

Supporting Information

Solid-State ^1H , ^7Li , and ^{13}C NMR Studied on A New Ionic Plastic Crystal of Crown Ether - LiTfSA Complex

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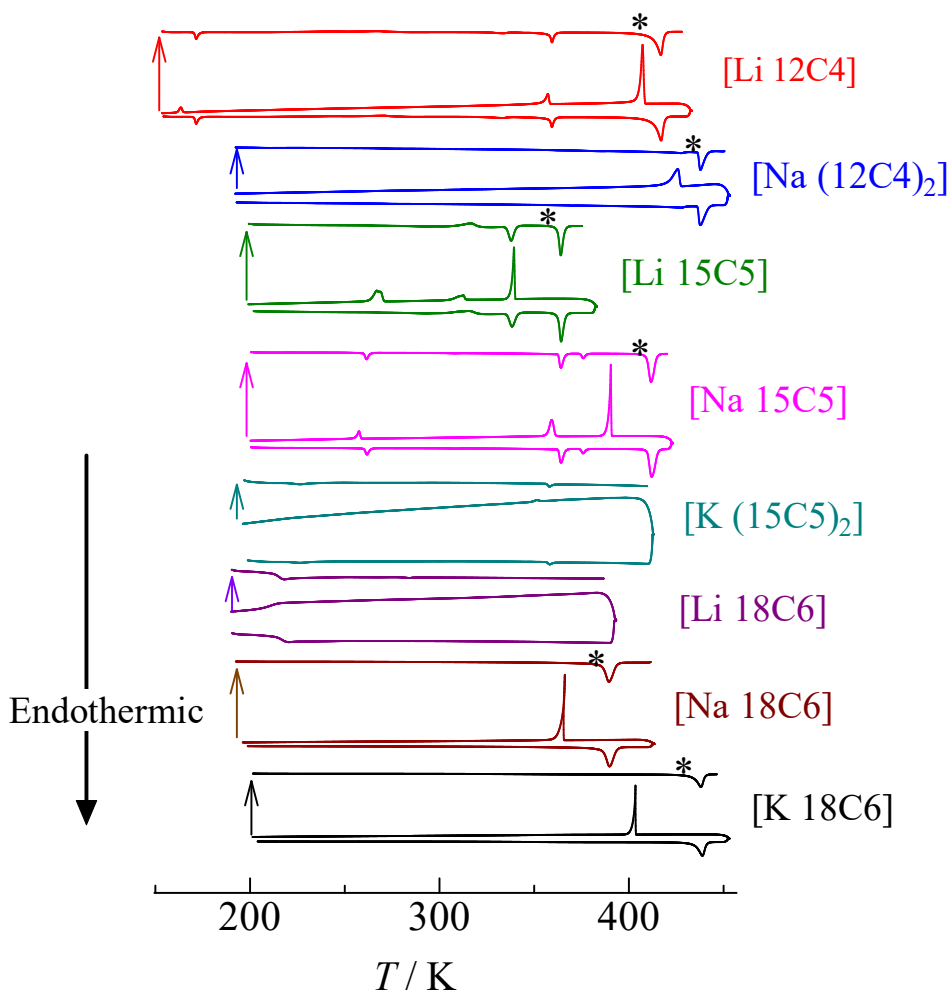


Fig. S1 DSC thermograms of $[\text{M} (3n)\text{C}_n]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}; n = 4-6$) in the 1st and 2nd heating and the 2nd cooling processes.

