Supporting Information

Li@C_{60} thin films: characterization and nonlinear optical properties

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Results from power dependence measurement

In order to determine the order of the peak of interest, the laser excitation power is changed and the corresponding change in peak intensity recorded. Subsequently, the intensity is plotted over laser excitation power and a power law (eq. 2 in main article) fitted on the data. By looking at the power, the order of the process can be determined.

Table S1. Results from power dependence measurements with the corresponding weighted averages and the expected values with SFG values used as validation. 1st and 2nd refer to two different independent measurements.

	820 nm dependence				1164 nm dependence			
	455 nm peak (1st)	455 nm peak (2nd)	SFG (1st)	SFG (2nd)	455 nm peak (1st)	455 nm peak (2nd)	SFG (1st)	SFG (2nd)
Measured k values ($y = ax^k$)	1.29 ± 0.13 1.37 ± 0.18 1.41 ± 0.01 1.26 ± 0.19 1.21 ± 0.16	1.12 ± 0.15 1.2 ± 0.3 0.83 ± 0.17 1.2 ± 0.5	1.02 ± 0.05 1.07 ± 0.05 1.15 ± 0.06 1.06 ± 0.05 0.99 ± 0.05	1.02 ± 0.06 0.89 ± 0.10 0.99 ± 0.06 1.23 ± 0.11	2.85 ± 0.21 3.87 ± 0.14 2.59 ± 0.19 4.46 ± 2.89 3.94 ± 0.16	2.97 ± 3.26 4.65 ± 8.46 3.92 ± 2.39 3.64 ± 1.69 4.21 ± 4.55 3.27 ± 3.59 4.38 ± 0.61	0.94 ± 0.04 1.42 ± 0.01 1.04 ± 0.02 1.24 ± 0.03 1.22 ± 0.03	0.62 ± 0.08 1.30 ± 1.86 0.83 ± 0.08 1.02 ± 0.07 0.87 ± 0.32 0.71 ± 0.12 0.72 ± 0.09
k weighted average	**1.38**	**1.05**	**1.05**	**1.02**	**3.4**	**4.0**	**1.2**	**0.80**
k standard deviation	± 0.06	± 0.16	± 0.05	± 0.11	± 0.6	± 0.5	± 0.2	± 0.15

Experimental values and FITs from which above values are derived can be seen here:

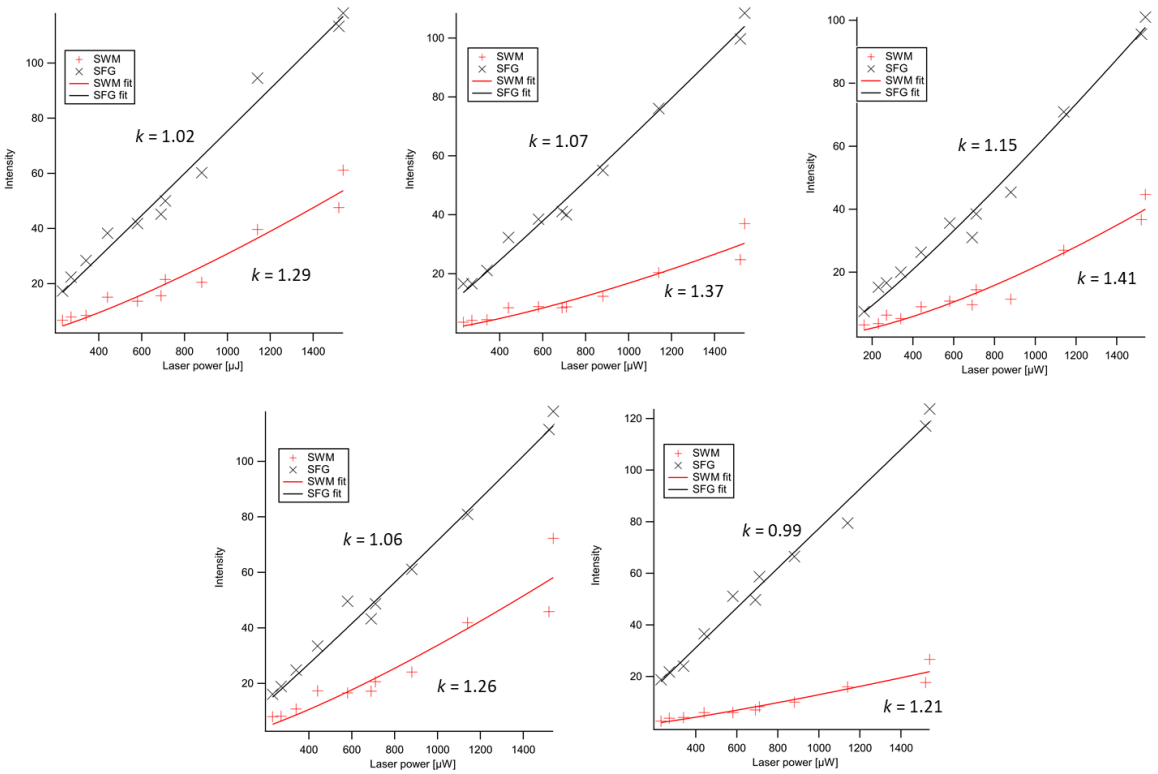

Figure S1 Experimental values and fits for “455 nm peak (1st)” and “SFG (1st)” under 820 nm dependence.

