Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

ESI: Large solubility of Lithium carboxylates reaching high rates of ^{6}Li incorporation in plastic scintillators for fast/thermal neutrons and gamma rays detection.

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Experimental

Materials and methods

Solvents were purchased from VWR; reagents were purchased from Sigma-Aldrich except for butyric acid, cyclopentanoic acid and cyclohexanoic acid, which were purchased from Acros. Monomers were distilled under reduced pressure to eliminate inhibitors and impurities. Other reagents were used without further purification. FTIR spectra were recorded on a Thermo Nicolet 8700 spectrometer with a Diamond ATR attachment.

Plastic scintillators were typically synthesized following 5 cycles of degassing under vacuum then sealed in glass vial under argon atmosphere and cured between 60 – 110 °C for several days. No initiator has been used.

Gamma pulse-height spectra were measured with a ^{137}Cs source and neutron/gamma pulse shape discrimination (PSD) were studied using a ^{252}Cf source shielded in its PET container, increasing the ratio of thermal to fast neutrons. Plastic scintillators were optically coupled to a Hamamatsu R7724-100 photomultiplier tube using RTV141A optical grease. In the case of gamma pulse height, the anode signal is collected through the lab own electronic board which collects pulse height as the maximal amplitude of each pulse and classified them into a histogram constituting the gamma pulse height spectra of a scintillator. In the case of n/γ PSD, the anode signal fed a CAEN DT5743 digitizer. Scintillation pulses were then recorded and post-processed with a homemade software where an optimized charge-comparison method is implemented and the mean Figure of Merit (i.e. evaluated at all incident energies) is calculated.

Synthesis

Part of this work is under patent application (FR 1856136).

Lithium carboxylates were synthesized as followed: 1 equivalent of $^{Nat/enriched}LiOH{\cdot}H_2O$ (1 g; 23.8 mmol) was dissolved in methanol (50 mL). 1 equivalent of carboxylic acid was progressively added to the mixture under stirring. The following product was concentrated by vacuum evaporation at 45 °C then precipitated with diethyl ether and filtered under pressure. $^{Nat/enriched}$Lithium carboxylates collected were then dried under vacuum at 60 °C for 12 h. Lithium carboxylates were obtained with yields between 45% and 90% (detailed below).

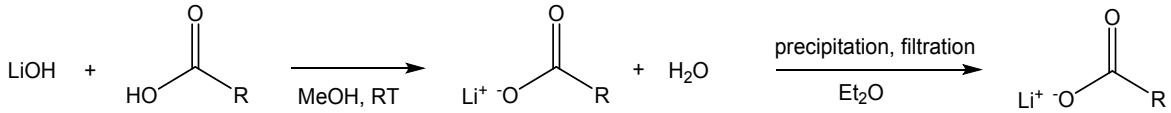


Figure S1. lithium carboxylates synthesis procedure

Lithium acrylate. The general procedure was followed with (1.63 mL) of acrylic acid (23.8 mmol). R=65%. FTIR (cm-1): 2980, 2933, 1643, 1550, 1428, 1335, 1276, 990, 959, 837.

Lithium methacrylate. The general procedure was followed with (2.02 mL) of methacrylic acid (23.8 mmol). R=60%. FTIR (cm-1): 2980, 2934, 1650, 1556, 1456, 1410, 1242, 1005, 933, 858, 839.

Lithium butyrate. The general procedure was followed with (2.19 mL) of butyric acid (23.8 mmol). R=47%. FTIR (cm-1): 2964, 2935, 2874, 1578, 1558, 1433, 1265, 1103, 900, 758,712.

Lithium pivalate. The general procedure was followed with (2.74 mL) of pivalic acid (23.8 mmol). R=58%. FTIR (cm-1): 2966, 2872, 1560, 1480, 1420, 1405, 1357, 894, 796.

Lithium pentanoate. The general procedure was followed with (2.59 mL) of pentanoic acid (23.8 mmol). R=80%. FTIR (cm-1): 2956, 2936, 2872, 1578, 1558, 1439, 1407, 1321, 1239, 1110, 932, 733, 695.

Lithium α-valerate. The general procedure was followed with (2.60 mL) of α-valeric acid (23.8 mmol). R=94%. FTIR (cm-1): 2968, 2936, 2877, 1558, 1462, 1407, 1370, 1301, 1251, 1092, 968, 906, 806, 773.

Lithium β-valerate. The general procedure was followed with (2.63 mL) of β-valeric acid (23.8 mmol). R=90%. FTIR (cm-1): 2957, 2872, 1573, 1401, 1380, 1366, 1342, 1322, 1260, 1223, 1108, 893, 718.

Lithium sorbate. The general procedure was followed with (2.67 g) of sorbic acid (23.8 mmol). R=45%. FTIR (cm-1): 3020, 1915, 1651, 1620, 1549, 1405, 1288, 1161, 997, 951, 887, 803, 728.

Lithium hexanoate. The general procedure was followed with (2.98 mL) of hexanoic acid (23.8 mmol). R=63%. FTIR (cm-1): 2953, 2929, 2871, 1578, 1557, 1439.

Lithium 2,2-dimethylbutyrate. The general procedure was followed with (2.99 mL) of 2,2-dimethylbutyric acid (23.8 mmol). R=64%. FTIR (cm-1): 2964, 2931, 2877, 1606, 1462, 1396, 1360, 1282, 1200,1055, 1007, 879, 794, 765.

Lithium 2-ethylbutyrate. The general procedure was followed with (3.00 mL) of 2-ethylbutyric acid (23.8 mmol). R=88%. FTIR (cm-1): 2966, 2939, 2877, 1587, 1461, 1410, 1307, 1289, 1274, 1251, 809.

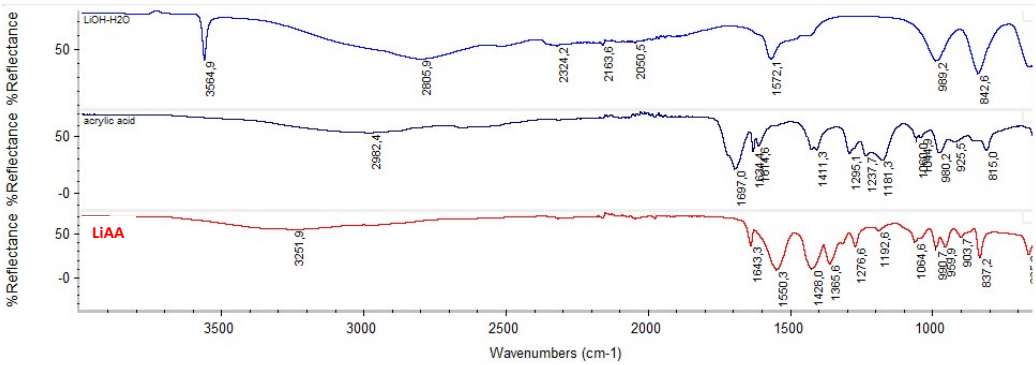
Lithium octanoate. The general procedure was followed with (3.77 mL) of octanoic acid (23.8 mmol). R=63%. FTIR (cm-1): 2954, 2921, 2852, 1578, 1557, 1441, 1404, 722.