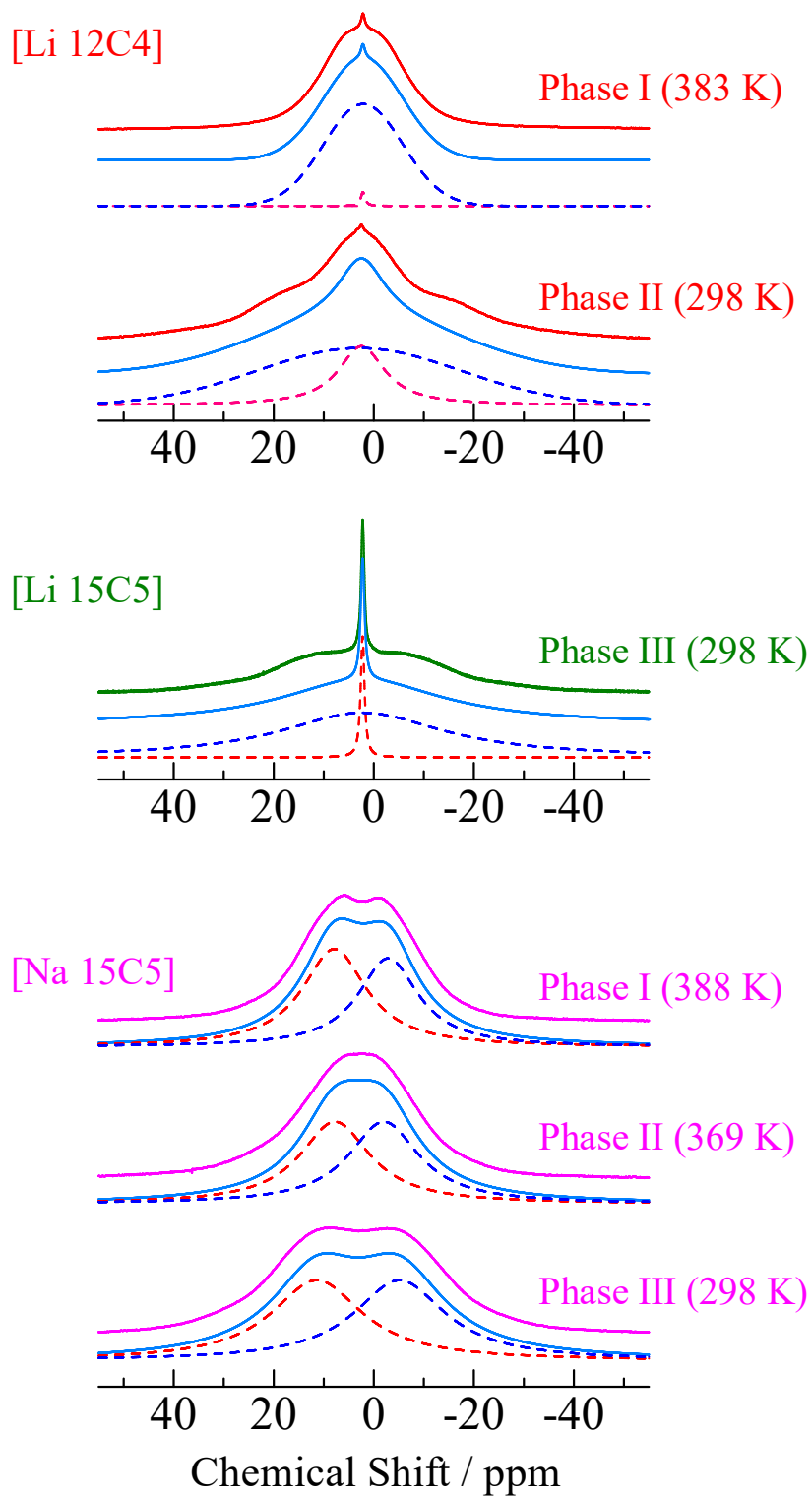


Fig. S2. Spectral analysis of ^1H NMR spectra for [Li 12C4], [Li 15C5], and [Na 15C5]. Here, blue solid lines are line envelope obtained by summing, and broken ones are analyzing lines.

Table S1 Values of the peak shift ν (ppm), the full width at half-maximum $\Delta\nu$ (kHz) and area ratio of the analyzed lines shown in Fig. S2.

	ν / ppm	$\Delta\nu$ / kHz	Area Ratio
[Li 12C4] 383 K	2.1	0.6	0.01
	2.1	18.6	0.99
[Li 12C4] 298 K	2.5	6.8	0.25
	2.5	28.8	0.75
[Li 15C5] 298 K	2.2	0.9	0.07
	2.2	40.0	0.93
[Na 15C5] 388 K	7.9	15.6	0.54
	-2.9	14.6	0.46
[Na 15C5] 369 K	7.8	17.1	0.50
	-2.0	17.1	0.50
[Na 15C5] 369 K	11.4	22.1	0.50
	-5.2	24.1	0.50

