MeLi + LiCl in THF: One heterodimer and no tetramers

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General considerations

Argon was dried and deoxygenated by bubbling through a commercial solution of butyllithium in hexane. Commercial diethyl ether and deuteriated tetrahydrofuran-d8 were distilled over sodium and benzophenone. 6Li (95%) was purchased from Aldrich and washed in freshly distilled pentane. Pentane and heptane were distilled over lithium aluminum hydride.

Instrumental considerations

All NMR experiments were performed on a Bruker Avance DMX 500 spectrometer, equipped with z-gradient unit and a 5 mm {^{1}H, ^{6}Li, ^{13}C and ^{15}N} quadruple-resonance probe. Measuring frequencies were 500 MHz (^{1}H), 125 MHz (^{13}C), 73 MHz (^{6}Li) and 50 MHz (^{15}N). ^{1}H and ^{13}C chemical shifts were referenced to the solvent THF-d_8 signals at δ 1.73 and δ 25.37 respectively. Lithium spectra were referenced to external 0.3 M ^{6}LiCl in THF-d_8 (δ 0.0).

1D NMR measurements

The proton and lithium one dimensional experiments were recorded with standard parameters. In order to remove heteronuclear scalar coupling, the one dimensional ^{1}H and ^{6}Li spectra were recorded with broad band ^{13}C decoupling, the one dimensional ^{13}C spectra were recorded with broad band ^{1}H decoupling or broad band ^{1}H and ^{6}Li decoupling.

2D NMR measurements

^{6}Li/^{6}Li EXSY:[1] The following parameters were used for acquiring and processing the spectra in phase sensitive-sensitive mode: 128 experiments with 2048 data points and 4 scans each were recorded; pure phase line shapes was obtained by using Time Proportional Phase Incrementation (TPPI) phase cycling, mixing time of 2s were used for the sample; one time zero filling in f_1; π / 2

shifted sine square window functions were applied to f_2 and f_1 dimension before Fourier Transformation.

^{6}Li/^{1}H HOESY:[2] The following parameters were used for acquiring and processing the spectra in phase sensitive-sensitive mode: 256 experiments with 2048 data points and 16 scans each were recorded; pure phase line shapes was obtained by using Time Proportional Phase Incrementation (TPPI) phase cycling; mixing times of 1.4s were used for the sample; one time zero filling in f_1; π / 2 and π / 3 shifted sine square window functions were applied to f_2 and f_1 dimension respectively before Fourier Transformation. Processing of NMR data was performed on PC computer, using the manufacturer's program Topspin1.3 (Bruker).

^{1}H DOSY:[3] The following parameters were used for acquiring the BPP-LED (Bipolar Pulse Pair-Longitudinal Eddy-current Delay) spectra: 32 experiments with 2048 data points and 8 scans each were recorded; Bipolar rectangular gradients were used with total durations of 1500 to 2700 μs. Gradient recovery delay was 5 ms. Diffusion times were between 100 and 600 ms. Processing of DOSY data was performed with the manufacturer's program Topspin2.1 (Bruker), using the processing method Gifa-MaxEnt.