Lithium cyclopentanoate. The general procedure was followed with (2.57 mL) of cyclopentanoic acid (23.8 mmol). R=69%. FTIR (cm-1): 2947, 2866, 1560, 1415, 1326, 1309, 1289, 769, 665.

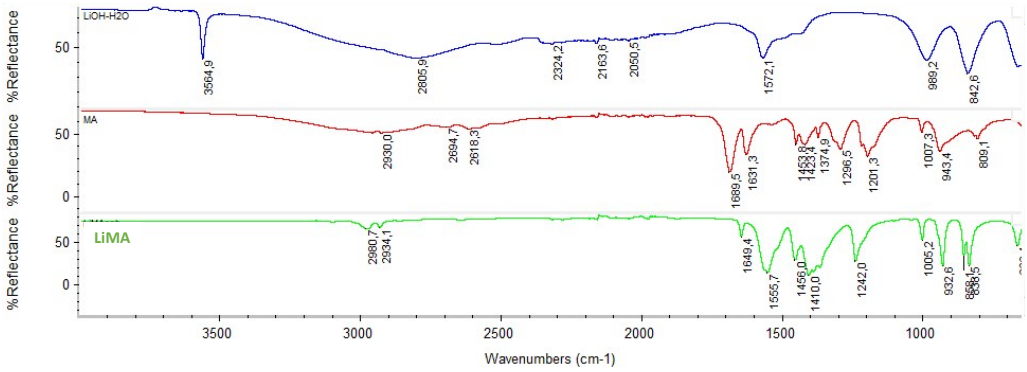
Lithium cyclohexanoate. The general procedure was followed with (2.94 mL) of cyclohexanoic acid (23.8 mmol). R=65%. FTIR (cm-1): 2937, 2859, 1693, 1447, 1422, 1313, 1255, 1210, 1181, 952, 923, 890.

Lithium salicylate. The general procedure was followed with (3.28 g) of salicylic acid (23.8 mmol). R=70%. FTIR (cm-1): 1630, 1569, 1486, 1455, 1391, 1244, 1145, 1029, 934, 859, 814, 748, 705.

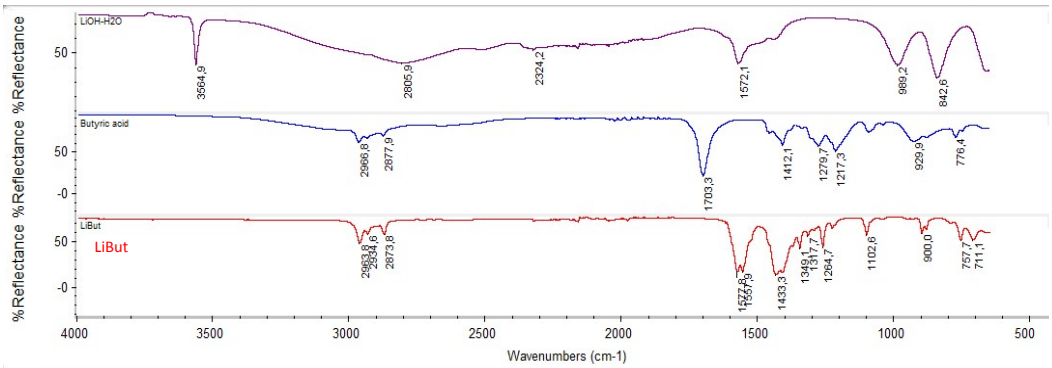
Lithium vinylbenzoate. The general procedure was followed with (3.28 g) of salicylic acid (23.8 mmol). R=77%. FTIR (cm-1): 1595, 1546, 1507, 1399, 1310, 1111, 1014, 989, 905, 875, 852, 798, 772, 721.



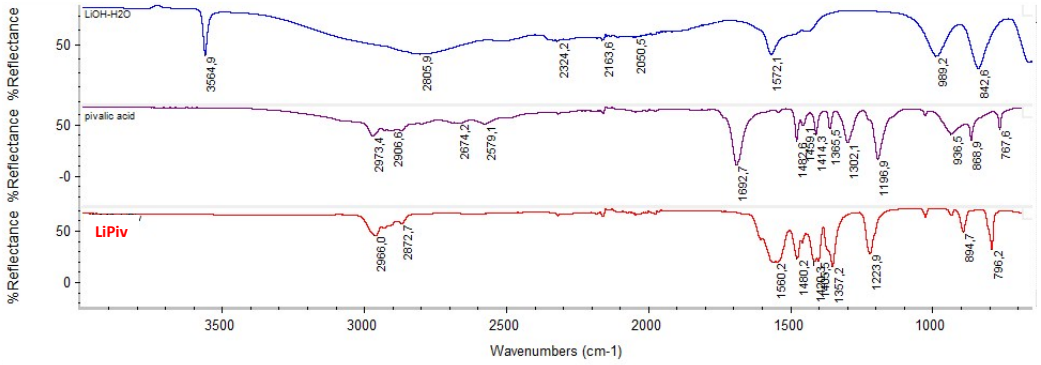
Lithium acrylate (cm^{-1}) : 2980, 2933, 1643, 1550, 1428, 1335, 1276, 990, 959, 837