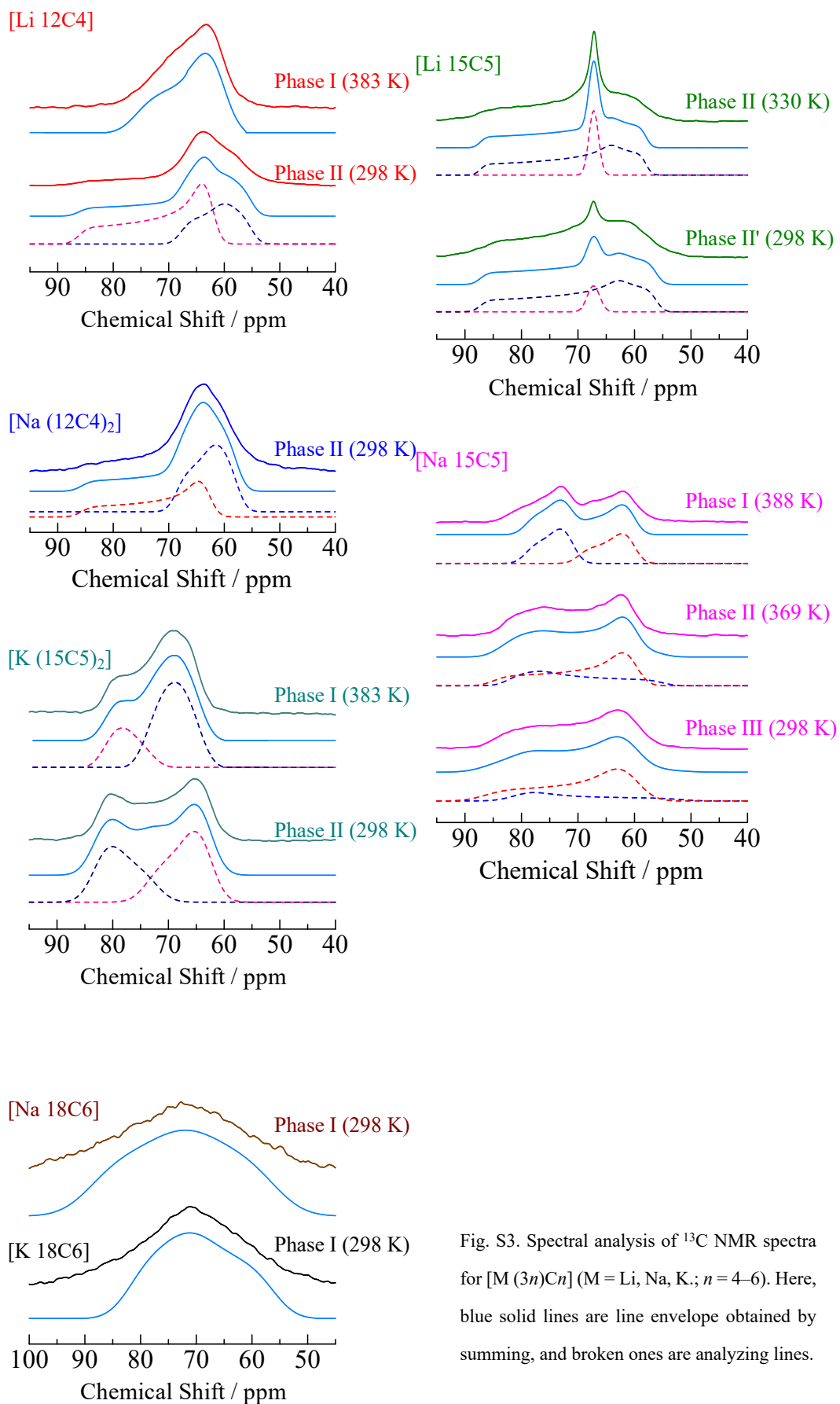


Fig. S3. Spectral analysis of ^{13}C NMR spectra for $[\text{M}(3n)\text{C}_n]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}; n = 4-6$). Here, blue solid lines are line envelope obtained by summing, and broken ones are analyzing lines.

