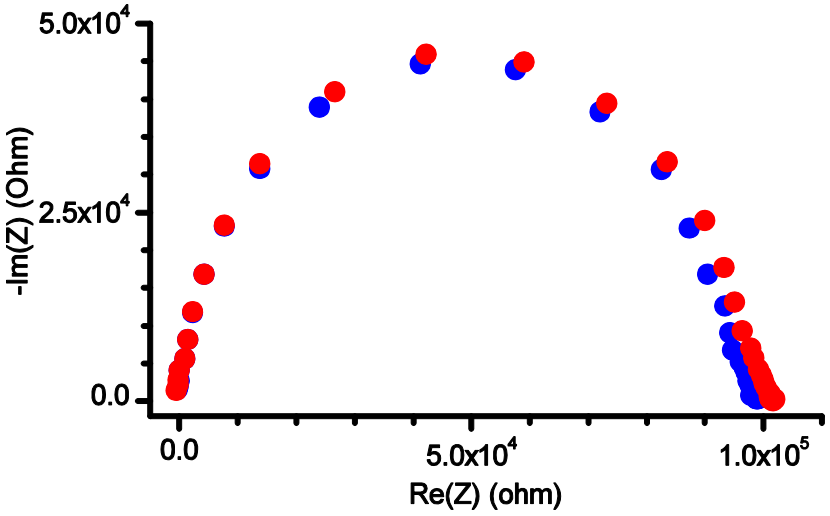

Fig. S6. Cole-Cole plots of **1** measured at 60 °C using lithium electrodes to evaluate t_{Li+} value (Blue: Before dc measurement, Red: After dc measurement).

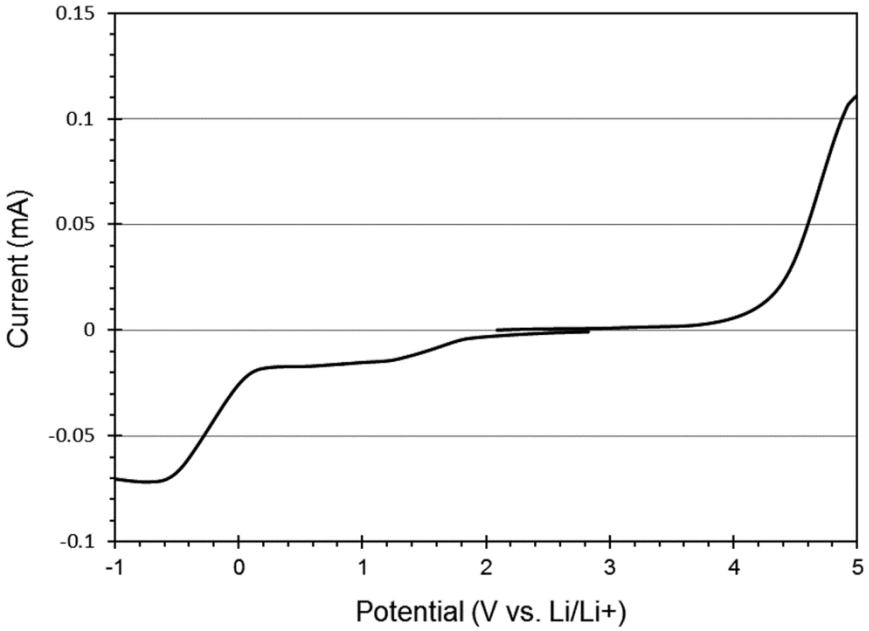

Fig. S7. Linear sweep voltammogram of **1**.