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Accurate Measurement of Effective Li-Li Scalar Coupling Constants: the NMR Missing Link for Alkyllithium Aggregates.

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1. General considerations:

Commercial Tetrahydrofurane-d_8, Diethylether-d_{10} and Toluene-d_8 were distilled over sodium and benzophenone. Argon was dried and deoxygenated by bubbling through a commercial solution of butyllithium in hexane. Commercial di-*n*-butylether was distilled overs CaH_2.

2. Experimental procedures

2.1. Alkyllithium salt-free solutions in tetrahydrofuran-d_8 or diethylether-d_{10}

A solution of Methyllithium in ether, Ethyllithium in cyclohexane or *n*-butyllithium in hexane was syringed in a tube fitted with a septum and flushed under dry argon. The tube was then placed under vacuum (20-25 mmHg) for 1 to 3 hours to evaporate all the solvent. The resulting solid was then dissolved in freshly distilled THF-d_8, Et_2O-d_{10} and placed under vacuum for 1h to evaporate the last traces of solvent. A new volume of solvent (2 to 3 mL) was added and the resulting solution was titrated (~0.5 to 0.7M) using a procedure reported by Duhamel.[1]

2.2. Alkyllithium salt-free solutions in dibutylether/toluene-d_8 (80 :20)

A solution of Methyllithium in ether, *n*-BuLi in hexanes or EtLi in cyclohexane was syringed in a tube fitted with a septum and flushed under dry argon. The tube was then placed under vacuum (20-25 mmHg) for 1 to 3 hours to evaporate all the solvent. The resulting solid was then dissolved in freshly distilled mixture of dibutylether/toluene-d_8 (ratio 4 :1). The resulting solution was titrated (~0.3 to 0.5M) according to the literature.[1]

2.3. Methyllithium / *n*-Butyllithium (ratio 1 : 1) in THF-d_8 solution

An equivalent of MeLi (~0.7M in THF-d_8) was added at -78°C to a solution of *n*-BuLi (~0.5M) in THF-d_8 (0.5 mL) placed into a dry 5-mm NMR tube, fitted with a septum and flushed under argon. The tube was vigorously shaken and was dropped in the pre-cooled NMR probe.

2.4. Methyllithium / Ethyllithium (ratio 1 : 0.8) in THF-d_8 solution

0.8 equivalent of EtLi (~0.5M in THF-d_8) was added at -78°C to a solution of MeLi (~0.7M) in THF-d_8 (0.5 mL) placed into a dry 5-mm NMR tube, fitted with a septum and flushed under argon. The tube was vigorously shaken and was dropped in the pre-cooled NMR probe.

2.5. Ethyllithium/ *n*-Butyllithium (ratio 1 : 0.8) in THF-d_8 solution

0.8 equivalent of *n*-BuLi (~0.5M) in THF-d_8 was added at -78°C to a solution of EtLi (~0.5M in THF-d_8) (0.5 mL) placed into a dry 5-mm NMR tube, fitted with a septum and flushed under argon. The tube was vigorously shaken and was dropped in the pre-cooled NMR probe.

2.6. Alkyllithium mixture (ratio 1 : 1) in Et_2O or (n-Bu)$_2$O solution

An equivalent of MeLi (~0.7M in Et_2O-d_{10}, ~0.5M in (n-Bu)$_2$O) was added at -78°C to a solution of *n*-BuLi or EtLi (~0.5M) in Et_2O-d_{10} or (~0.3M) in (n-Bu)$_2$O (0.5 mL) into a dry 5-mm NMR tube, fitted with a septum and flushed under argon. The tube was vigorously shaken and was dropped in the pre-cooled NMR probe.

2.7. NMR parameters and conditions:

All NMR experiments were recorded on a Bruker Avance DMX 500 spectrometer operating at 500.13 MHz for ^{1}H and 194.4 MHz for ^{7}Li. Experiments were run under Topsin (version 2.1) with a BBFO {^{1}H,X} probe and a z gradient unit.

1D NMR Measurements: Lithium one dimensional experiments were recorded with standard parameters, 32 scans, an acquisition time of 5s and a relaxation delay of 10s.

2D ^{7}Li-^{7}Li EXSY: The following parameters were used for acquiring and processing the spectrum: 256 experiments with 2048 data points and 16 scans each were recorded. The relaxation time was 5s. Pure phase line shapes was obtained by using time proportional phase incrementation (TPPI) phase cycling. The mixing time was τ_m = 0.4s to τ_m = 1s. One time zero filling was applied to obtain a digital resolution of 0.94 Hz/point in f1 and 0.94 Hz/point in f2. The temperature range was between 205K and 175K.