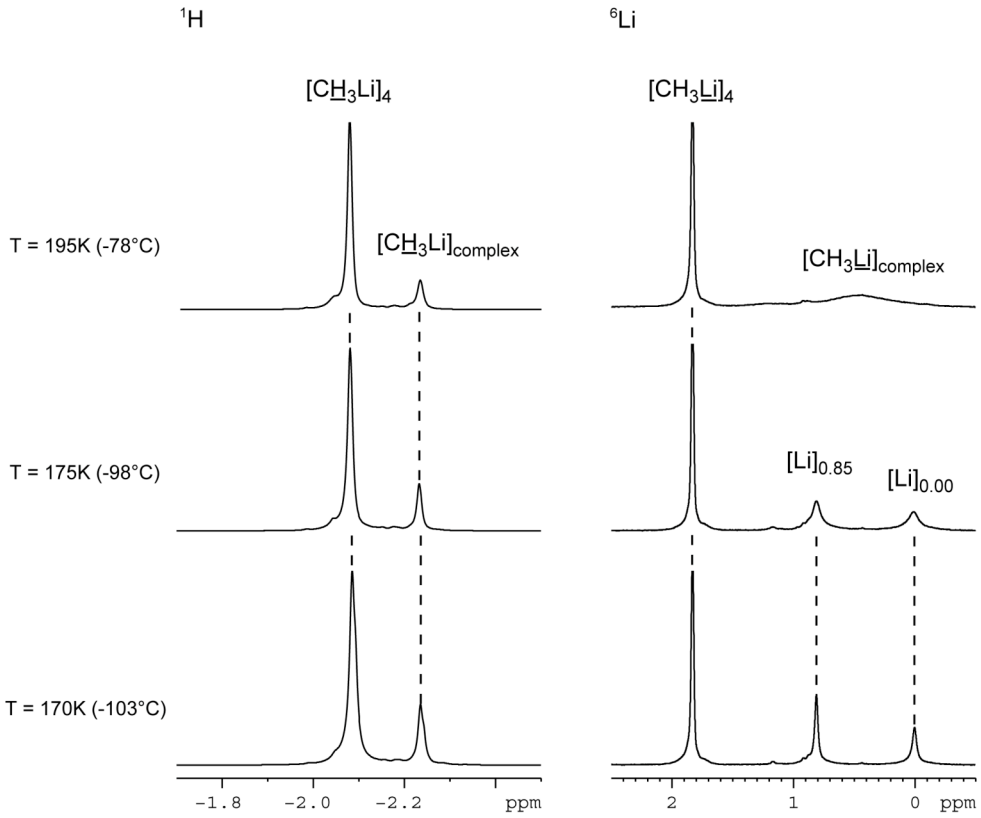


Figure 1S. Comparison of the ^{1}H methyllithium spectra registered at 195K, 175K and 170 K.

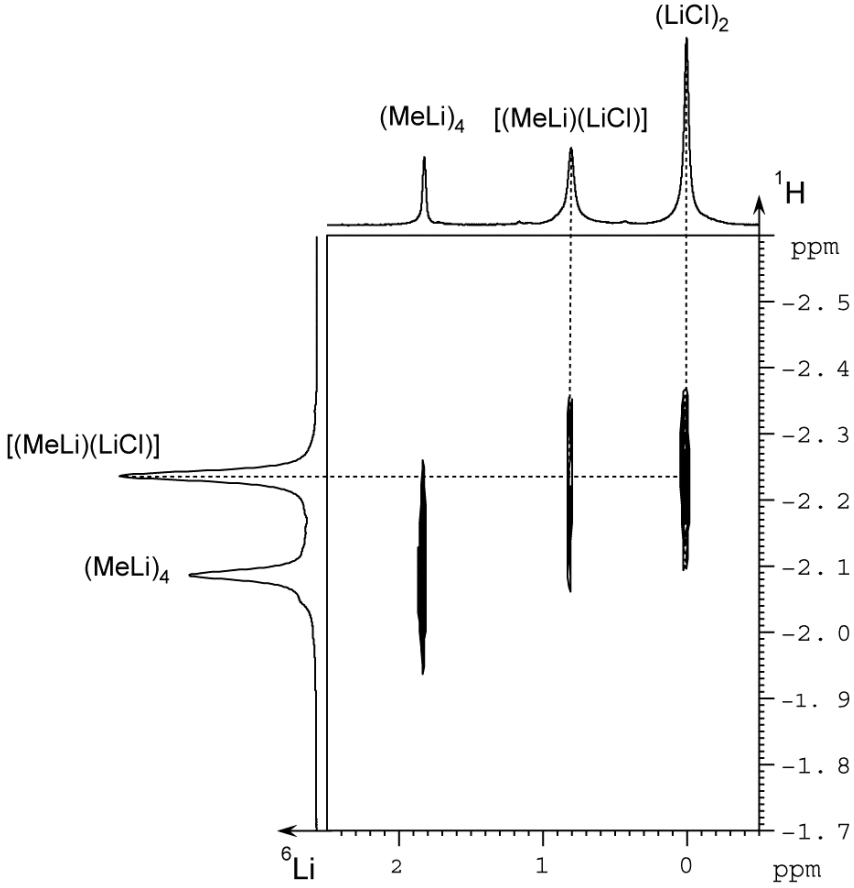


Figure 2S: HOESY spectrum of a 1:2 MeLi/LiCl sample in THF (170K). The correlation observed between the signal at 0.00 ppm (LiCl) and the mixed-aggregate proton signal at -2.22 ppm is due to a strong exchange between $(LiCl)_2$ and (MeLi)(LiCl).