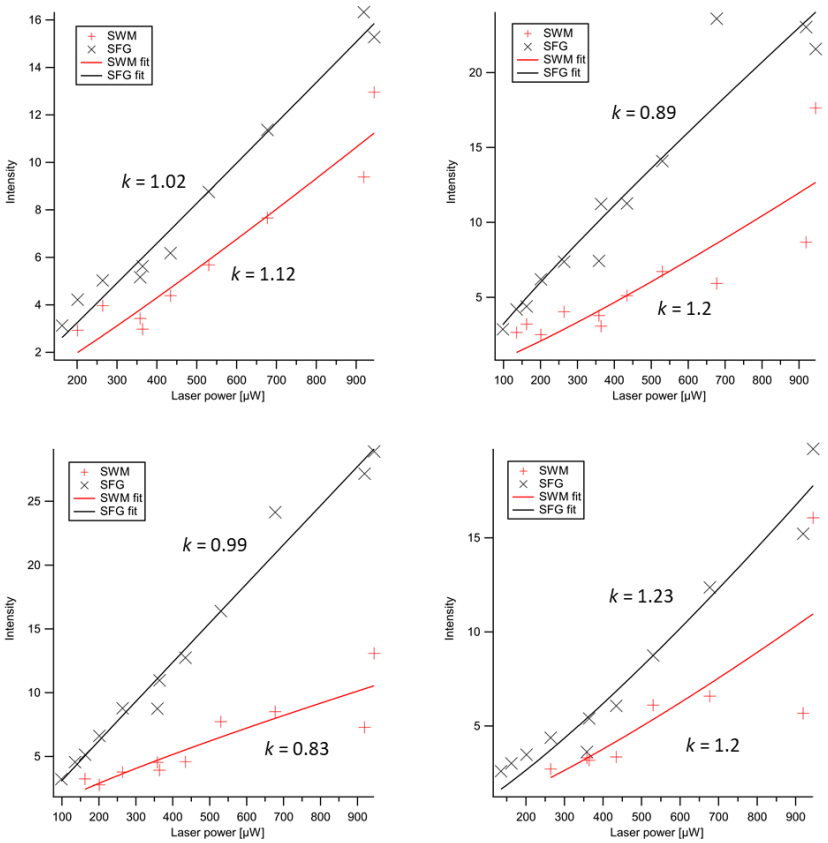

Figure S2 Experimental values and fits for “455 nm peak (2nd)” and “SFG (2nd)” under 820 nm dependence.

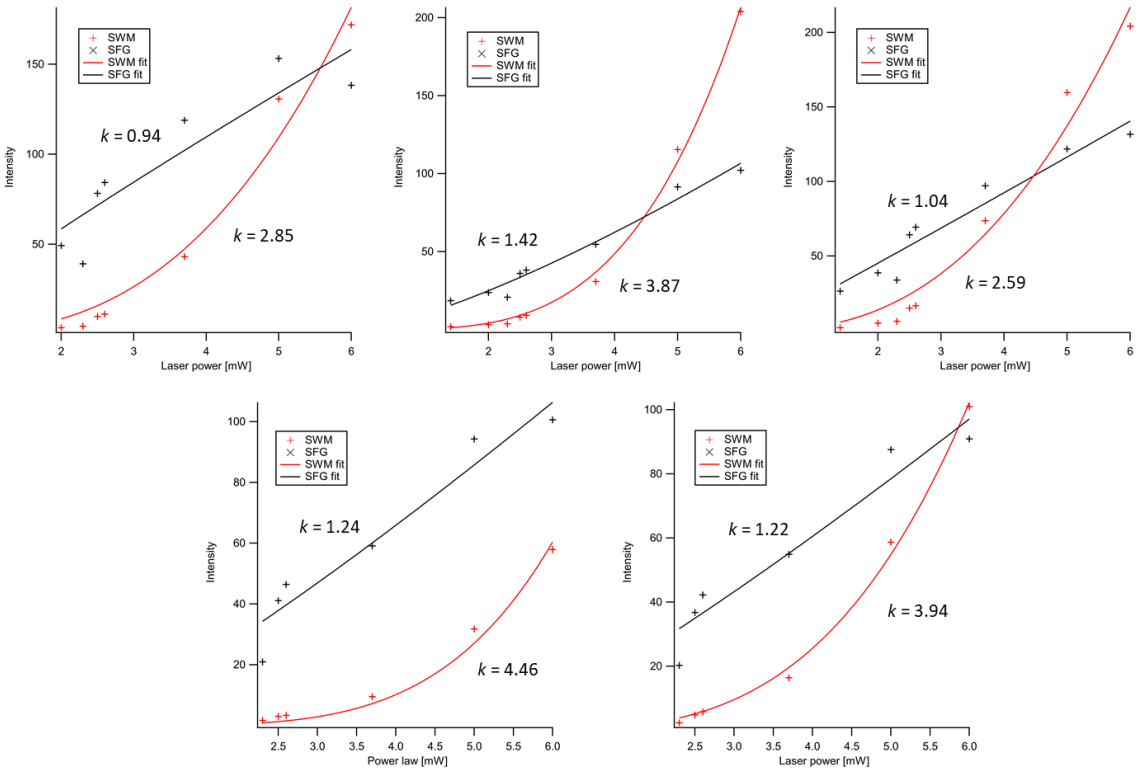

Figure S3 Experimental values and fits for “455 nm peak (1st)” and “SFG (1st)” under 1164 nm dependence.