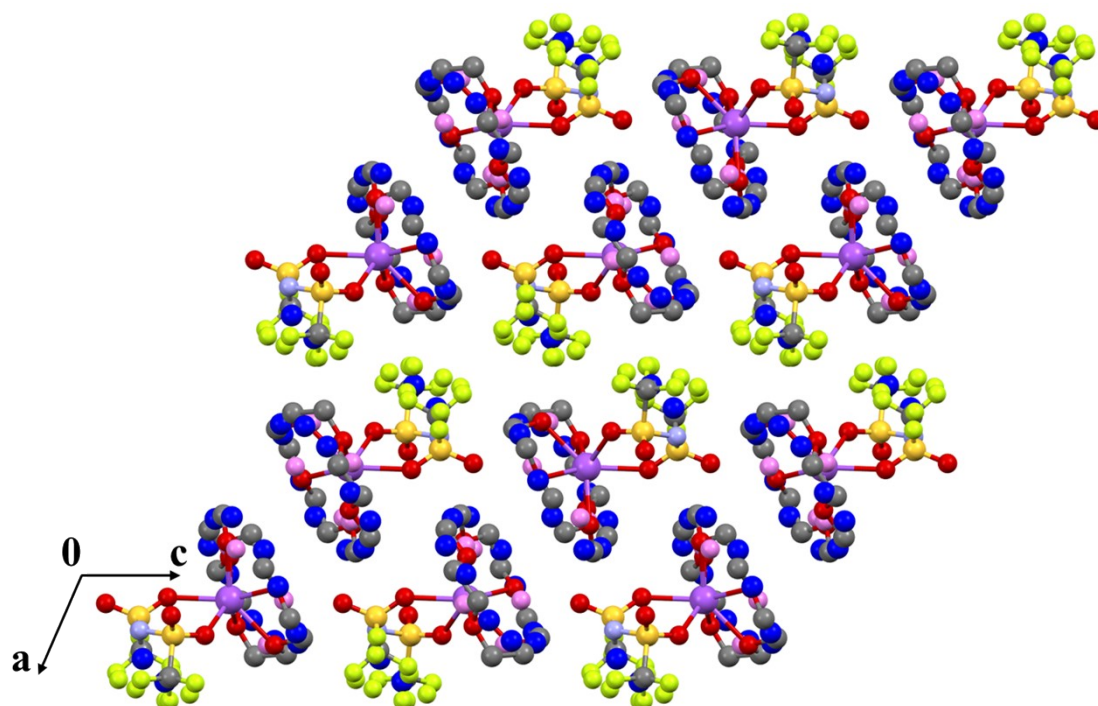


Fig. S4. A crystal packing diagrams of [Na 15C5] at 253K. The low occupancy part of the disordered molecules carbon, oxygen and fluorine are coloured as blue, violet and green, respectively. Hydrogens are omitted for clarity.

Table S1 Na-O distances and O-C-C angles determined by the SCXRD measurement at 253K.

	Structure A (High Occupancy)	Structure B (low Occupancy)
Na-O(1A) Distance	2.427 Å	2.465 Å
Na-O(2) Distance	2.409 Å	2.365 Å
Na-O(3) Distance	2.478 Å	2.430 Å
Na-O(4) Distance	2.417 Å	2.386 Å
Na-O(5) Distance	2.409 Å	2.436 Å
O(1)-C(1)-C(2) Angle	108.81°	109.11°
O(2)-C(3)-C(4) Angle	104.23°	92.94°
O(3)-C(5)-C(6) Angle	106.57°	123.68°
O(4)-C(7)-C(8) Angle	110.15°	110.73°
O(5)-C(9)-C(10) Angle	110.58°	111.17°

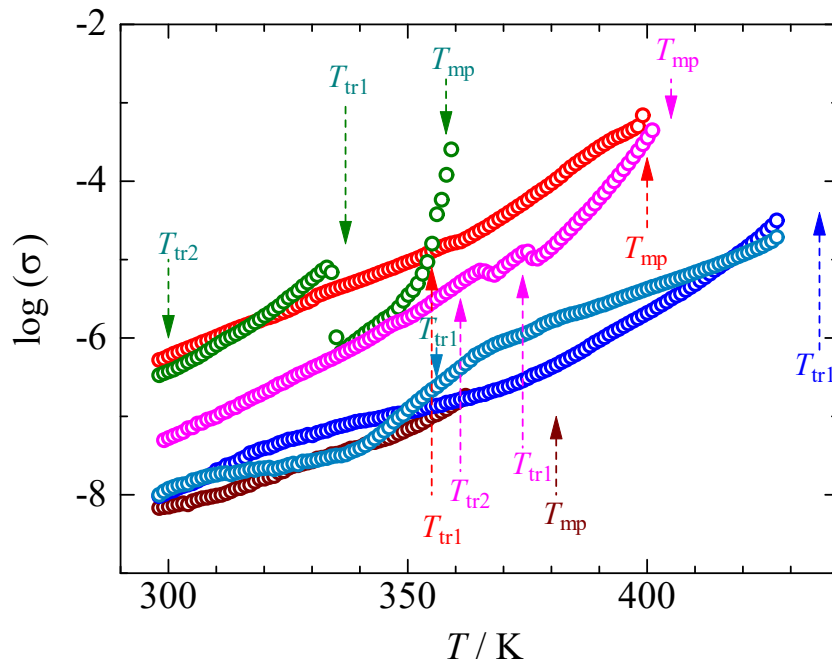


Fig. S5. Electrical conductivity σ of [Li 12C4] (○), [Na (12C4)₂] (○), [Li 15C5] (○), [Na 15C5] (○), [K (15C5)₂] (○), and [Na 18C6] (○) as a function of temperature.