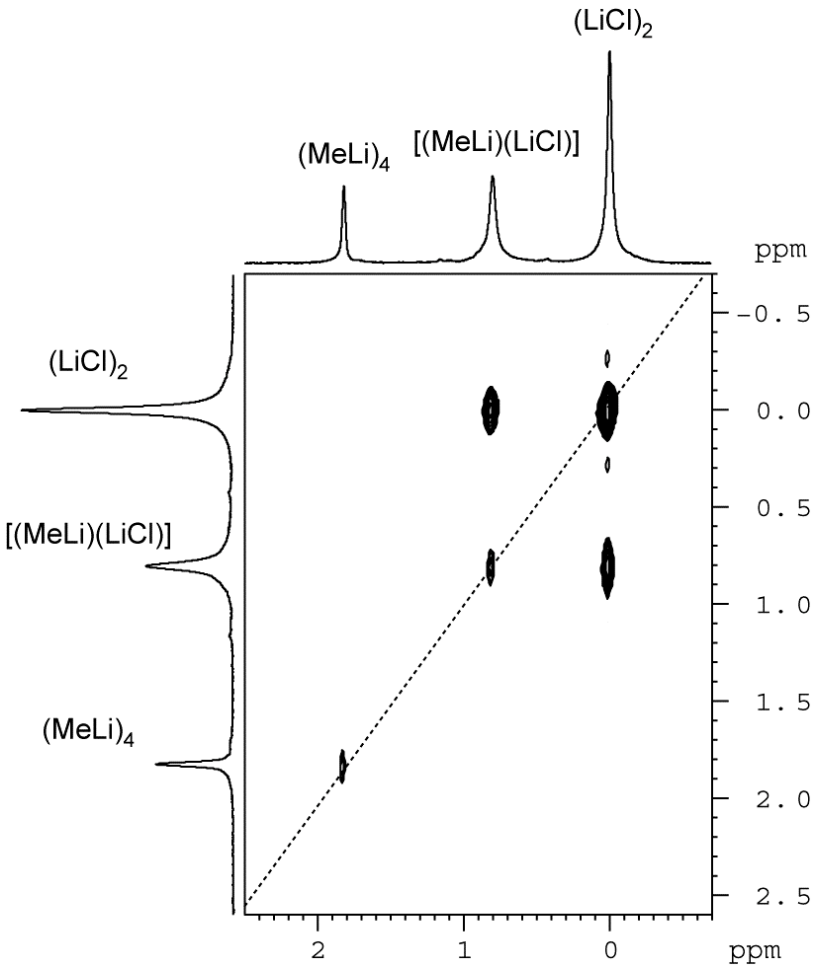
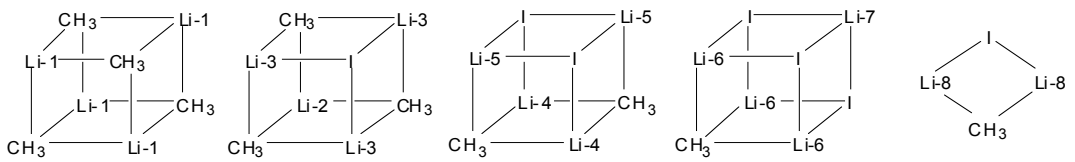


Figure 3S: EXSY spectrum of a 1:2 MeLi/LiCl sample in THF (170K). Mixing time = 2s.