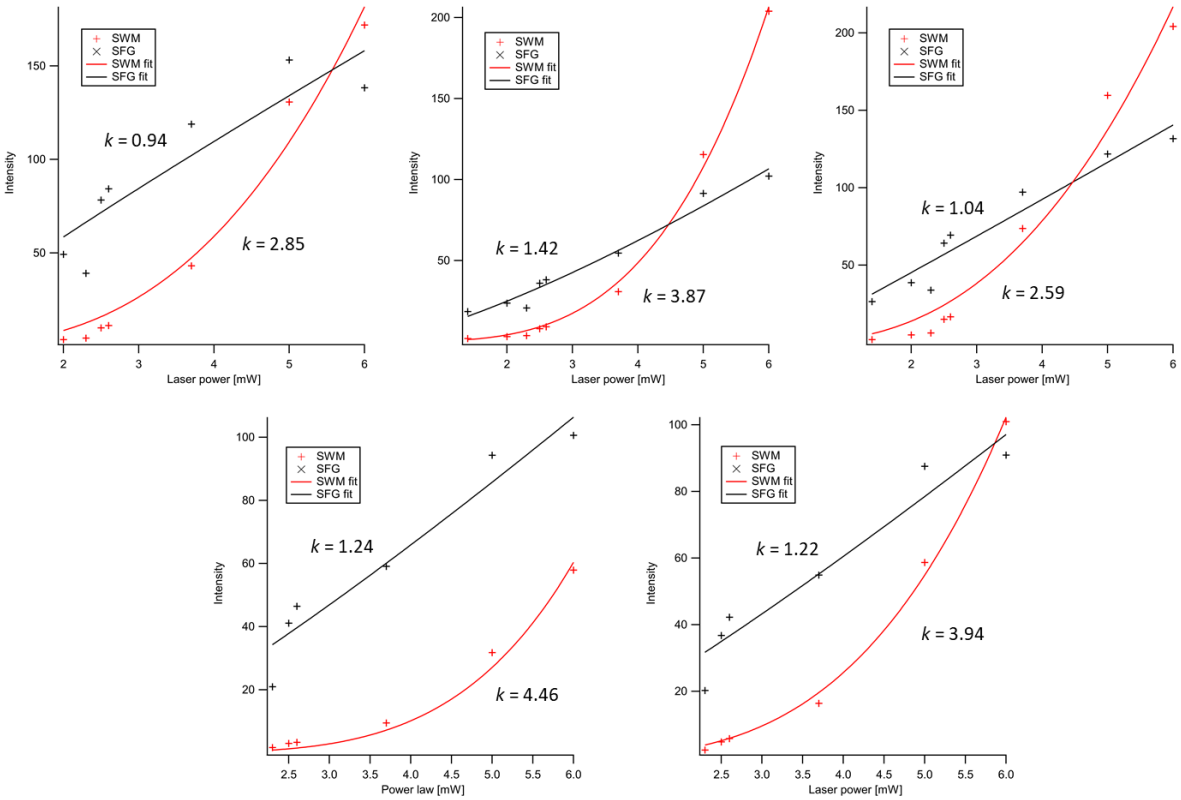

Figure S4 Experimental values and fits for “455 nm peak (2nd)” and “SFG (2nd)” under 1164 nm dependence.

Raman measurements from Li@C_{60} films, C_{60} powder and Li@$C_{60}[PF_6^-]$ powder

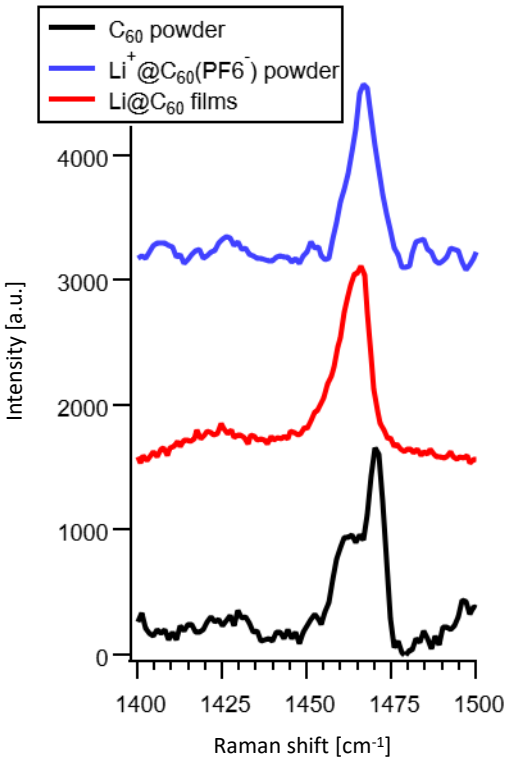

Figure S5. Raman measurements from Li@C_{60} films (red), $Li^+@C_{60}(PF_6^-)$ powder (blue) and C_{60} powder (red). Excitation wavelength was 633 nm. Raman of $Li^+@C_{60}(PF_6^-)$ powder and C_{60} powder were background corrected using a Savitzky–Golay filter.