2D ^{7}Li-^{7}Li CT-COSY: The following parameters were used for acquiring and processing the spectrum: 256 experiments with 2048 data points with 4 scan each were recorded. The relaxation time was 5s. The delta delai was between 40ms and 500ms. One time zero filling in f1 to obtain a digital resolution of 0.47 Hz/point in f1 and 1.33 Hz/point in f2.

3. References

(1) Duhamel, L.; Plaquevent, J.-C. *J. Organomet. Chem.* **1993**, *448*, 1-3.

4. NMR Data

Figure 1S: Variable temperature NMR 1D ^{7}Li spectra of MeLi/*n*-BuLi mixture in THF-d_8.

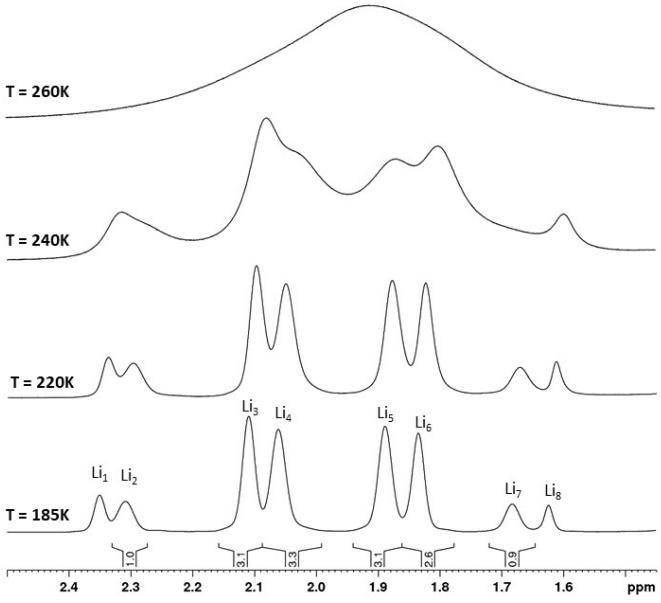


Figure 2S: Plot of the intensity ratio I_{cross}/I_{diag} versus constant time for $(MeLi)_{4-n}(n\text{-BuLi})_n$ mixed aggregates.

