Supplementary Information

Angle-Resolved Photoelectron Spectroscopy and Scanning Tunnelling Spectroscopy Studies of the Endohedral Fullerene Li@C₆₀

M. Stefanou,^a H. J. Chandler,^b B. Mignolet,^c E. Williams,^a S. A. Nanoh,^b J. O. F. Thompson,^a F. Remacle,^c R. Schaub,^b E. E. B. Campbell^{a,d,*}

a: EaStCHEM and School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, U.K.

b: EaStCHEM and School of Chemistry, University of St. Andrews, St. Amdrews KY16 9ST, U.K.

c: Theoretical Physical Chemistry, Research Unit MOLSYS, University of Liège, B4000 Liège, Belgium

d: Division of Quantum Phases and Devices School of Physics, Konkuk University, Seoul 143-701, South Korea.

*: Corresponding author: Eleanor.campbell@ed.ac.uk



Fig. S1. Fs photoionisation mass spectra obtained as a function of time from $[Li^+C_{60}]PF_6^$ heated in a quartz capillary tube to a temperature of ca. 600 K. After heating for a number of hours the impurities in the spectra that arise from the endohedral material disappear leaving the parent fullerene species.



Fig. S2. Intensities of the parent molecular ions as a function of laser power for ionisation with 35 fs duration laser pulses at a wavelength of 540 nm. The different slopes indicate the different ionisation energies of the two molecules. C_{60} (ionisation energy 7.6 eV) requires 4 photons to ionise while Li@C₆₀ (ionisation energy 6.5 eV) only requires 3 photons.



Fig. S3. Oven temperature dependence of the molecular ion intensity of C_{60} and $Li@C_{60}$ for ionisation with 540 nm, 35 fs laser pulses. The change of slope for $Li@C_{60}$ indicates the onset of thermal decomposition.

SI.2. Population distributions and rotational coordinations for C₆₀ and Li@C₆₀

adsorbed on Au(111).

The population distributions of C_{60} and $Li@C_{60}$ and their rotational coordinations to Au(111) are reported in **Fig. S4**. The data is based on statistical analysis of over 3000 molecules from many STM images acquired at different voltages. The $Li@C_{60}$ are differentiated from C_{60} thanks to the bright circular feature appearing at +2.5 V. Statistical analysis reveals that 13% of all adsorbed fullerenes are $Li@C_{60}$. The rotational coordinations of the fullerenes with respect to the Au(111) surface are deduced from the shape and symmetry of features observed in the STM images at all tunnelling voltages, as reported by Gardener and co-workers¹. The data acquired at -2.5 V allow to identify the fullerene faces (C_6 , C_6 - C_6 , and C-apex) in contact with the support^{2,3}, and hence those furthest from the support (indicated by blue shadings in the ball-and-stick models). The data acquired at +1.0 V indicate that the C_6 species (both empty and Li-filled) adsorb in two orientations rotated by 180° (as seen from the triangular or trefoil shapes), one of them being predominant (roughly 90% versus 10%), as a result of second-layer effects of the gold substrate. We refer to these mirror-symmetric orientations as majority (M- C_6) and minority (m- C_6) species. Most importantly, whilst the C_{60} molecule are seen to adsorb in three possible coordinations (C_6 , C_6 - C_6 , and C-apex, with the C_6 - C_5 and C_5 coordinations never observed on Au(111), contrary to e.g. $Cu(100)^4$), Li@ C_{60} is only observed in the C_6 coordination.

	Species	Model	STM Data: -2.5 V / +1.0 V / +2.5 V	% Туре	% Total
Li@C60	M-C ₆			91 %	12 %
	m-C ₆			9 %	1 %
Ceo	M-C ₆			86 %	36 %
	m-C ₆	200 - 200 200 - 200 200 - 200 200 - 200 200 - 200 200 200 - 200 200 200 200 200 200 200 200 200 200		14 %	6 %
	C_6 - C_6				21 %
	C-apex				24 %
	C ₆ -C₅ & C₅		Not observed		0 %

Fig. S4. Li@C₆₀ and C₆₀ species identified on the Au(111) surface. Ball-and-stick models, STM images (acquired over the same area at -2.5 V, +1.0 V and +2.5 V from left to right), population ratios. For the bottom two C₆₀ species, C₆-C₆ and C-apex, the rotational orientations on the surface are ignored.