SEM and EDX point spectrum

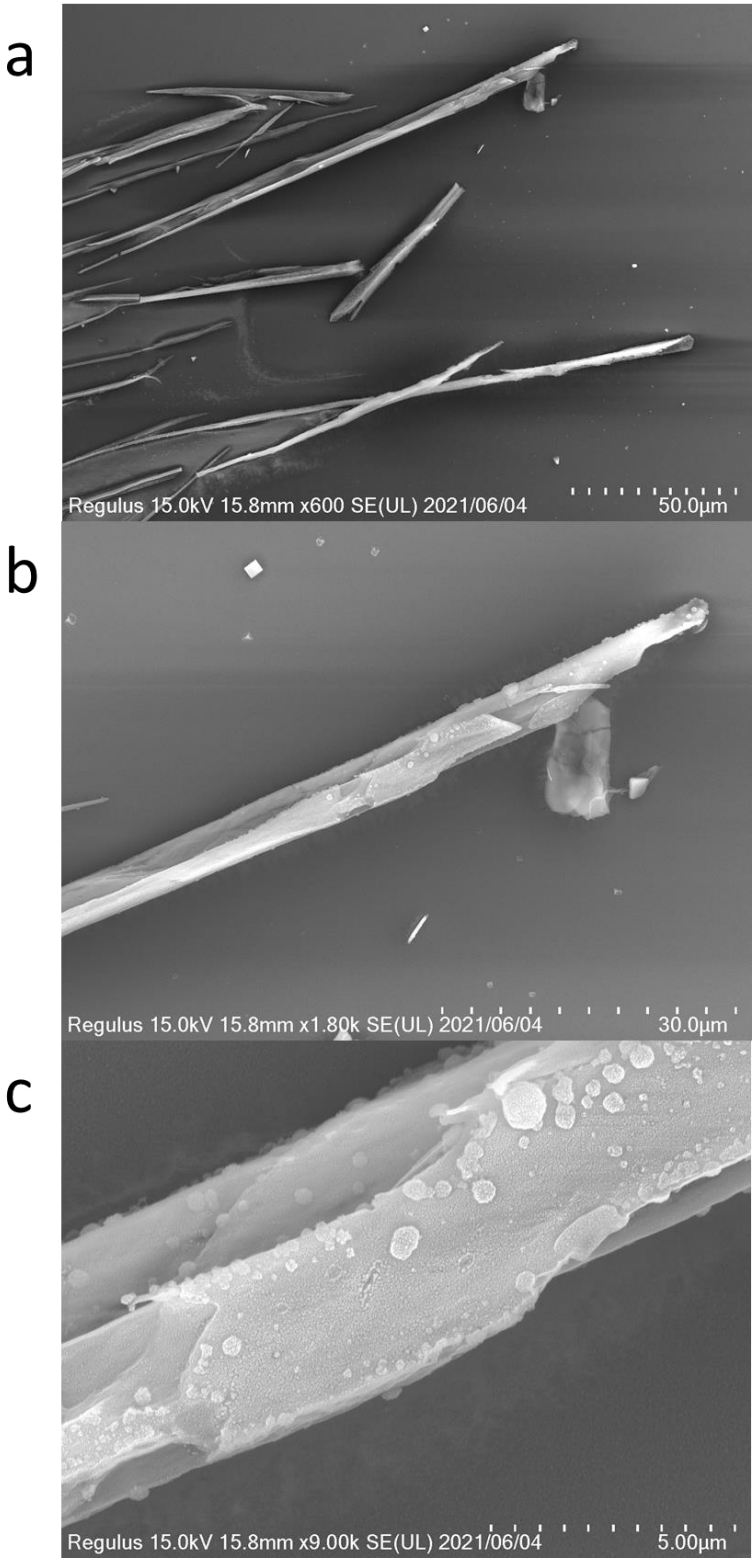

Figure S6. Scanning electron microscope (SEM) images of films made using NaI with increasing zoom from a) to c). Scale bars are given in the bottom right of each image.

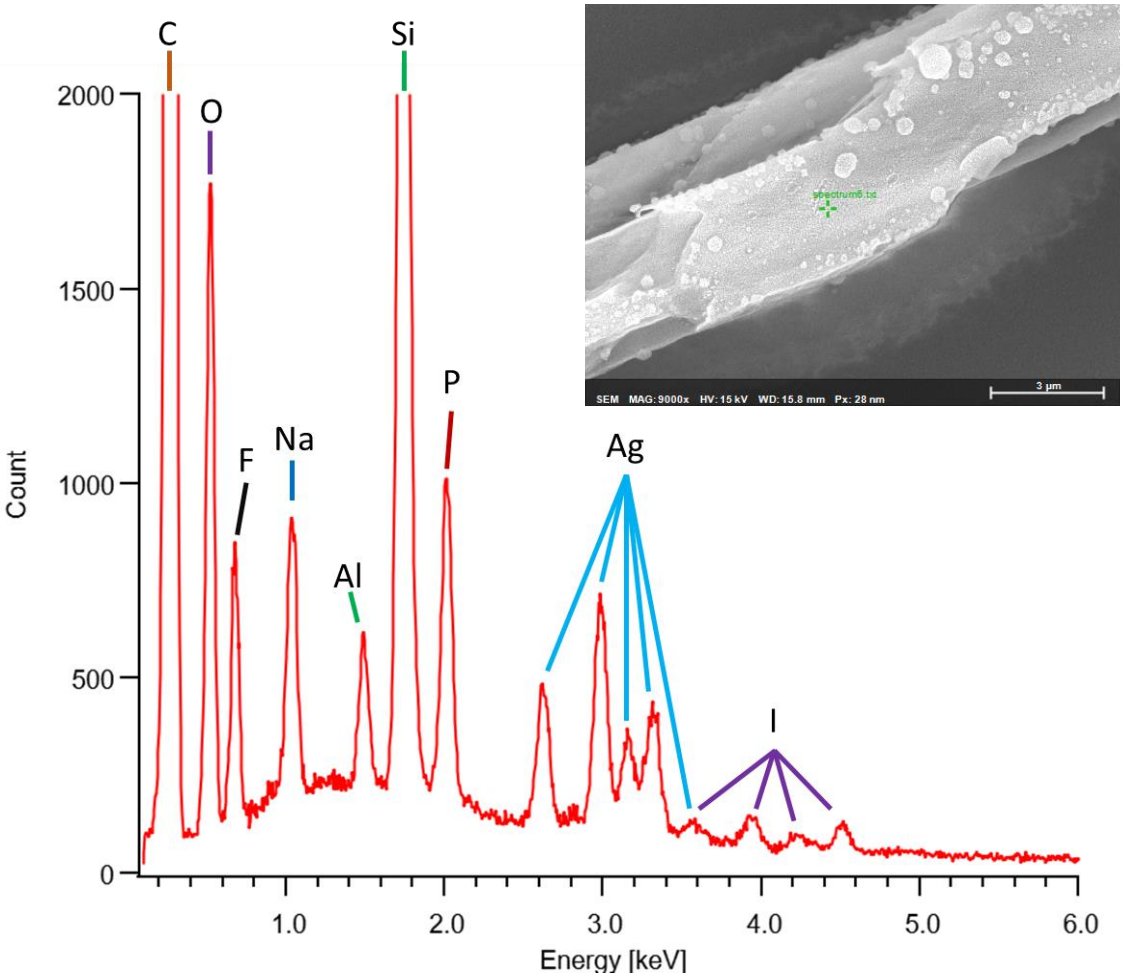

Figure S7. EDX spectrum obtained from the spot marked with a green cross in the SEM image (inlet). Elements observed are C, O, F, Na, Al, Si, P, Ag and I. O and Si are observed due to the glass substrate, Ag due to sputtering, Al due to the sample holder. Accelerating voltage was 15 kV.