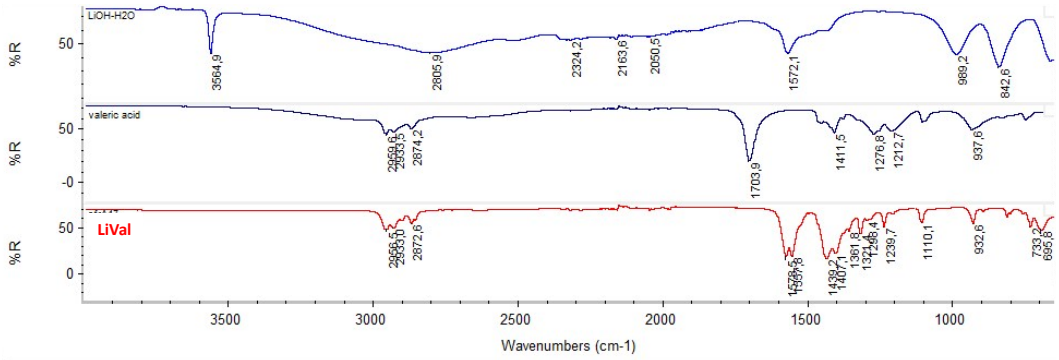
Lithium methacrylate (cm^{-1}) : 2980, 2934, 1650, 1556, 1456, 1410, 1242, 1005, 933, 858, 839



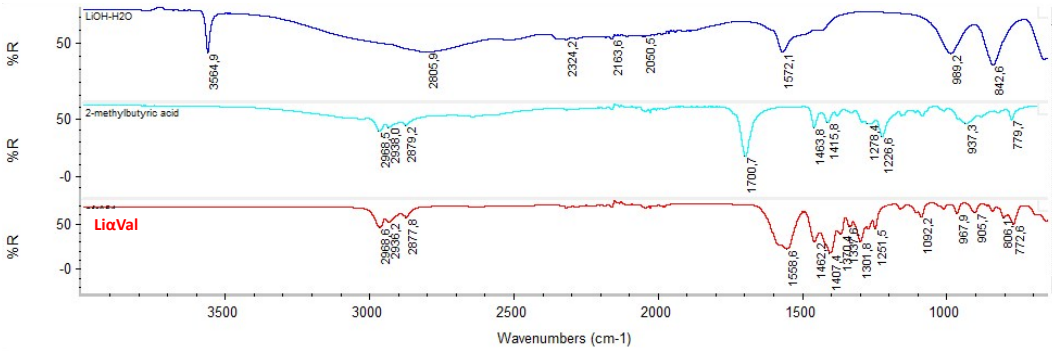
Lithium butyrate (cm-1) : 2964, 2935, 2874, 1578, 1558, 1433, 1265, 1103, 900, 758,712



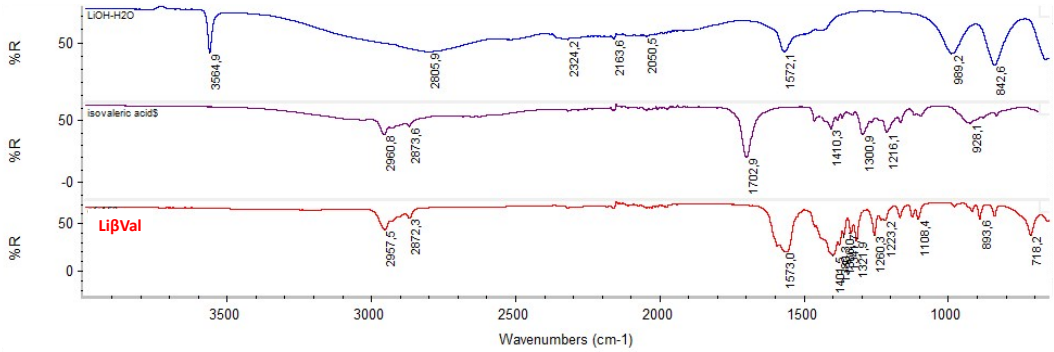
Lithium pivalate (cm^{-1}) : 2966, 2872, 1560, 1480, 1420, 1405, 1357, 894, 796



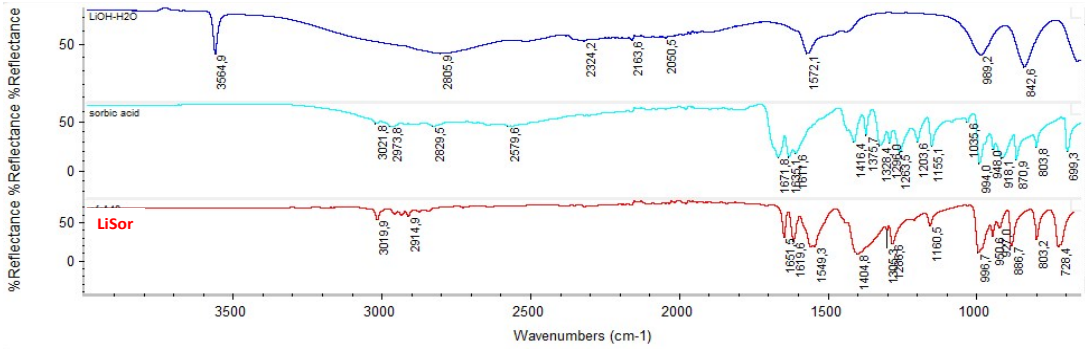
Lithium pentanoate (cm^{-1}) : 2956, 2936, 2872, 1578, 1558, 1439, 1407, 1321, 1239, 1110, 932, 733, 695



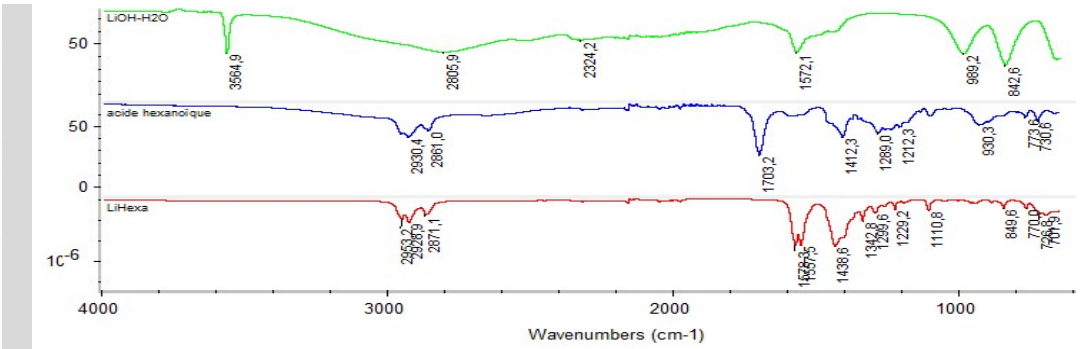
Lithium α-valerate (cm^{-1}) : 2968, 2936, 2877, 1558, 1462, 1407, 1370, 1301, 1251, 1092, 968, 906, 806, 773