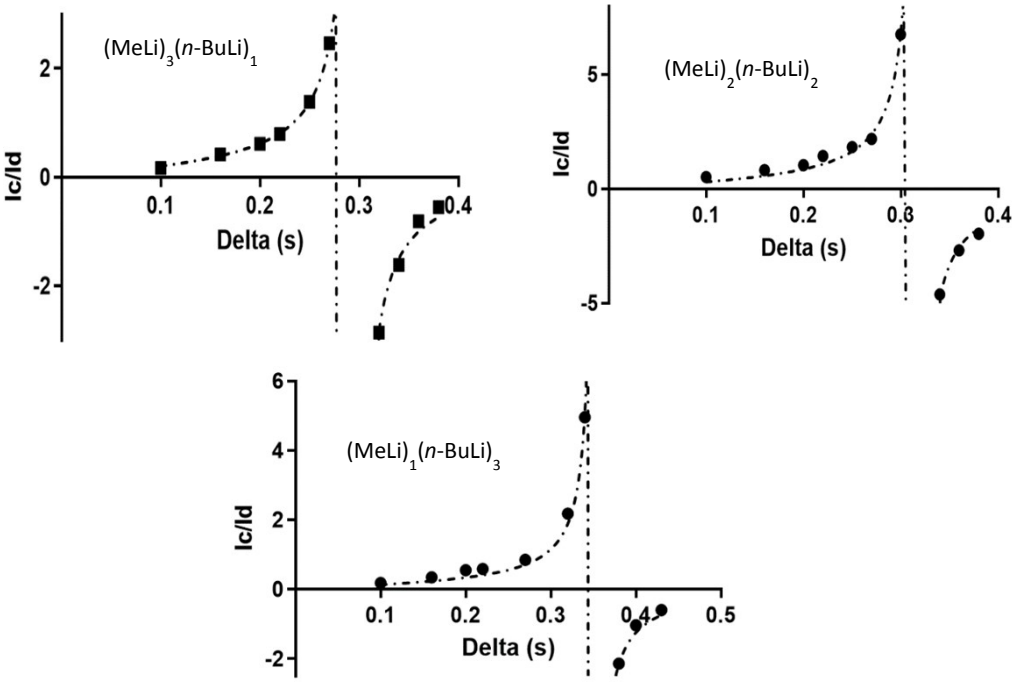
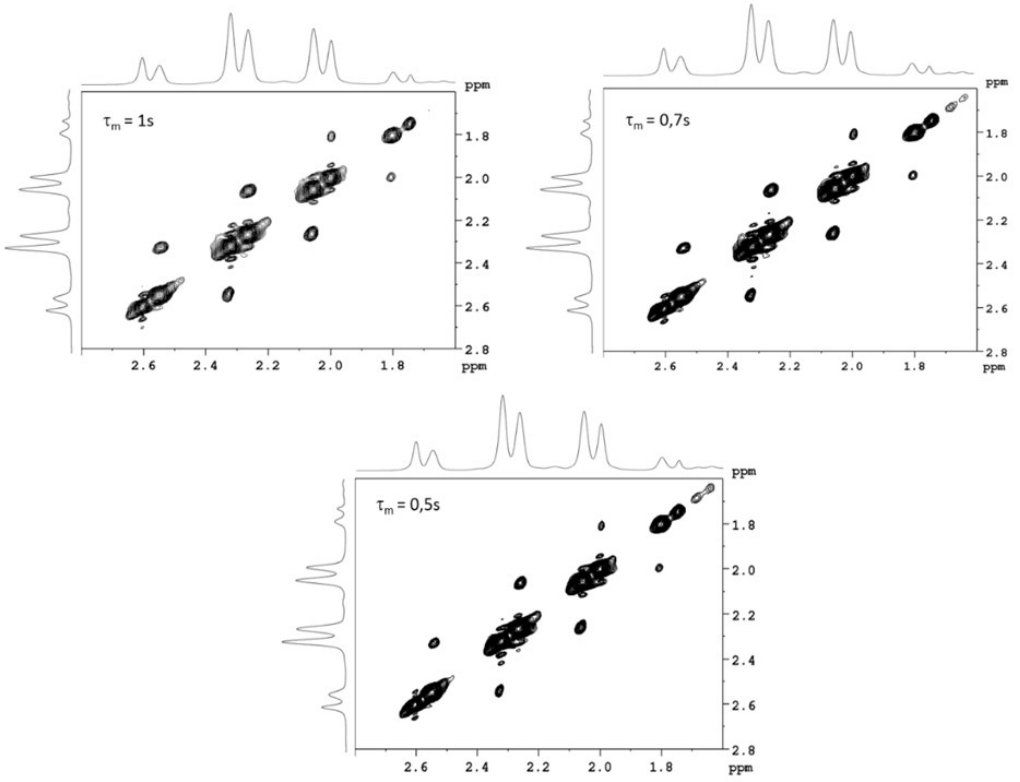


Figure 3S: (a) 2D ^{7}Li-^{7}Li EXSY (mixing times τ_m = 0.5s, 0.7s and 1s) spectra of MeLi/*n*-BuLi (1:1) in THF-d_8 at 185K. (b) Build-up ^{7}Li exchange curves of mixed aggregates $(MeLi)_{4-n}(n\text{-}BuLi)_n$ obtained from 2D ^{7}Li-^{7}Li EXSY experiments at 185K.

(a)



(b)