$(MeLi)_m(LiI)_n$ Günther's aggregates

(MeLi)(LiCl) + traces of $(MeLi)_m(LiI)_n$ aggregates

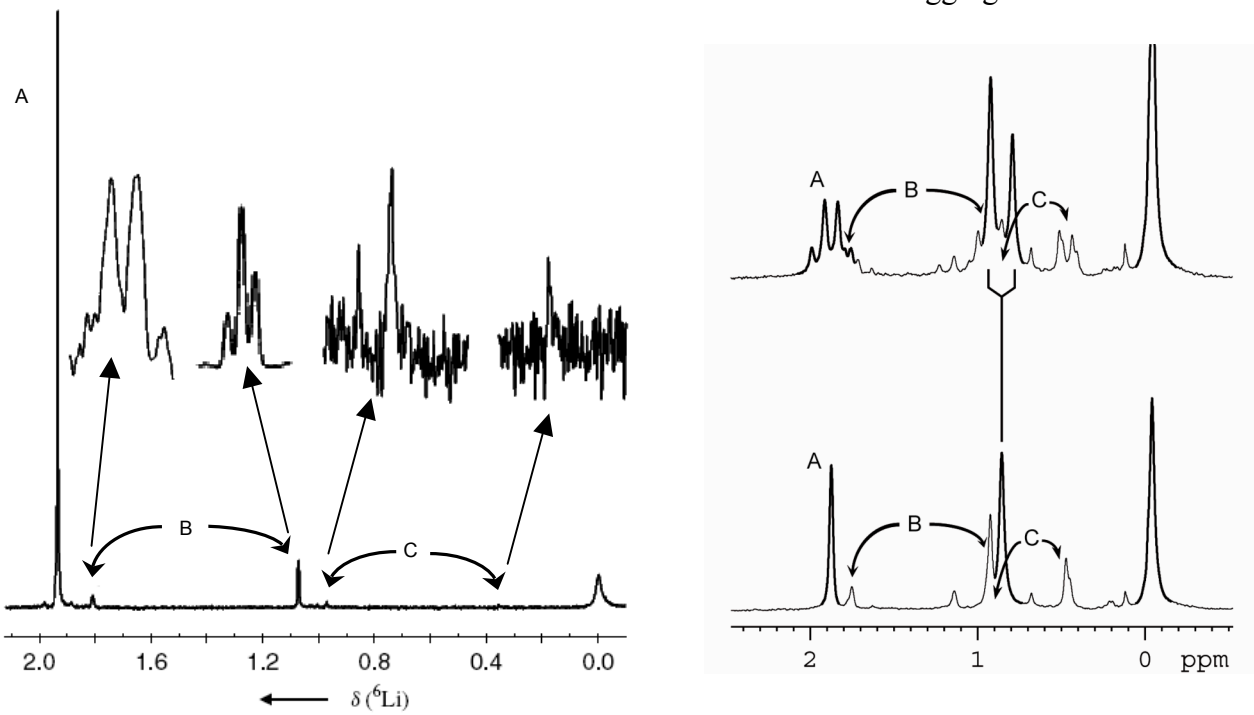


Figure 4S. Identification of the MeLi / LiI mixed aggregates described by H. Günther.[4]