Li@C_{60} film formation under different conditions

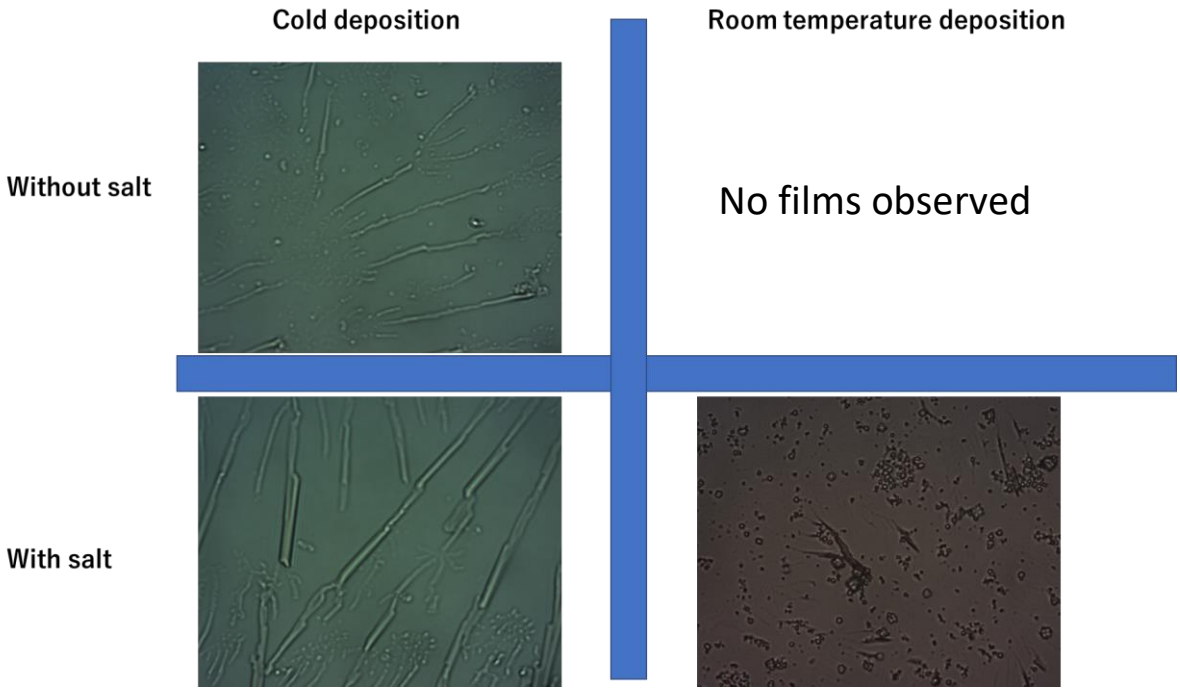

Figure S8. Optical transmission images of Li@C_{60} films prepared under different conditions.

Optical transmission images of C_{60} crystals and C_{60}-Ad films

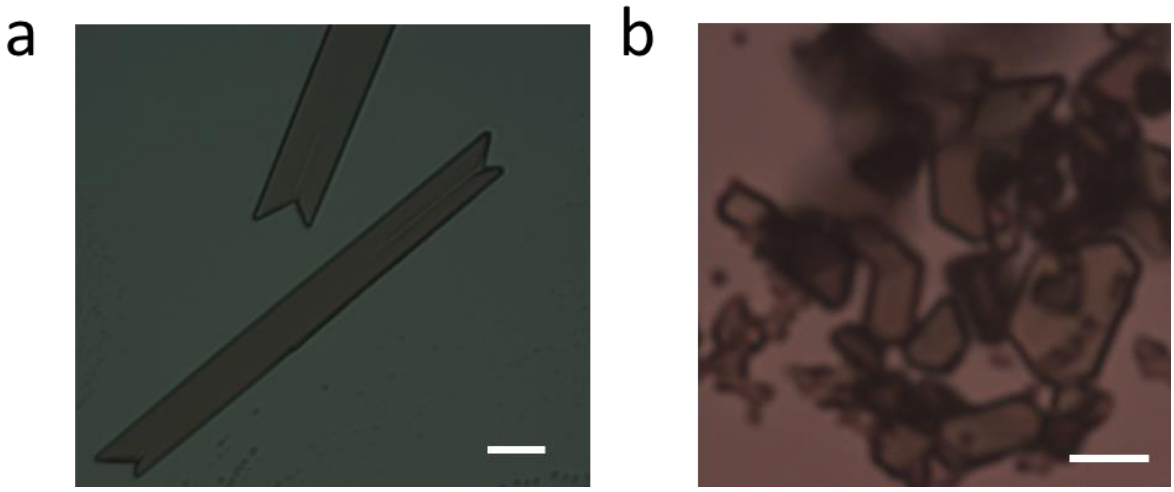

Figure S9. Optical transmission image of C_{60}-Ad films (a) and C_{60} crystals (b). Scale bars are 5 µm.
C_{60}-adamantylidene (C_{60}-Ad) was synthesized and characterized according to the literature.[1]