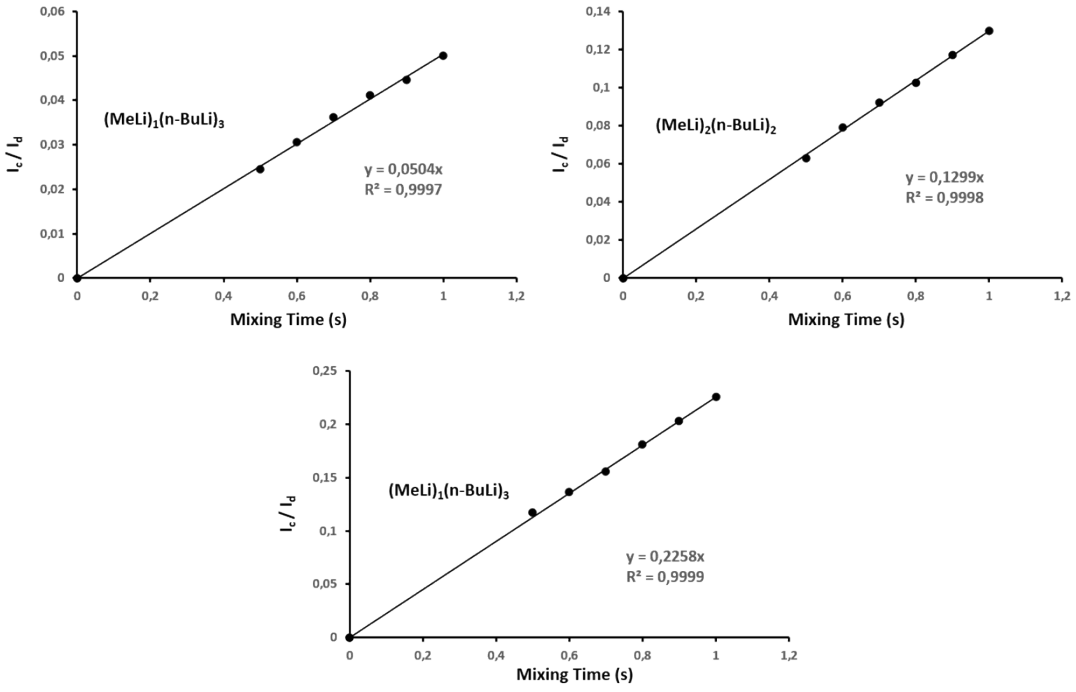


Figure 4S: 1D ^{7}Li spectra of EtLi/RLi mixtures (R = *n*-Bu (top), Me (bottom)) in THF-d_8 at 185K.