SI.3 Scanning Tunnelling Microscopy and Spectroscopy Details

Constant-current (c.c.) dI/dV spectra were acquired on many different C_{60} and $Li@C_{60}$ molecules (acquisition conducted with different tips, different days, and different sample preparations). The molecules were either isolated from any other neighbours, or condensed in extended, highly ordered, molecular islands.

Preparation of isolated molecules

As discussed in the main text, the preparation of molecular islands involves post-deposition anneal to elevated temperatures so as to induce molecular motion and subsequent two-dimensional condensation into molecular islands. This procedure also serves to selectively sublime unwanted pollution (e.g. fragments of stabilising ligands). The preparation of isolated molecules involves post-deposition anneal to moderate temperatures so as to prevent significant molecular motion but enough to selectively desorb unwanted pollution. This procedure easily yields isolated molecules. However, the vast majority of these are $Li@C_{60}$. The C_{60} molecules are found to coalesce in islands. This is due to C_{60} and $Li@C_{60}$ exhibiting drastically different diffusivities on the Au(111) surface, with $Li@C_{60}$ diffusivity very much reduced (due to the Li atom) as compared to C_{60} . Due to the difficulty in finding isolated C_{60} molecules on the Au(111) surface, only a handful of c.c. dl/dV spectra could be acquired, whereas many spectra could be acquired over $Li@C_{60}$.

Representative large scale images showing isolated molecules on both Au(111) and $Cu(110)-(2\times1)O$ surfaces are shown below in **Fig. S5**. The high magnification images reported in **Figs. 8** and **9** of the manuscript are extracted from images similar to the ones shown here.



Figure S5: STM images of large areas showing isolated C_{60} and $Li@C_{60}$ molecules. (**left**) The Cu(110)-(2×1)O surface, 1.0 V and 0.1 nA. (**right**) The Au(111) surface, 2.5 V and 0.1 nA. The herringbone reconstruction visible. Pollution leftovers can be observed on both surfaces.

Reproducibility of spectroscopy data

The reproducibility of c.c. dI/dV spectra acquired over isolated molecules of same species on a given surface is remarkable, as demonstrated in **Fig. S6**. This reproducibility is key in aiding to identify SAMO resonances in a reliable and confident manner. We can assign the minor differences observed for identical species/surface configurations to local effects (e.g. isolated molecules likely adsorbed on different surface sites on the Au(111) surface such as fcc or hcp sites). This is more pronounced for the lower energy resonances, e.g. P_z -SAMOs. Nevertheless, the reproducibility of the data allows for

unambiguous identification of SAMO resonances. Furthermore, the spectra also allow for the different species to be discriminated (or even identified). The reproducibility of the spectra is also very good when the molecules are condensed in islands, as shown in **Fig. S7** for the Au(111) surface only.



Comparison of C60 and Li@C60 species

Fig. S8 below compares representative constant-current d/dV spectra (extracted from **Fig. S6**) for isolated C₆₀ and Li@C₆₀ molecules on both the Au(111) and Cu(110)-(2×1)O surfaces in order to highlight similarities and/or differences. This set of comparisons allows us to draw several conclusions. First, the SAMO resonances for C₆₀ (top-left panel) are similar in appearance when the molecule is adsorbed on either surface, with an apparent energy shift of the peaks. The SAMOs lie at lower energies, by approximately 400 meV, when the support is the Cu(110)-(2×1)O surface. The same conclusion (same appearance with an energy shift of about 400 meV) can be drawn for the Li@C60

Figure S6: Constant-current dI/dV spectra acquired on (left panels) isolated C₆₀ molecules, and (right panels) isolated Li@C60 molecules. The red and blue traces are for molecules adsorbed on the Cu(110)-(2×1)O surface, and the green and orange traces are for molecules adsorbed on the Au(111) surface. As discussed above, note that there are only very few spectra for C₆₀/Au(111) due to these molecules being difficult to find in isolation. Every spectrum reported here is composed of a back and a forward trace (in relation to the voltage sweep). On the scale of the present figure, the two traces are virtually indistinguishable.