Raman from C_{60}-Ad films and C_{60} crystals

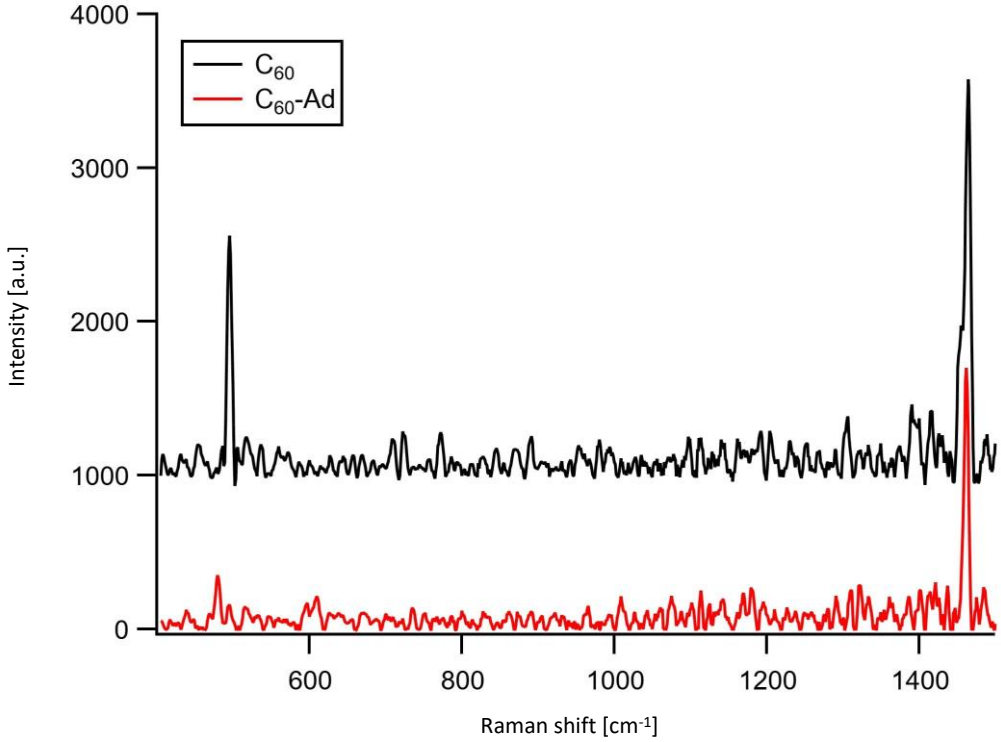

Figure S10. Raman measurements from C_{60}-Ad (red) and C_{60} crystals (black). Excitation wavelength was 633 nm. Both spectra were background corrected using a Savitzky–Golay filter.

AFM measurements

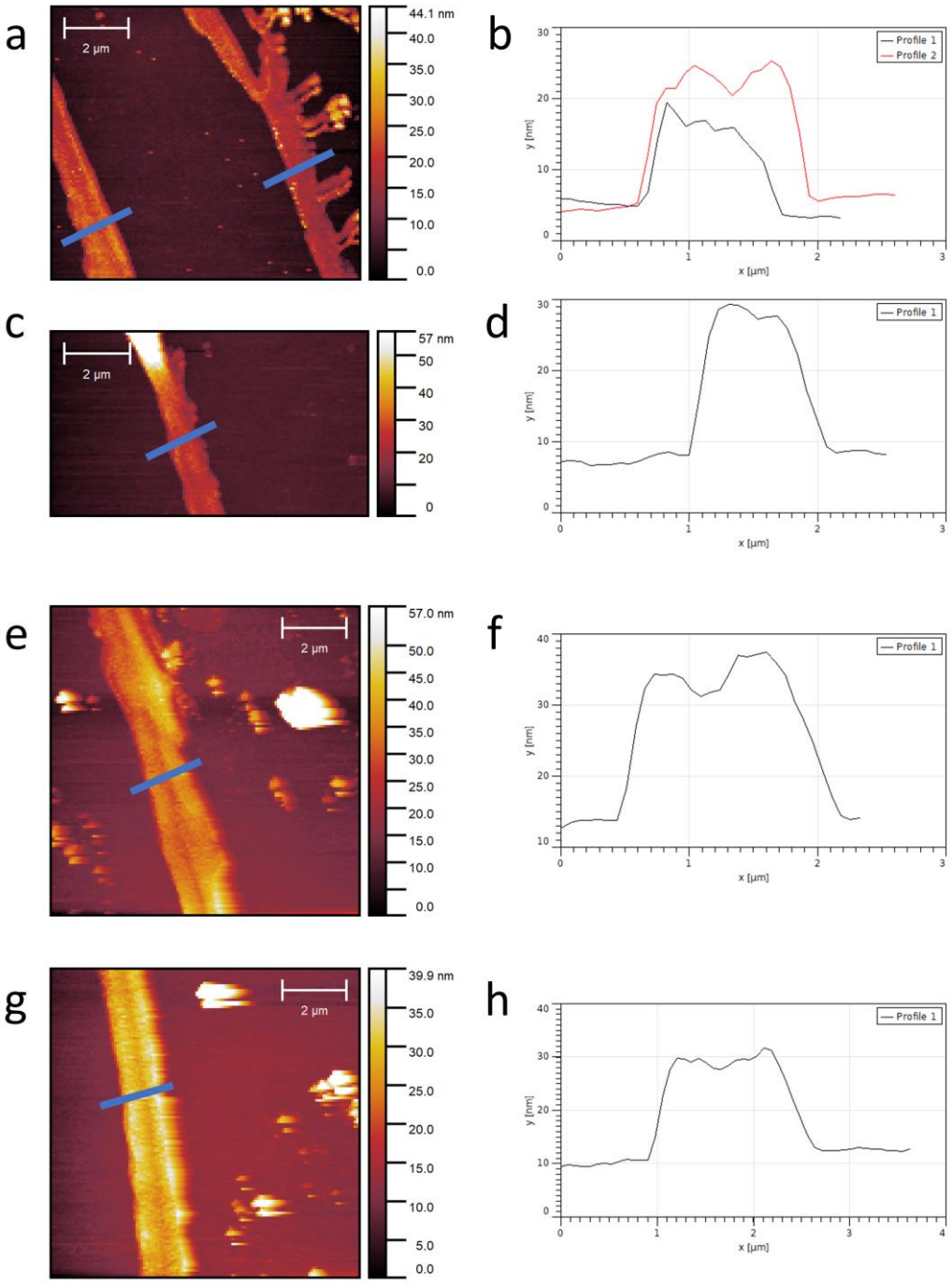

Figure S11. a) c) e) g) AFM images of a Li@C_{60} films (**sample 1**), b) d) f) h) height profiles taken from a, c, e and g respectively.