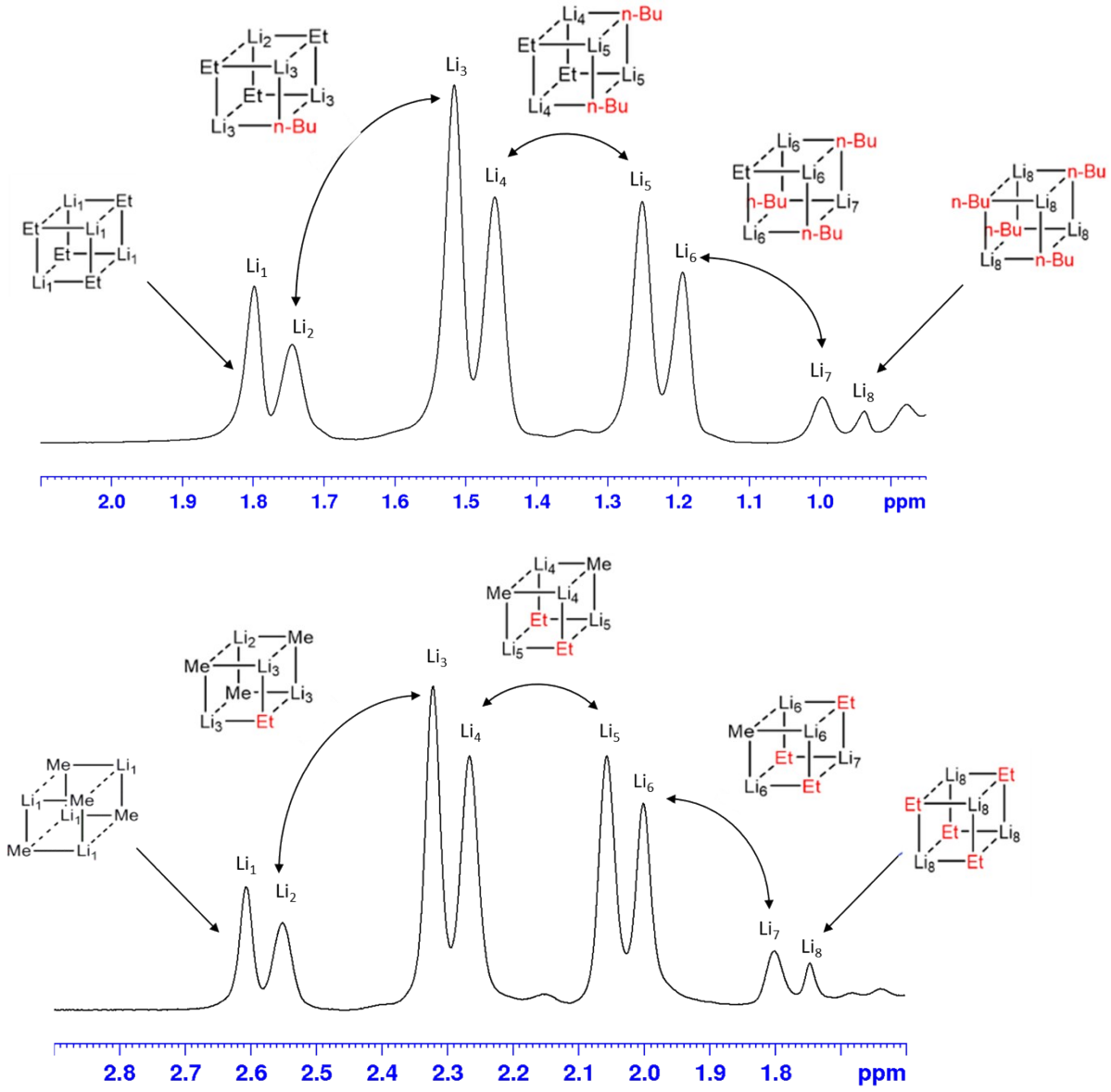
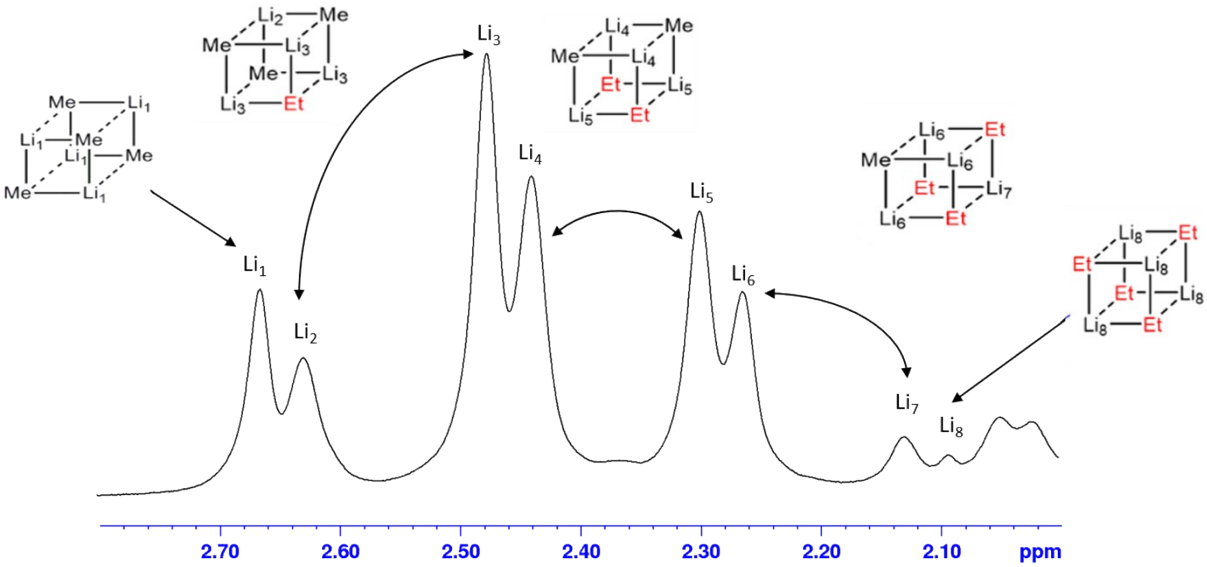


Figure 5S: 1D ^{7}Li spectra of EtLi/RLi mixtures (R = Me (top), *n*-Bu (bottom)) in Et_2O-d_{10} at 185K.