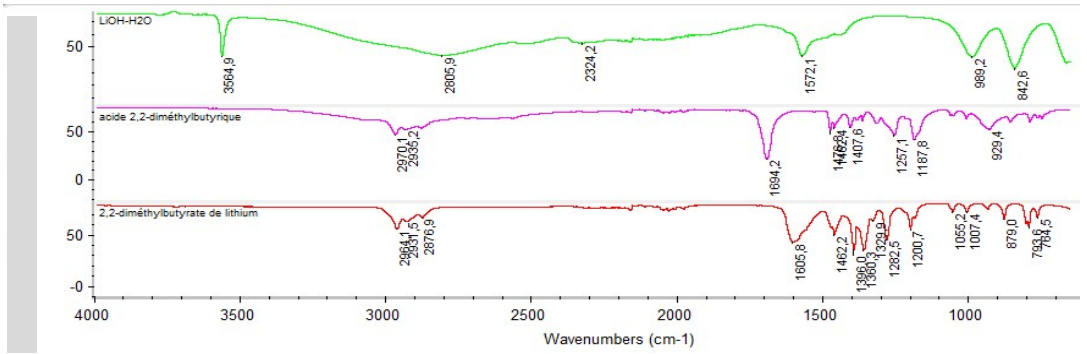
Lithium β-valerate (cm^{-1}) : 2957, 2872, 1573, 1401, 1380, 1366, 1342, 1322, 1260, 1223, 1108, 893, 718



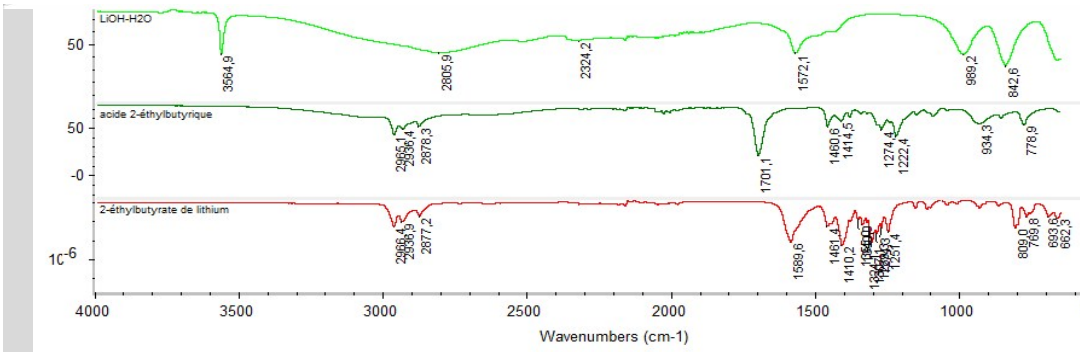
Lithium sorbate (cm^{-1}) : 3020, 1915, 1651, 1620, 1549, 1405, 1288, 1161, 997, 951, 887, 803, 728



Lithium hexanoate (cm^{-1}) : 2953, 2929, 2871, 1578, 1557, 1439



Lithium 2,2-dimethylbutyrate (cm^{-1}) : 2964, 2931, 2877, 1606, 1462, 1396, 1360, 1282, 1200,1055, 1007, 879, 794, 765



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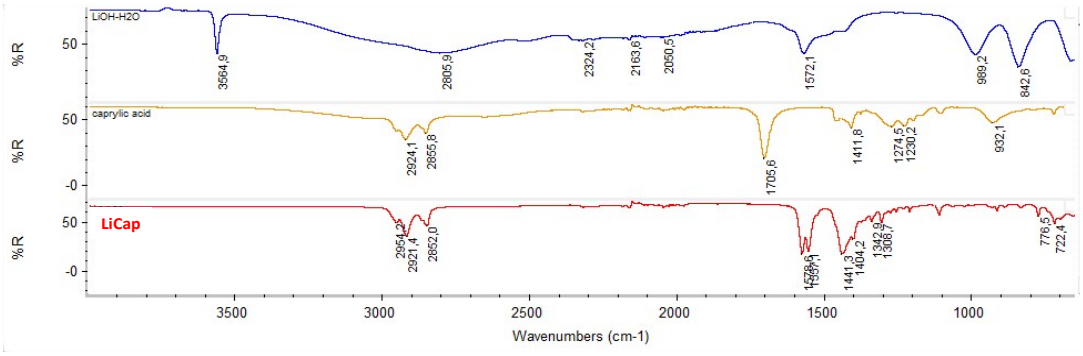
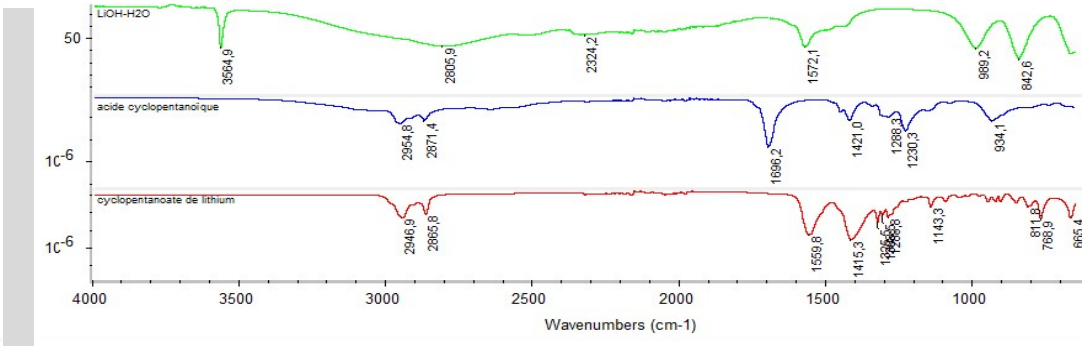
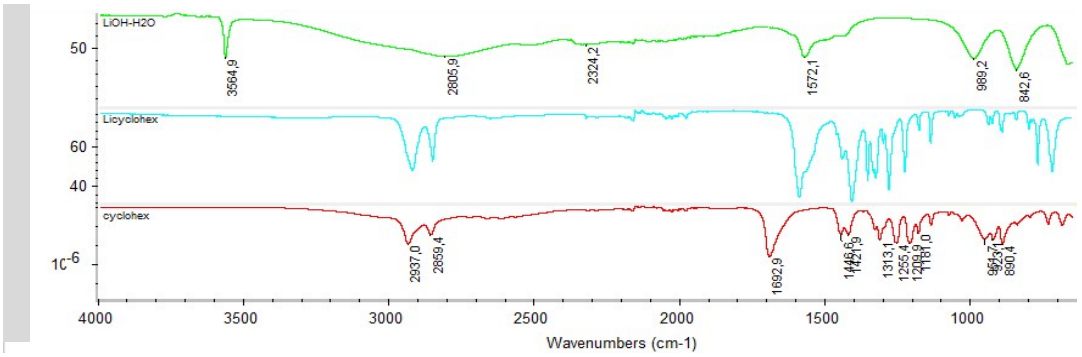