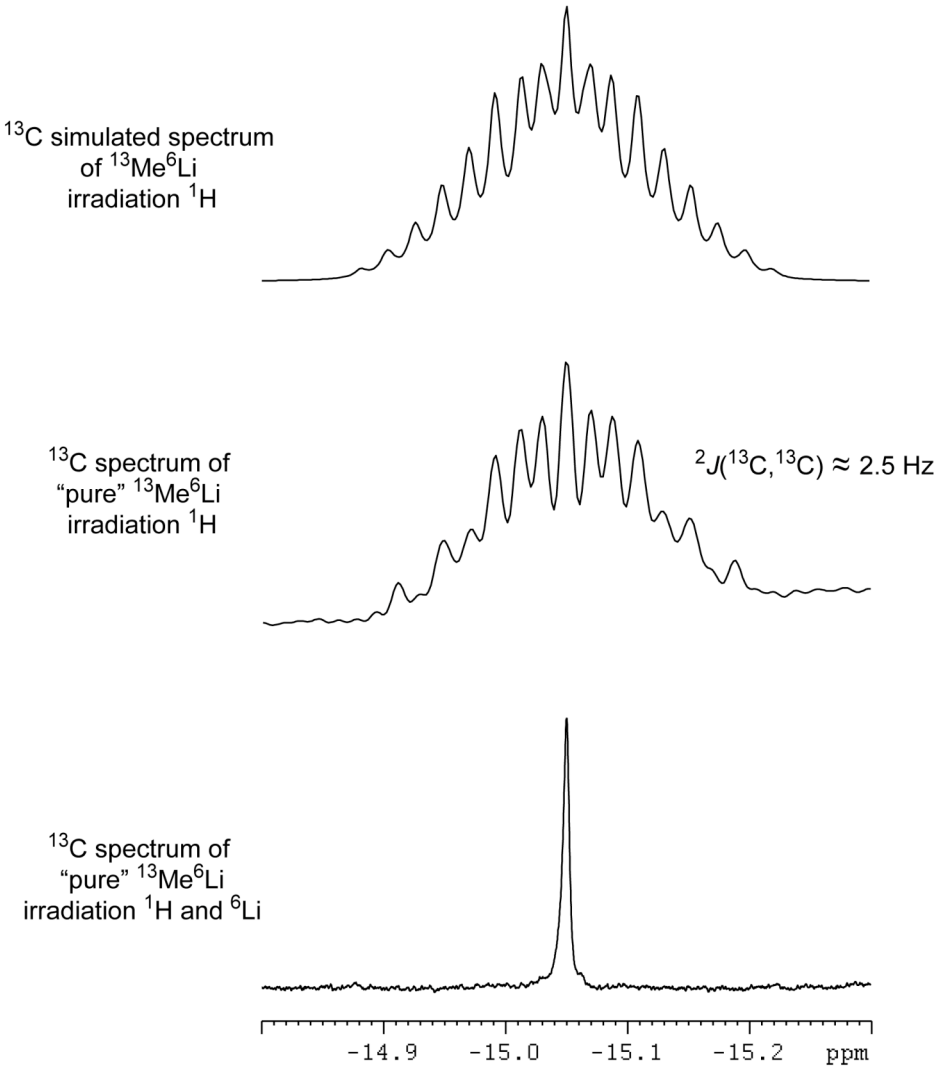


Figure 5S. Simulated (top) and recorded (middle and bottom) ^{13}C spectra of $^{13}CH_3{}^{6}Li$ in THF.