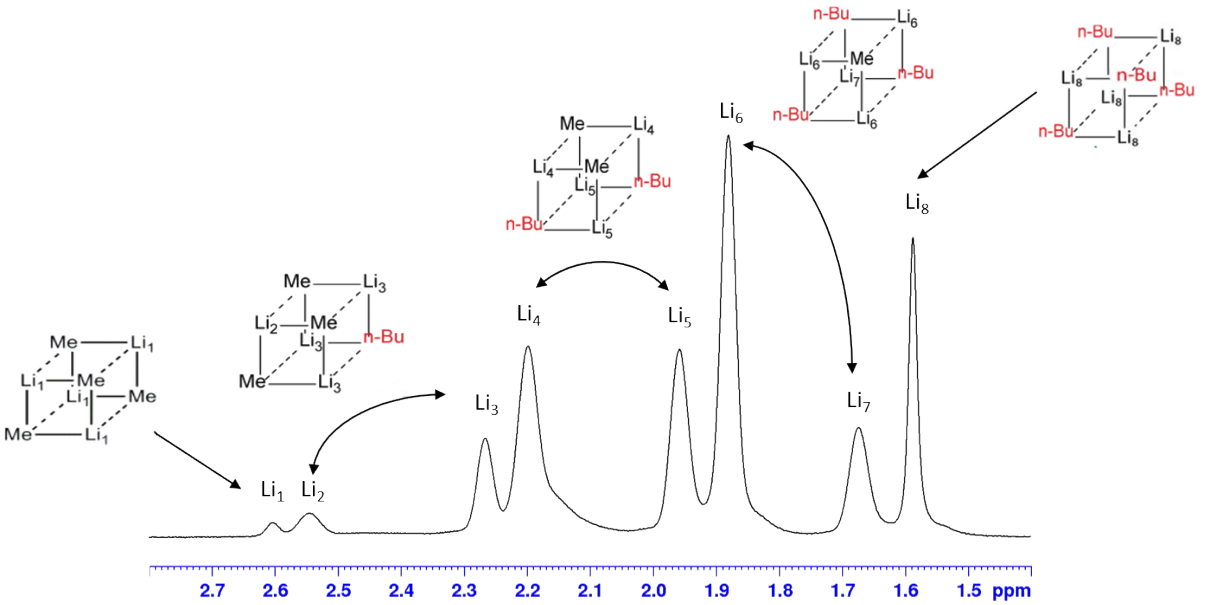
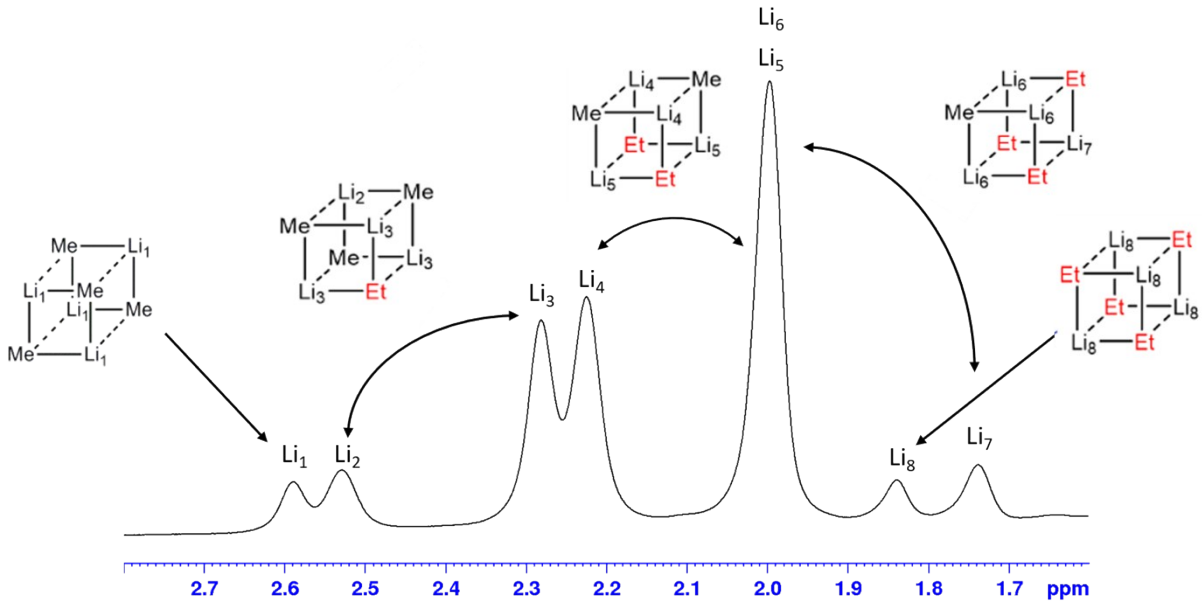


Figure 6S: 1D ^{7}Li spectra of MeLi/RLi mixture (R = Et (top), *n*-Bu (bottom)) in *n*-Bu_2O/Tol-d_8 at 185K.