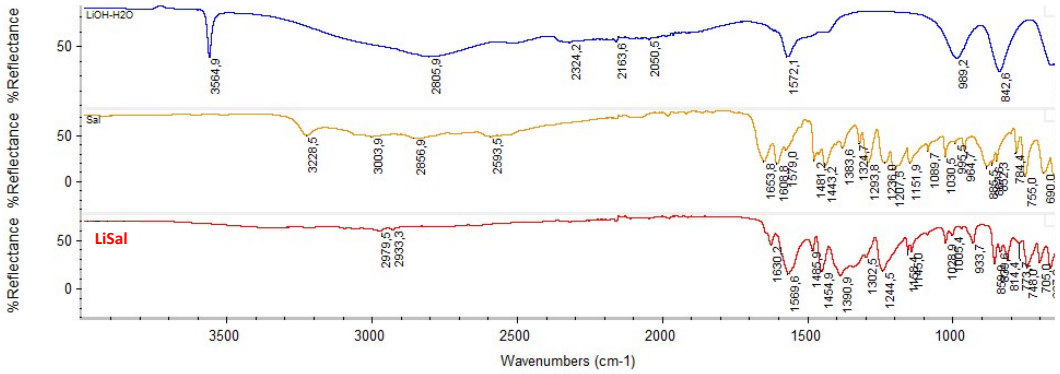
Lithium octanoate (cm^{-1}) : 2954, 2921, 2852, 1578, 1557, 1441, 1404, 722



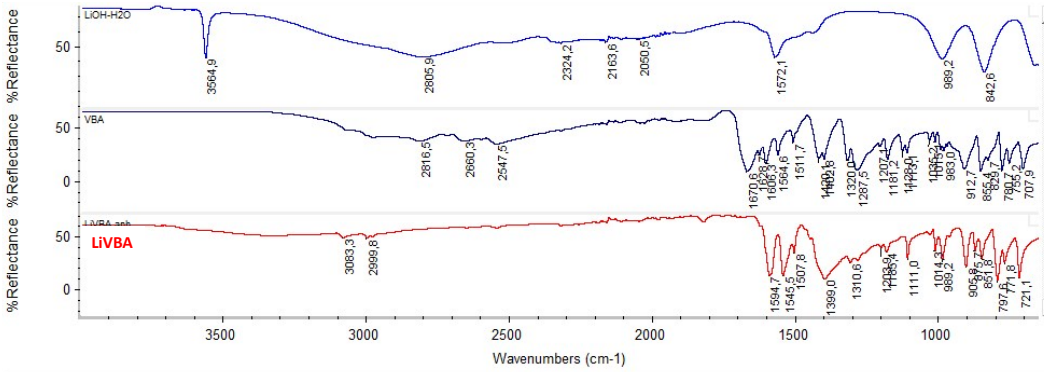
Lithium cyclopentanoate (cm^{-1}) : 2947, 2866, 1560, 1415, 1326, 1309, 1289, 769, 665



Lithium cyclohexanoate (cm^{-1}) : 2937, 2859, 1693, 1447, 1422, 1313, 1255, 1210, 1181, 952, 923, 890



Lithium salicylate (cm^{-1}) : 1630, 1569, 1486, 1455, 1391, 1244, 1145, 1029, 934, 859, 814, 748, 705

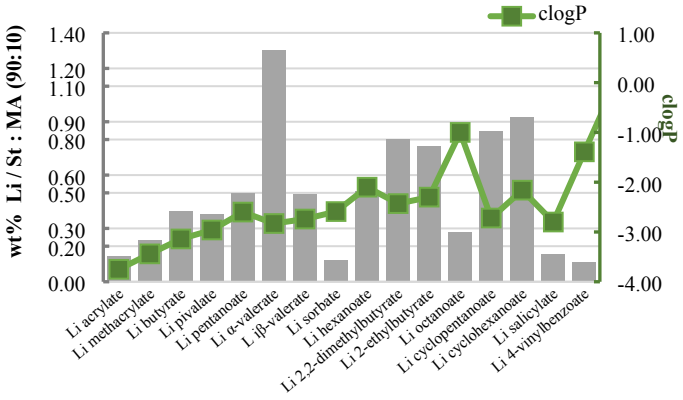


Lithium 4-vinylbenzoate (cm^{-1}) : 1595, 1546, 1507, 1399, 1310, 1111, 1014, 989, 905, 875, 852, 798, 772, 721

ClogP and Hanssen solubility parameters

We additionally evaluate predictive clogP values as well as Hanssen solubility parameters (see below). Accordingly, we did not find any predictable explanation about the LiαVal high solubility.

A.



B.

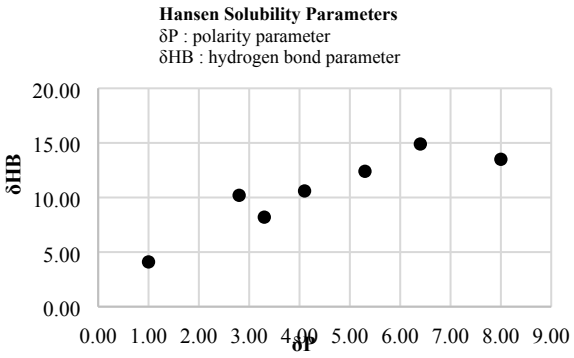


Figure S2. A. Li-carboxylates solubility and clogP comparison; B. Hansen solubility parameters of carboxylic acid moieties

Pictures and hardness of PSs #1 to #9

Highly transparent PSs were received for all St : MA (60 : 40) matrices even at high doping amount of ^{6}LiαVal (50 wt% LiαVal). For other St : MA compositions (90 : 10, 80 : 20, 70 : 30), a relatively high turbidity were received but did not prevent from qualitative photophysical results.