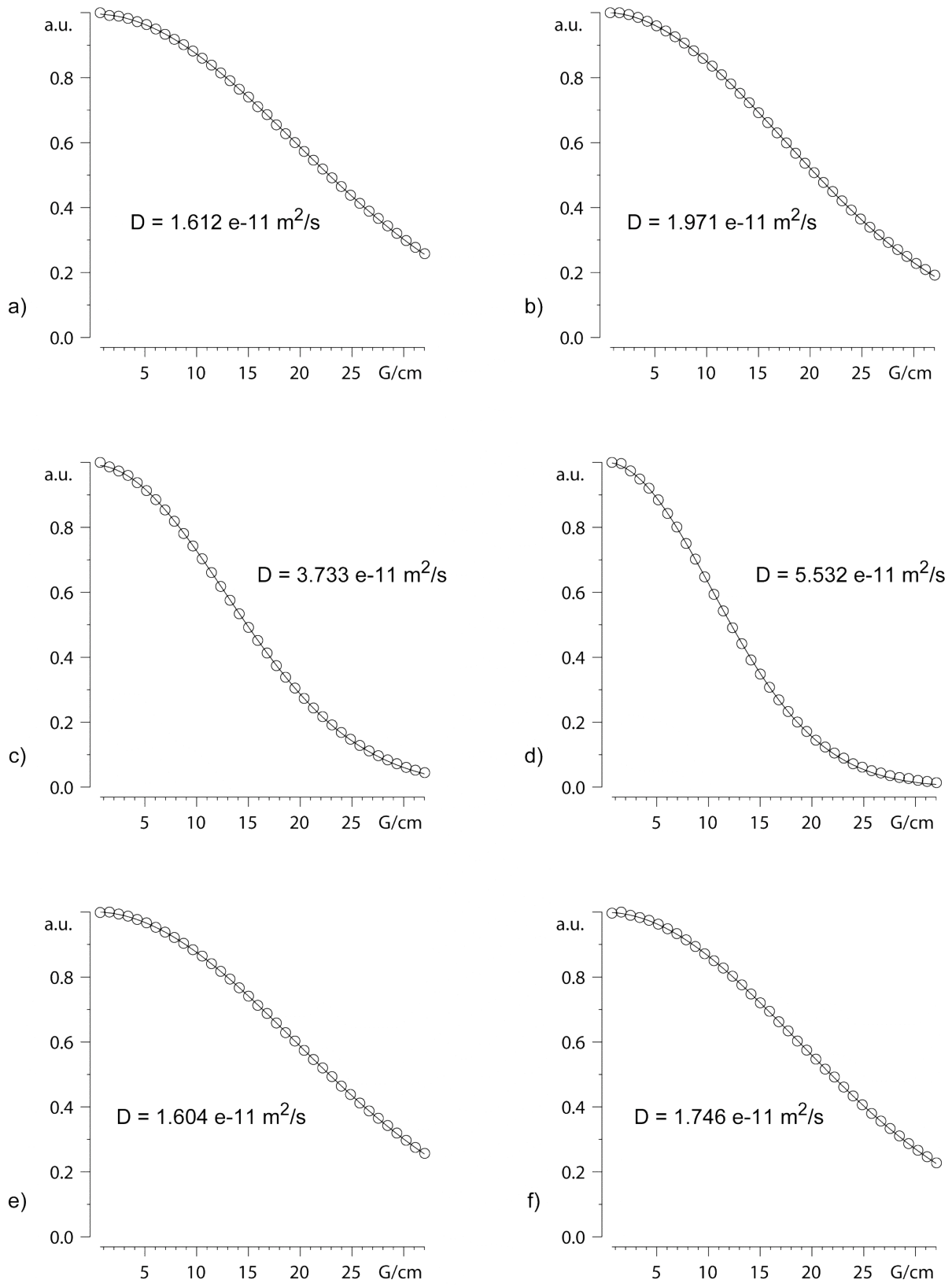


Figure 6S. Signal attenuation curves from ^{1}H-DOSY data for a) Triphenylbenzene, b) Tritertbutylbenzene, c) Trimethylbenzene, d) Ether, e) $(MeLi)_4$, f) mixed dimer (MeLi)(LiCl).

Computational Details

The geometry optimizations were carried out using the Gaussian 03 program.[5] According to the procedure validated previously,[6,7] geometries were optimized at the BLYP/6-31++G** level. In addition, comparisons of this functional to the most widely used B3LYP for a set of molecules relevant to this study are given in Table 1S (next page). Full geometry optimizations were systematically conducted with no symmetry restraint. Solvation was taken into account by including explicit solvent molecules either dimethylether (Me_2O) used as a simple model (for discussion of the validity of this model, see Ref [8]) or tetrahydrofurane (THF). Frequencies were evaluated within the harmonic approximation and are used to evaluate Gibbs free energy unscaled according to the standard procedure implemented in Gaussian. Computations were carried out either at 170 K, which is the temperature used in the experiments. Corrections were also added to the gas phase free energies of the macrosystems in order to evaluate the reaction free energies within the framework of the dilute solute approximation.[9] This was done by adding a RT.ln(RT) term to the free energy term of any molecule, as well as a RT.ln[THF] term (computed using the values of reference 9b) to the free energy term of each explicit solvent molecule. The NMR coupling constants were computed at the BLYP on the BLYP/6-31++G** optimized geometries using the 6-311+G** basis set, according to the procedure validated previously.[7]

Comparison of the BLYP and B3LYP functionals

Table 1S: Energies (in kcal.mol^{-1}) at the BLYP and B3LYP level (full geometry optimization was carried out at both levels) for various representative processes.