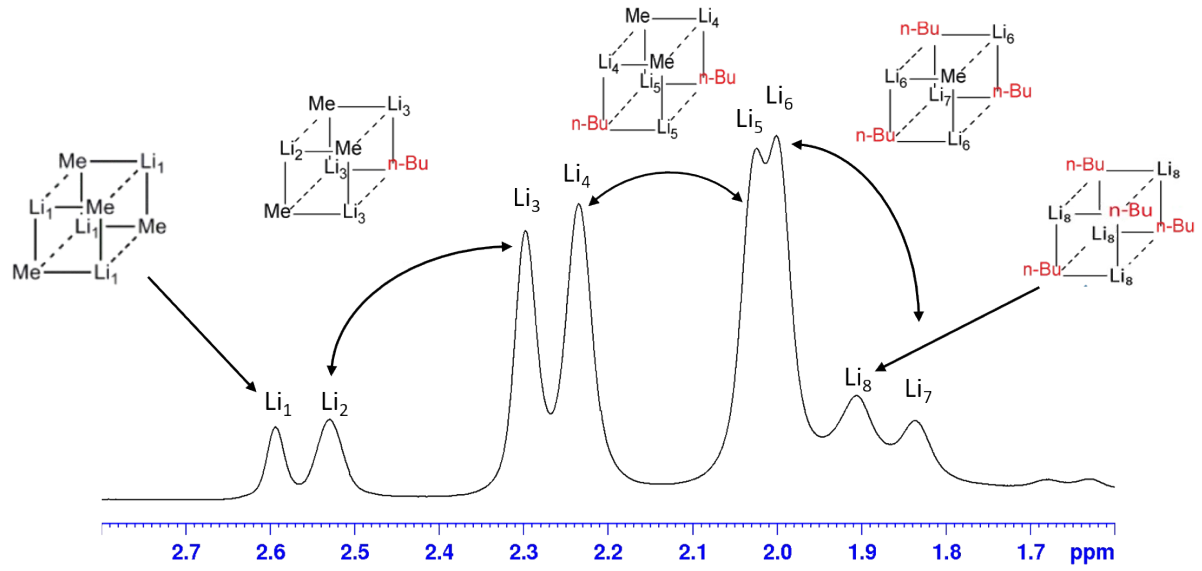
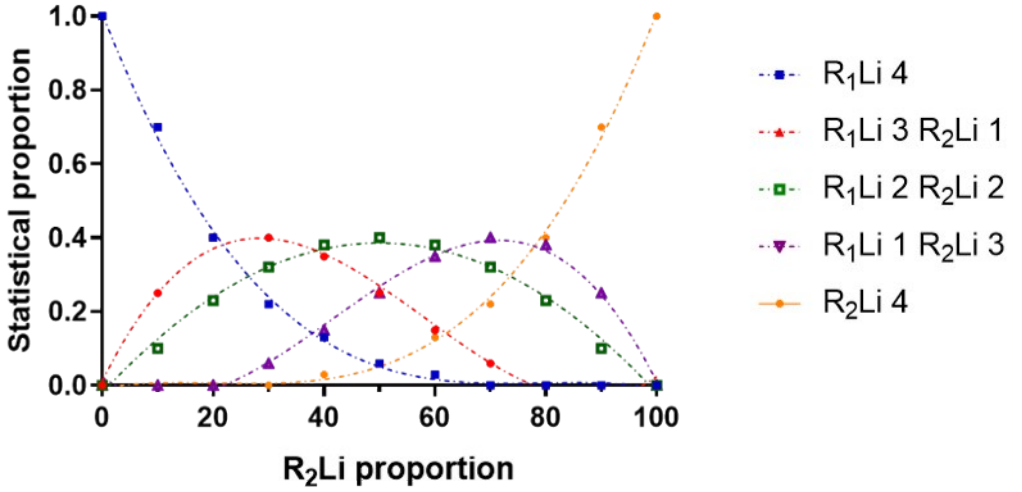
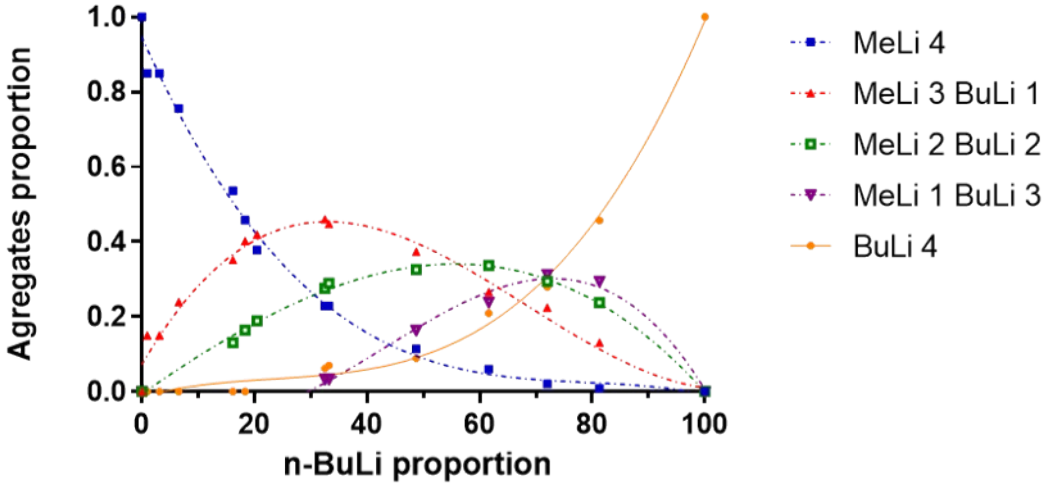