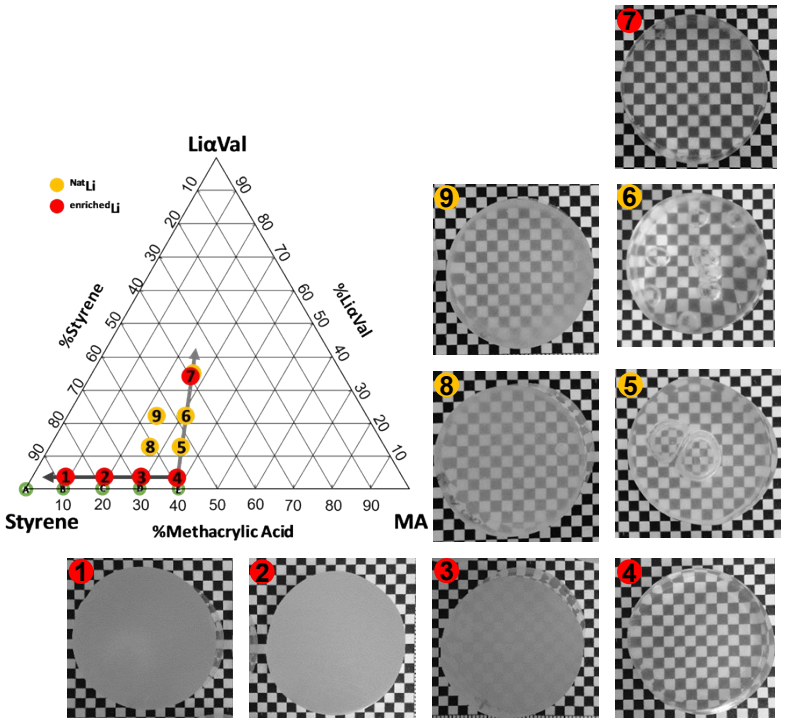


Figure S3. Pictures of PS #1 to #9

Table S1. Hardness of PSs #1 to #9

PS #	#1	#2	#3	#4	#5	#6	#7	#8	#9
Hardness (Shore-D)	66	84	88	87	89	78	59	85	79

NB: Shore-D (EJ-200) =97

LiαVal non-loaded PSs study

A serie of non-loaded PSs was synthesized with +3%wt PPO and +0.03%wt POPOP, without LiαVal. This study pointed out that the samples turbidity relies on the monomers composition (see Figure S4). Additionally, increasing amounts of methacrylic acid leads to lower radioluminescence light yields (see Figure S5).

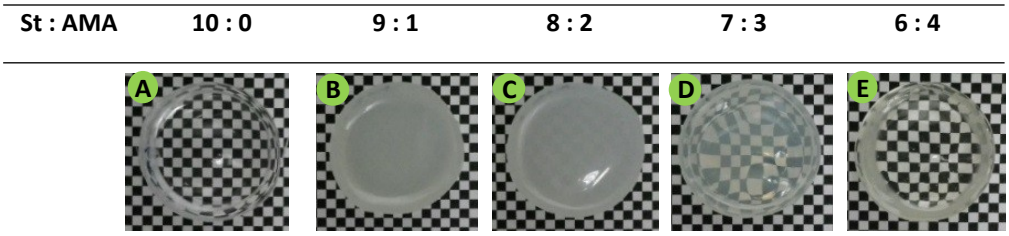


Figure S4. pictures of PS A to E (without LiαVal; +3%wt PPO, +0.03%wt POPOP)

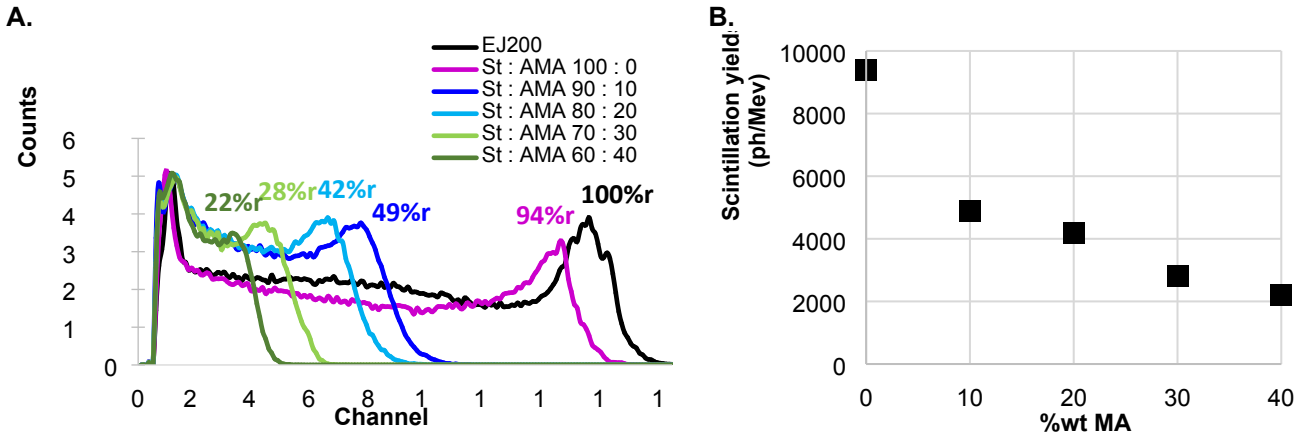


Figure S5. A. Pulse height spectra of sample #A to #E; B. corresponding radioluminescence light yields; ^{137}Cs source