Figure S7: Constant-current dI/dV spectra acquired on (left panel) C₆₀ molecules, and (right panel) Li@C₆₀ molecules. Both molecules are condensed in islands on the Au(111) surface. For the C₆₀ molecules, the spectra encompass the various rotational registries as discussed in the main text. The rotational alignment is known to induce minor energy shifts for the LUMO+1 resonances near 2.0 V, as discussed in ref.⁴

molecule (top-right panel). This demonstrates that both surfaces exhibit different reactivities towards the molecules. Second, irrespective of the support, the SAMO resonances of $Li@C_{60}$ and C_{60} are very different (see bottom panels). These differences are discussed in the main text.



Figure S8: Comparing the molecules and comparing the metal supports. Representative constant-current dI/dVspectra are reported in the (top-left panel) to compare the effect of the metal substrate on the C₆₀ SAMOs, in the (top-left panel) to compare the effect of the metal substrate on the Li@C60 SAMOs, in the (bottom-left panel) to compare the effect of the Li encapsulation in the C₆₀ cage on the SAMOs when supported on the Cu(110)-(2×1)O surface, and finally, in the (bottom-right panel) to compare the effect of the Li encapsulation in the C₆₀ cage on the SAMOs when supported on the Au(111) surface.

Figure S9: Comparing the molecules supported on Au(111) when isolated and condensed in two-dimensional islands. Representative constant-current dI/dV spectra are reported in the (**left panel**) for C₆₀, and in the (**right panel**) for Li@C₆₀.

Comparison of c.c. dI/dV spectra for isolated or condensed molecules on Au(111) is reported in **Fig. S9**. When the molecules are condensed in large two-dimensional islands, the SAMO resonances are shifted downwards by a few 100 meV. In the case of C₆₀, a noticeable difference is the significant increase in intensity for the band near 5.0 V, that is almost absent in isolation. For Li@C60, the P_{x,y}-SAMO band becomes better resolved but the LUMO+2,+3 band is not detectable anymore.

SAMO peak assignment for C₆₀

The first attempt to assign SAMO peaks was reported by the Petek group in their seminal paper⁵, based on a combination of constant-current spectroscopy and DFT calculations. However, we note here that the spectroscopy was acquired at 77 K, rendering it poorly resolved. Similar measurements by Reecht *et al.*⁶ were later performed, and in combination with orbital imaging (that is, dI/dV imaging), the SAMO peak assignment was revised. Our data (see **Fig. S10** below) is full in agreement with this latest research. Hence, we adopt for C₆₀ the same SAMO peak assignment, as reported in the c.-c. spectrum shown in the bottom-left of **Fig. S10** and **Table SI-1**.



Figure S10: (Top-left) Constant-current STM image of an isolated C_{60} molecule on the Cu(110)-(2×1)O surface. (Bottom-left) Constant-current dI/dV spectrum on the C_{60} molecule. The SAMO resonance labelling is based on identification of collection of the dI/dV images (modulation amplitude of 10 mV and frequency of 520 Hz) shown to the right acquired at different voltages. See ref.⁶ for details.

