Extended Supplementary Information

On the Structural and Vibrational Properties of Solid Endohedral Metallofullerene Li@C_{60}

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Equation S1

The Murnaghan equation-of-state (eq. 1) expressed as *V*(P) – volume as a function of pressure:

$$V = V_0[1 + P(K_0'/K_0)]^{-1/K_0'} \quad \text{(S1)}$$

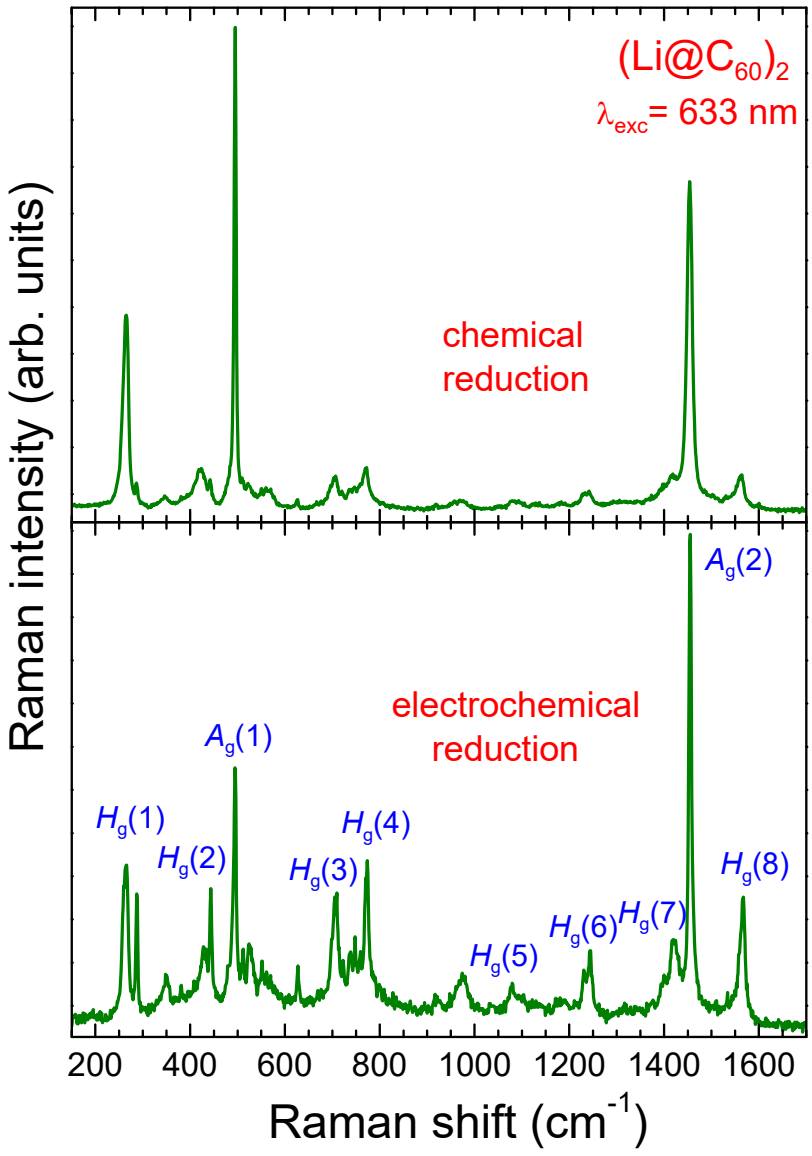

Figure S1. The Raman spectrum of $(Li@C_{60})_2$ obtained by electrochemical reduction compared to that obtained by chemical reduction. The mode assignment refers to the irreducible representations of the C_{60} molecule in I_h symmetry.

Table S1. Tentative assignment of the observed Raman peaks and their frequencies for monomeric solid C_{60} and $(Li@C_{60})(PF_6)$ and for dimeric solid $(C_{59}N)_2$ and $(Li@C_{60})_2$. The $A_g(2)$ mode is shown in bold.

Mode[a]	C_{60}	$(Li@C_{60})(PF_6)$	$(C_{59}N)_2$	$(Li@C_{60})_2$
$H_g(1)$	266	269	257	259
	272		263	263
			266	267
			269	
			286	287
$G_u(1)$			344	338
$G_g(1)$			352	350
			375	370
				381
			396	397
$H_u(1)$			417	408
$H_g(2)$	432	434	424	422
				428
			432	434
$G_g(1)$			446	444
			469	
$H_u(2)$	485	488		
$A_g(1)$	496	497	490	494
$F_{1g}(1)$			512	512
$G_g(2)$			522	524
				530
$F_{2g}(1)$			548	552
$F_{1u}(2)$				561
				569
$F_{2u}(2)$				579
$G_g(3)$			623	627
$H_u(4)$			669	
			682	
				698
$H_g(3)$	711	714	704	704
			710	709
			717	722
			730	
			735	735

Table S1. (continued)

Mode[a]	C_{60}	$(Li@C_{60})(PF_6)$	$(C_{59}N)_2$	$(Li@C_{60})_2$
$G_u(2)$			738	739
			743	
$H_g(4)$	773	774	754	748
			761	758
			768	769
			773	774
$\omega(1)$				922
$\omega(2)$				973
$G_u(4)$				1079
$H_g(5)$	1100	1101	1091	1100
			1106	
$H_g(6)$	1251	1246	1183	1176
			1190	1189
			1237	1231
				1244
$H_u(4)$				1399
$H_g(7)$	1423	1423	1415	1421
			1424	
			1439	
$G_g(5)$			1457	
	1458			
$A_g(2)$	**1468**	**1465**	**1462**	**1455**
$G_u(6)$			1553	
$H_g(8)$	1573	1573		1561
			1566	1567
			1575	
$H_u(7)$			1586	

[a]Mode assignment refers to the irreducible representations of the C_{60} molecule in I_h symmetry and is in accordance to that of Ref. [24].

Table S2. Refined parameters of the Rietveld analysis (using the Fullprof suite) of the synchrotron X-ray powder diffraction data of $(Li@C_{60})_2$ prepared by electrochemical reduction at 300 K The space group is $P6_3/mmc$. The lattice constants and the unit cell volume are: a = 10.0432(3) Å, c = 16.135(9) Å, and V = 1409.5(1) Å^3. The $Li@C_{60}$ units were modelled as spherical shells with a radius of 3.54 Å residing at the 2d (⅔,⅓,¼) lattice sites. The CH_2Cl_2 solvent molecules were modelled by introducing an isoelectronic Mo atom (Z = 42) residing at the 2a (0,0,0) lattice sites. The refined stoichiometry of the material is $(Li@C_{60})_2 \cdot (CH_2Cl_2)_{0.81(2)}$. The weighted-profile and expected R factors are R_{wp} = 5.79% and R_{exp} = 1.48%, respectively.

	x/a	y/b	z/c	N	B_{iso} (Å^2)
C_{60}	⅔	⅓	¼	1	11.7(8)
CH_2Cl_2	0	0	0	0.404(8)	14(1)