Figure of Merit description

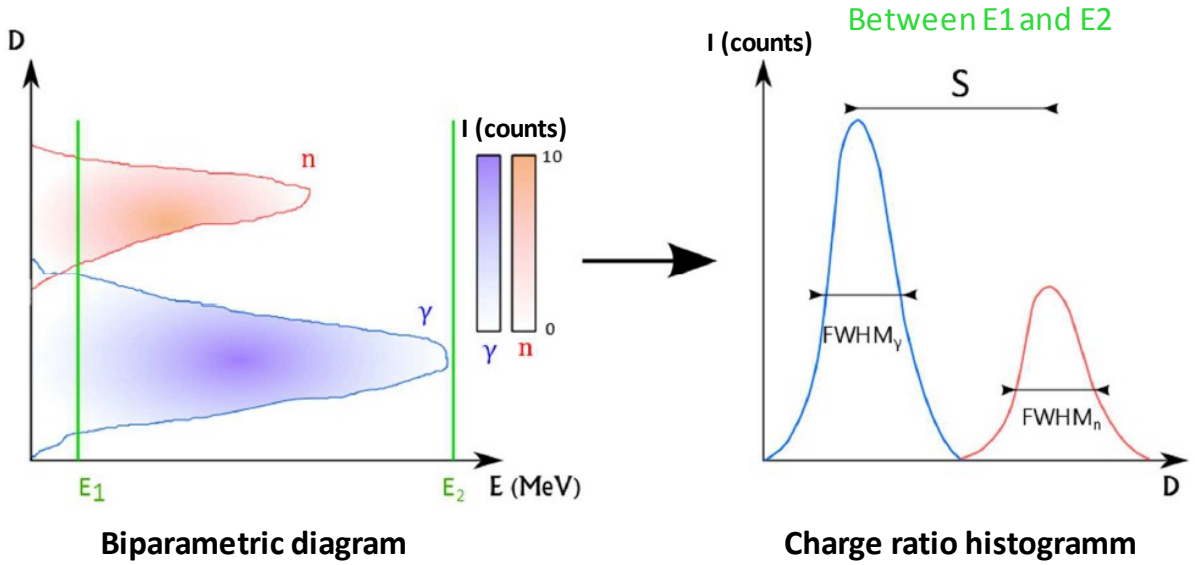


Figure S6. Biparametric diagramm and corresponding charge ratio histogramm

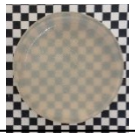
$$FoM = \frac{S}{FWHN_n + FWHN_\gamma} \quad \text{(Equation 1)}$$

Photophysical characterizations extended to other ^{6}Lithium carboxylates

A study of Li^{6}-doped plastic scintillators were conducted with 8 other ^{6}Li carboxylates (^{6}Li-methacrylate, ^{6}Li-pivalate, ^{6}Li-pentanoate, ^{6}Li-βvalerate, ^{6}Li-hexanoate, ^{6}Li-2,2dimethylbutyrate, ^{6}Li-salicylate, ^{6}Li-octanoate) which presents acceptable solubility to be synthesized at this amount (+0.15wt% ^{6}Li). The composition of these PSs were chosen such as the %wt^{6}Li remains constant at 0.15%wt^{6}Li for all the Li^{6} carboxylates chosen for this study. 9 PSs of 10g were then synthesized simultaneously and cured together in the same oven in order to compare them properly. The photophysical characterization are displayed below.

Similar to the ^{6}LiαVal PS #1, relatively turbid PSs were received. Acceptable results were obtained for all ^{6}Li-carboxylates except for ^{6}Li-methacrylate and ^{6}Li-salicylate, which displayed poorer photophysical features. Once again, similar trends of scintillation yields and FoM values are observed, like in pure fast neutron / gamma discrimination where better scintillation yields favours a better FoM. ^{6}LiαVal presents the best scintillation light yield and one of the best FoM value.
^{6}Li pivalate, ^{6}Li α-valerate, ^{6}Li 2,2-dimethylbutyrate and ^{6}Li octanoate present the best FoM values, whereas ^{6}Li methacrylate and ^{6}Li salicylate display lower FoM.

Table S2. PSs composition of ^{6}Li carboxylates study on photophysical properties for equivalent wt%Li (0.15%wt Li).

PS #	**#10**	**#11**	**#12**	**#13**	**#14**	**#15**	**#16**	**#17**	**#18**
^{6}Li carbox.	**^{6}Li methacrylate**	**^{6}Li pivalate**	**^{6}Li pentanoate**	**^{6}Li α-valerate**	**^{6}Li β-valerate**	**^{6}Li hexanoate**	**^{6}Li 2,2dimethyl Butyrate**	**^{6}Li salicylate**	**^{6}Li octanoate**
									
wt% St	73	72.8	72.8	72.8	72.8	72.5	72.5	72	71.9
wt% MA	8.1	8.1	8.1	8.1	8.1	8	8	8	8
wt% PPO	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7	16.7
wt% POPOP	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
wt% ^{6}Li carbox.	2.1	2.4	2.4	2.4	2.4	2.8	2.8	3.3	3.4
wt% ^{6}Li	*0.15*	*0.15*	*0.15*	*0.15*	*0.15*	*0.15*	*0.15*	*0.15*	*0.15*
Scintillation yield (Ph/MeV)	2090	3290	3160	3670	2910	2970	3350	1520	3160
FoM	0.88	1.09	1.02	1.15	0.98	0.97	1.15	0.66	1.13
Hardness (Shore-D)	80	87	85	85	85	86	81	86	84

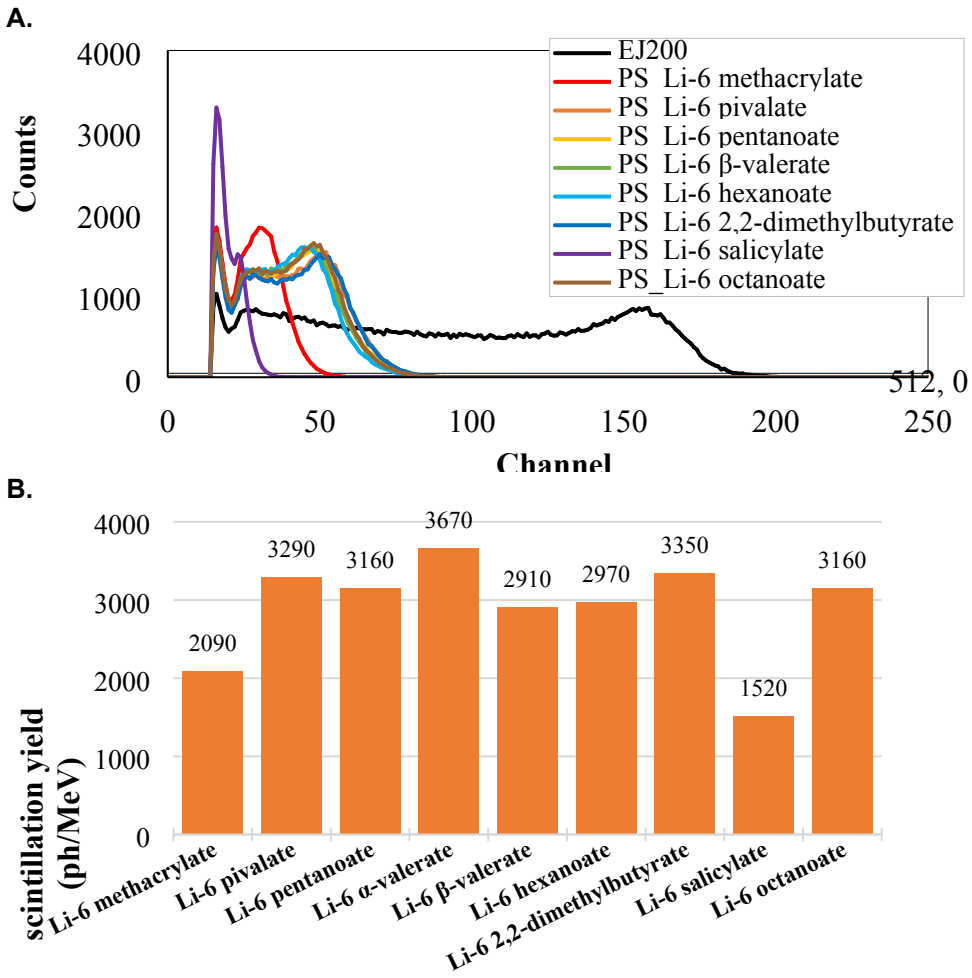


Figure S8. A. pulse height spectra of PSs with ^{6}Li carboxylates as listed in Table 1; B. corresponding scintillation yields calculated from EJ200; ^{137}Cs source.