	C ₆₀			Li@C ₆₀	
Peak	Cu(110)-(2×1)O	Au(111)	Peak	Cu(110)-(2×1)O	Au(111)
L+1	1.6 V	2.0 V	Pz, L+1	1.3 V	1.8 V
L+2, L+3	3.2 V	3.4 V	S	2.1 V	2.3 V
S	3.9 V	4.2 V	L+2, L+3	3.1 V	3.2 V
Pz	5.0 V	4.9 V	Px,y	4.6 V / 5.0 V	4.8 V / 5.3 V
Px,y	5.4 V	5.7 V	D	5.8 V	>6 V
S Pz Px,y	3.9 V 5.0 V 5.4 V	4.2 V 4.9 V 5.7 V	S L+2, L+3 Px,y D	2.1 V 3.1 V 4.6 V / 5.0 V 5.8 V	3.2 V 4.8 V / 5.3 V > 6 V

Table SI-1: Peak assignment and corresponding energy for isolated C₆₀ and Li@C₆₀ SAMOs.

Constant-current versus constant-height spectroscopy in relation to establishing LDOS

The representative c.c. d/dV spectra reported in **Fig. S8** (also shown in **Figs. 8** and **9** of the main text) are used for direct comparison with the PES data. However, local density of states (LDOS) is most commonly extracted from constant-height (c.h.) d/dV spectroscopy measurements. Berndt and coworkers show that the two different modes of operation (c.c. and c.h. d/dV) significantly affect peak positions.⁷ They show experimentally that the relative peak difference one can observe is of the order of 100-150 meV. The authors also devise a normalisation procedure to retrieve the LDOS from c.c. d/dV data. To compare our results to those of the Berndt group, we have reproduced their measurements by acquiring both c.c. and c.h. d/dV spectra on the same C₆₀ molecule (same tip, same conditions). The data is reported in **Fig. S11** below. Comparison of this figure and Fig. 1 of ref.⁷ shows that our data is in all aspects equivalent to theirs, as also summarised in **Table SI-2** below. From this, we most importantly conclude that the error (at most 200 meV) we make in the main text when comparing SAMO energies measured by PES and STS is negligible considering the absolute values of the energies (> 1.0 V).



Figure S11: Constant-height (both dashed and solid red traces) and constant-current (orange trace) dI/dV spectra together with its displacement curve $\Delta z(V)$ (blue trace) acquired on an isolated C₆₀ molecule on the Au(111) surface. Two different set-point conditions (or tunnel gaps) are used to acquire the two c.h. dI/dV spectra, optimised for providing a good signal in a narrow and low voltage range (0 to 3 V – solid red trace – 2.5 V and 10 nA) and in a large voltage range (0 to 5 V – dashed red trace – 2.5 V and 0.1 nA). The set point condition used for the c.c. dI/dVspectrum covering the large voltage range (0 to 5 V) is made identical to the c.h. spectra, that is, 2.5 V and 0.1 nA.

Table SI-2: Peak energy shifts (in meV) observed when comparing constant-current and constant-height dI/dV spectra acquired over an isolated C_{60} molecule on Au(111). The peak numbers refer to the assignment shown in **Fig. S11**. Peak 3 is not resolved in our c.h. spectra.

Peak	Our work	Data from Ref. ⁷
1	140 meV	110 meV
2	40 meV	70 meV
3		
4	170 meV	
5	60 meV	

References

- 1. J.A. Gardener, G.A.D. Briggs and M.R. Castell, *Phys. Rev. B* 2009, **80**, 235434.
- 2. M. De Menech, U. Saalmann and M. E. Garcia, *Physical Review B*, 2006, **73**, 155407.
- 3. X. Lu, M. Grobis, K. H. Khoo, S. G. Louie and M. F. Crommie, *Physical Review B*, 2004, **70**, 115418.
- 4. G. Schull, N. Néel, M. Becker, J. Kröger and R. Berndt, *New Journal of Physics*, 2008, **10**, 065012.
- 5. M. Feng, J. Zhao and H. Petek, *Science*, 2008, **320**, 359-362.
- 6. G. Reecht, H. Bulou, F. Scheurer, L. Limot and G. Schull, *New Journal of Physics*, 2017, **19**, 113033.
- 7. M. Ziegler, N. Néel, A. Sperl, J. Kröger and R. Berndt, *Physical Review B*, 2009, **80**, 125402.