Figure 7S: (a) Statistical distribution of mixed aggregates $(R_1Li)_{4-n}(R_2Li)_n$ as a function of R_2Li molar proportion. Experimental (based on 1D ^{7}Li NMR signal integrations) distribution of mixed aggregates $(MeLi)_{4-n}(R_2Li)_n$ (R_2=*n*-BuLi, Et) in *n*-Bu_2O/Tol-d_8 at 185K as a function of R_2Li molar proportion : (b) $(MeLi)_{4-n}$(*n*-BuLi)$_n$; (c) $(MeLi)_{4-n}(EtLi)_n$.

a)



b)



c)

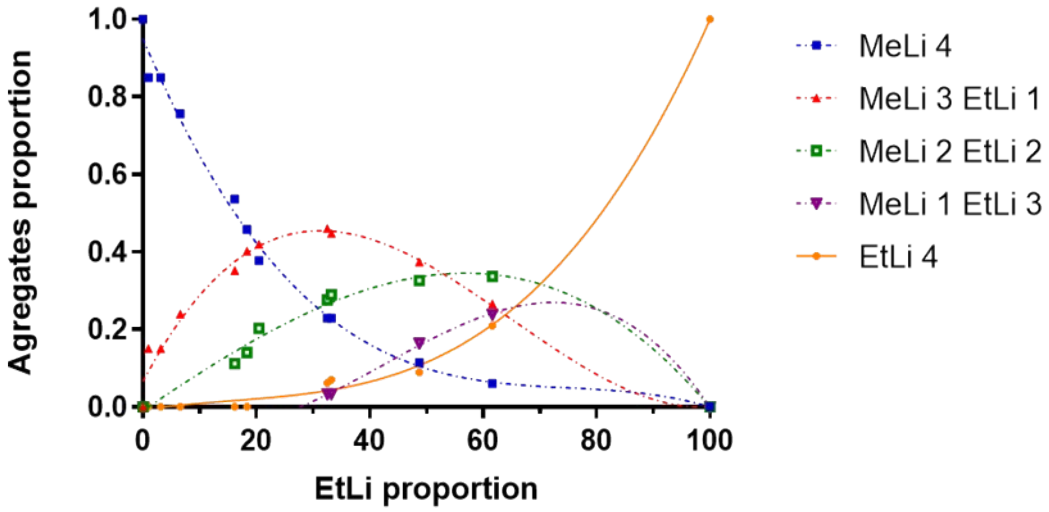


Table 1S: Value of coupling constant ($^2J_{Li-Li}$) and exchange rate for mixed aggregates $(MeLi)_{4-n}(n\text{-BuLi})_n$ in THF-d_8 at different temperature.

	$(MeLi)_3(n\text{-BuLi})_1$		**$(MeLi)_2(n\text{-BuLi})_2$**		**$(MeLi)_1(n\text{-BuLi})_3$**	
T (K)	$^2J_{Li-Li}$ (Hz)	k (s^{-1})	$^2J_{Li-Li}$ (Hz)	k (s^{-1})	$^2J_{Li-Li}$ (Hz)	k (s^{-1})
175	0.5614 ±0.0009	0.033	0.5265±0.0009	0.093	0.4733±0.0009	0.194
180	0.5612±0.0007	0.041	0.5263±0.0009	0.102	0.4726±0.0010	0.225
185	0.5610±0.0008	0.050	0.5260±0.0009	0.130	0.4730±0.0009	0.215
190	0.5609±0.0005	0.056	0.5253±0.0010	0.136	0.4717±0.0004	0.250
193	0.5606±0.0010	0.066	0.5243±0.0005	0.179	0.4715±0.0003	0.281
198	0.5593±0.0008	0.118	0.5215±0.0008	0.349	0.4662±0.0008	0.635
200	0.5579±0.0007	0.172	0.5166±0.0010	0.576	0.4597±0.0003	1.020
205	0.5577±0.0008	0.183	0.5144±0.0006	0.699	0.4580±0.0004	1.184