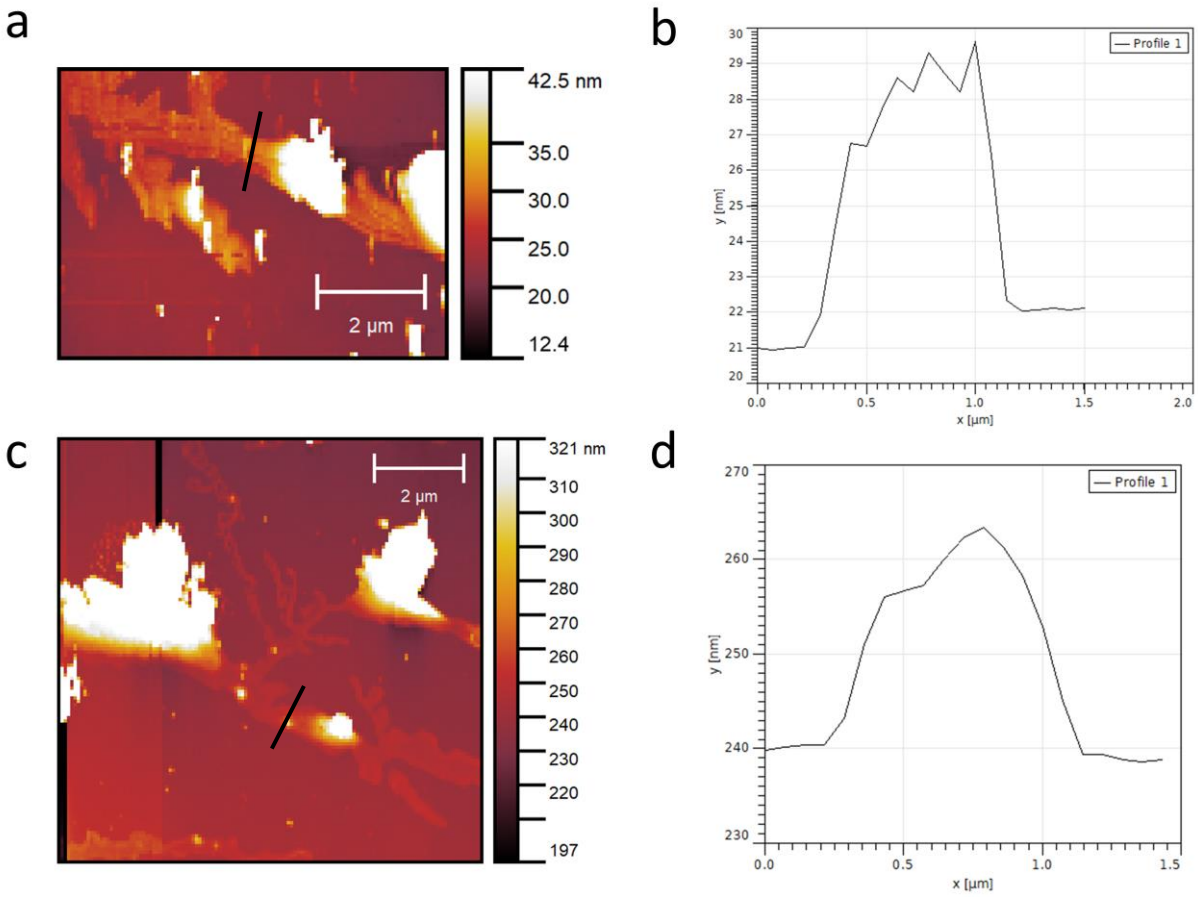

Figure S12. a) c) AFM images of a Li@C_{60} films (**sample 2**), b) d) height profiles taken from a and c respectively.

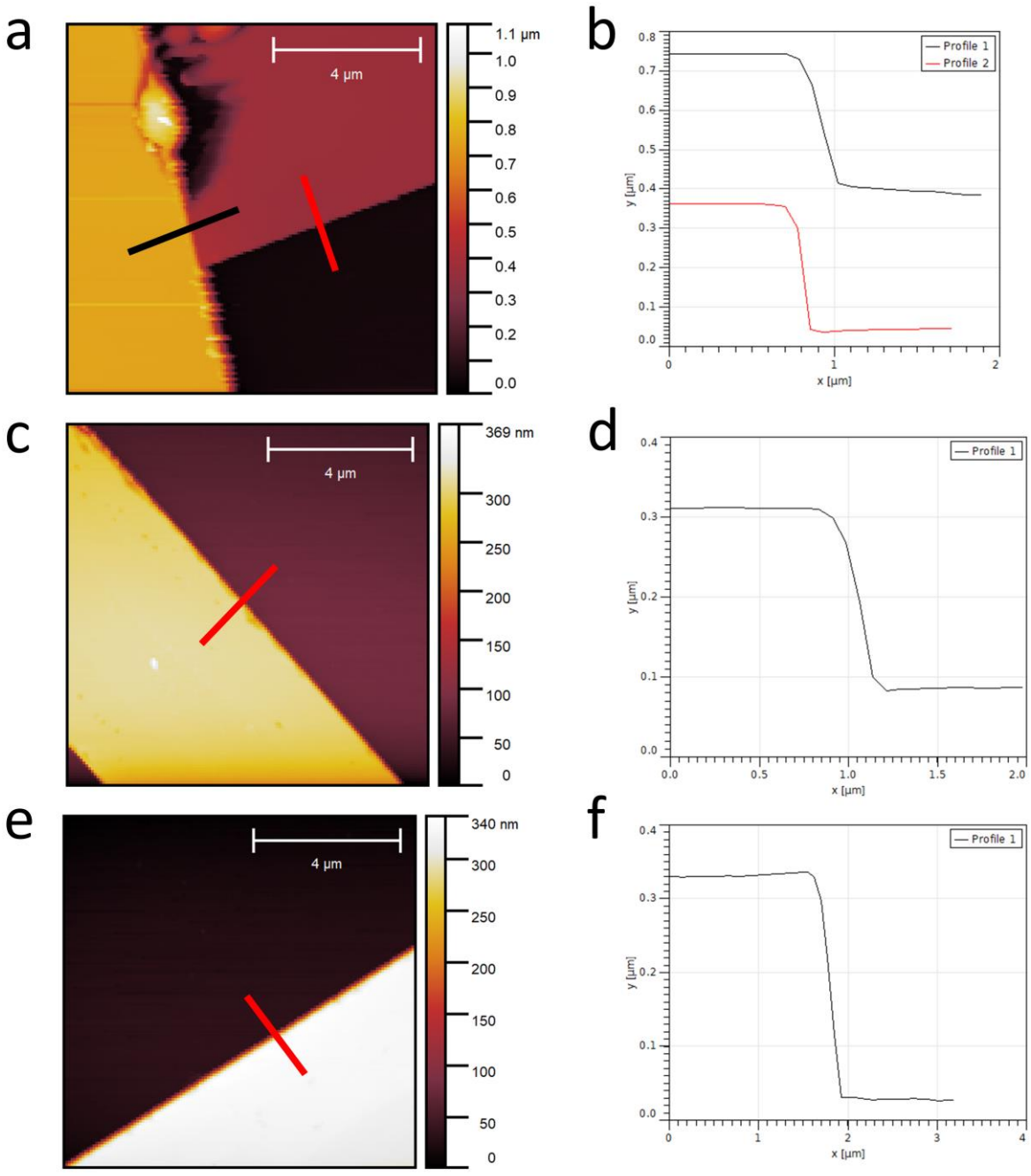

Figure S13. a) c) e) AFM images of a C_{60}-Ad films, b) d) f) height profiles taken from a, c and e respectively.