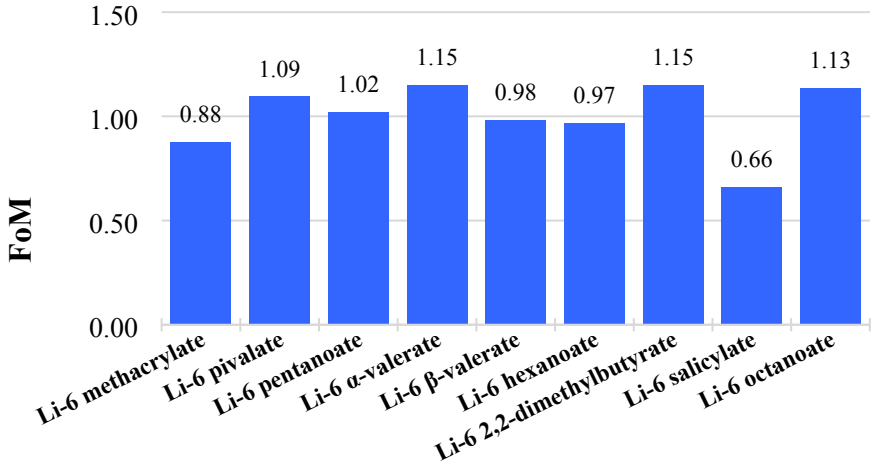
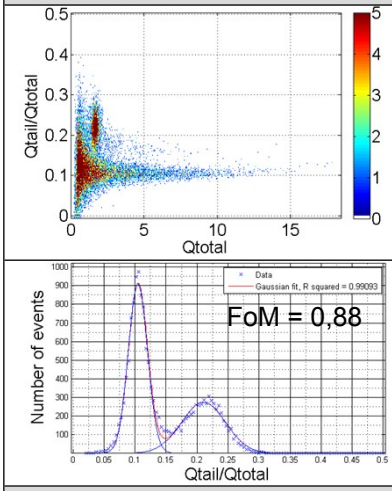
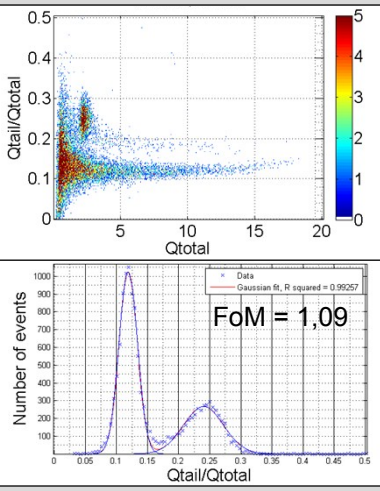
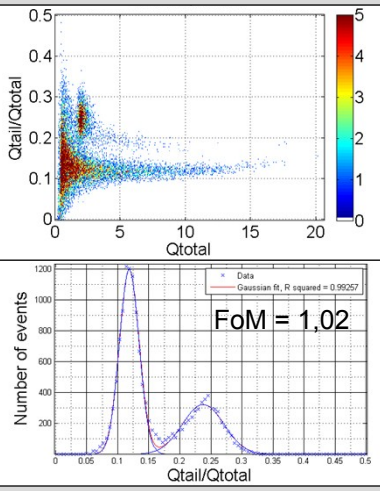
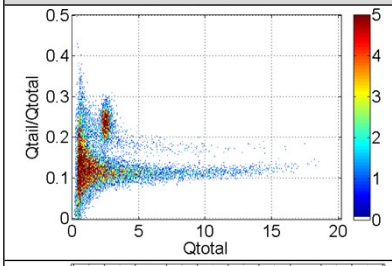
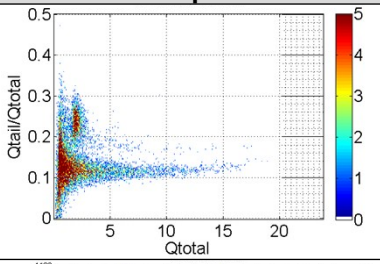
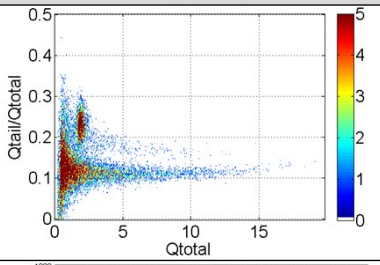
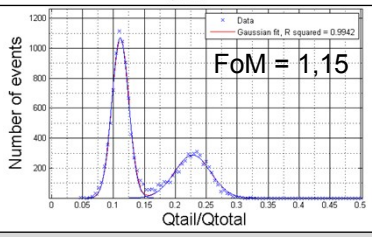
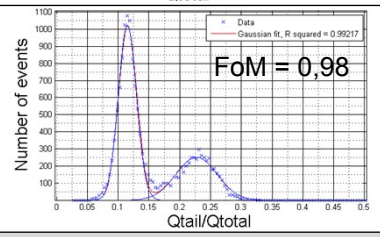
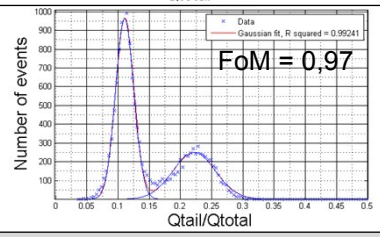


Figure S9. FoM (n/γ) for Qtotε[1-2;15] corresponding to biparametric diagram from Table 2.

Table S3. biparametric diagrams of ^{6}Li-carboxylates doped PSs.

^{6}LiMA	^{6}LiPiv	^{6}LiVal
		
^{6}LiαVal	**^{6}LiβVal**	**^{6}LiHex**
		
		
^{6}Li2,2αVal	**^{6}LiSal**	**^{6}LiOct**