	BLYP	**B3LYP**
Equations probing aggregation energies (See Figure 7)		
½ Li_4Me_4 + ½ Li_4Cl_4 = $Li_4Cl_2Me_2$	0.1	0.1
½ Li_4Me_4 + ½ Li_4Br_4 = $Li_4Br_2Me_2$	0.4	0.4
½ Li_4Cl_4 = Li_2Cl_2	20.2	21.2
½ Li_4Br_4 = Li_2Br_2	27.1	28.3
Li_2Me_2 + Li_2Cl_2 = 2 Li_2MeCl	-1.4	-1.5
Li_2Me_2 + Li_2Br_2 = 2 Li_2MeBr	-1.6	-1.6
Equations probing solvent coordination		
Li_2Cl_2 + 4 OMe_2 = $[Li_2Cl_2].[OMe_2]_4$	-50.7	-56.1
Li_4Cl_4 + 4 OMe_2 = $[Li_4Cl_4].[OMe_2]_4$	-54.6	-60.1
Li_4Me_4 + 4 OMe_2 = $[Li_4Me_4].[OMe_2]_4$	-35.4	-41.1

Relative energies and free enthalpies of $[(MeLi)_2(LiCl)_2]. [Me_2O]_n$

Table 2Sa: Energies of various structures and solvation degrees for the $Li_4Cl_2Me_2$ mixed aggregates, in kcal.mol^{-1}, relative to the most stable isomers that is the cubic tetrasolvated species.

ΔE	**n = 0**	**n = 2**	**n = 3**	**n = 4**
Cube	46.2	Not computed	Not computed	0.0
Plane	54.1	Not found	Not found	Not found
Ladder	56.1	23.5	16.0	8.9
Distorded	Not computed	Not computed	15.4	Not computed

Table 2Sb: Free enthalpies (gaz phase expression of the activities is used) of various structures and solvation degrees for the $Li_4Cl_2Me_2$ mixed aggregates, in kcal.mol^{-1}, relative to the most stable isomers that is the cubic tetrasolvated species.

ΔG (170 K)	**n = 0**	**n = 2**	**n = 3**	**n = 4**
Cube	18.6	Not computed	Not computed	0.0
Plane	23.9	Not found	Not found	Not found
Ladder	25.6	7.2	6.8	7.0
Distorded	Not computed	Not computed	5.6	Not computed

Comparison of binding energies in Cl and Br aggregates

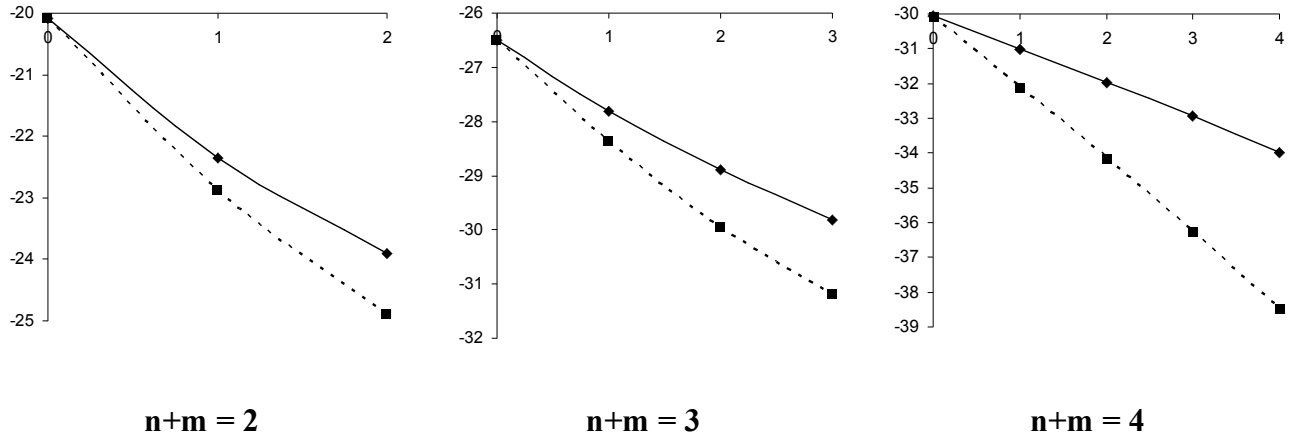


Figure 7S. ΔE (ΔE = E(A)/(n+m), with E(A) reaction energy for n LiX + m MeLi → $Li_{n+m}X_nMe_m$, kcal/mol), binding energy per lithium atoms for the $Li_{n+m}X_nMe_m$ aggregates, as a function of n for dimer (left), trimer (center) and cubic tetramer (right). Losange and plain lines for X = Cl, square and dotted lines for bromine.

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