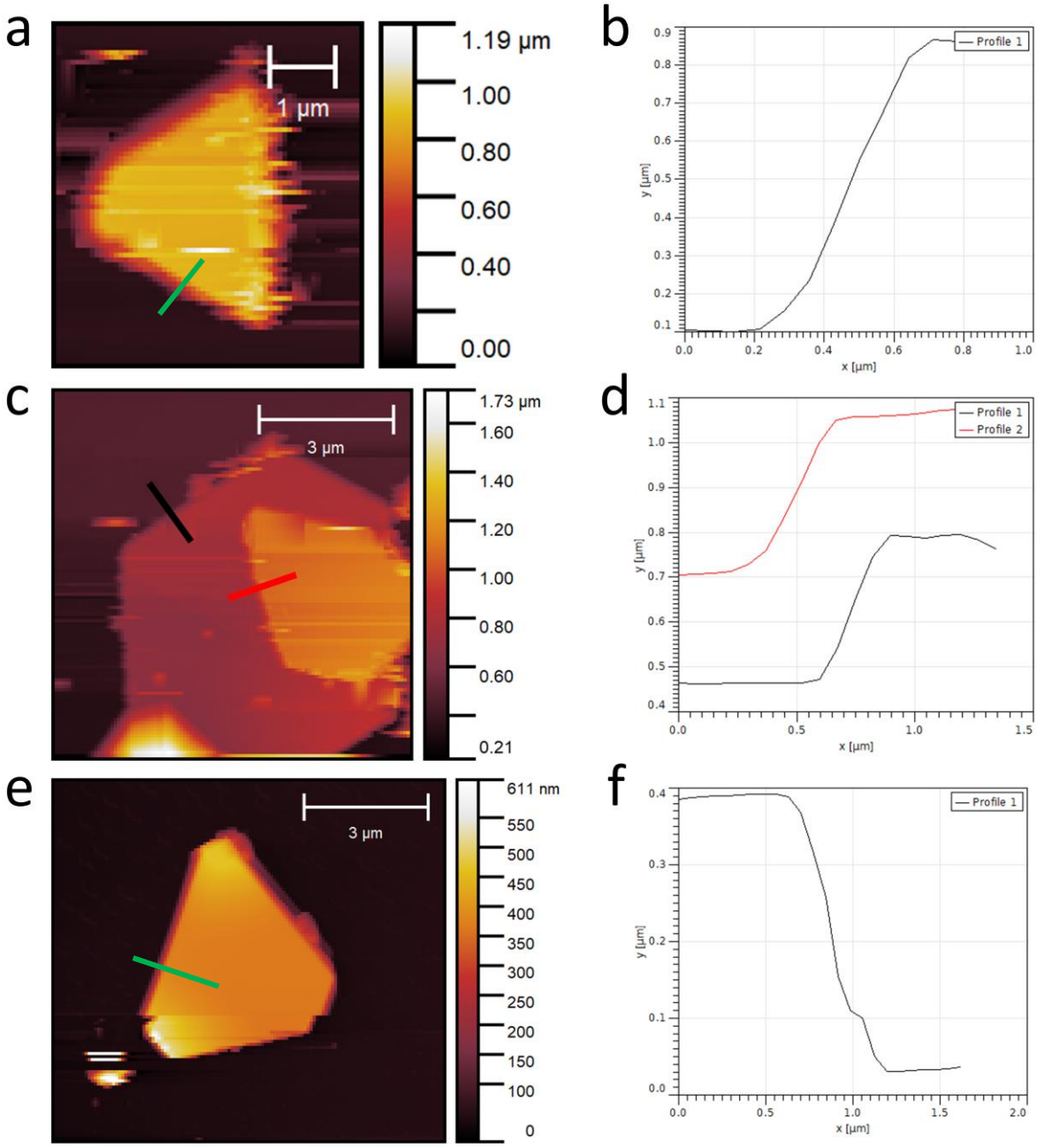

Figure S14. a) c) e) AFM images of a C_{60} crystals, b) d) f) height profiles taken from a, c and e respectively.

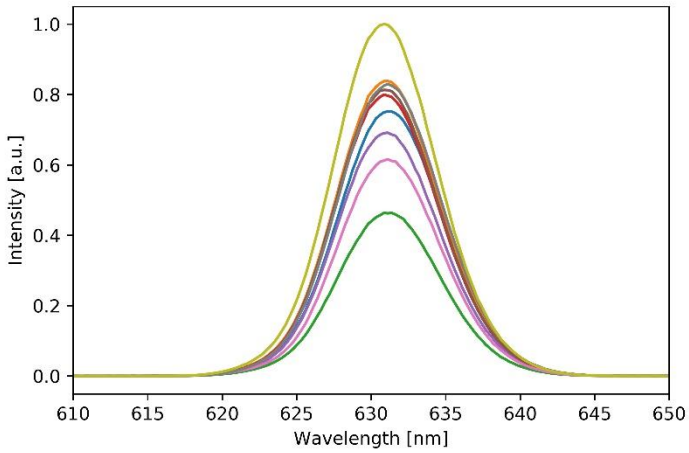

Figure S15 Normalized spectra obtained from Li@C_{60} films. The spectra have been obtained from films with varying orientation in relation to the excitation beams.

Figure S15 shows all nine spectra that went into the average spectra for DFWM of Li@C_{60} thin films. The spectra have been obtained from films with varying orientations in relation to the polarization of the excitation beams. Aside from two outliers (one on top, one on bottom), the intensities are relatively uniform. From AFM measurements on Li@C_{60} sample 1, we know the thicknesses are relatively uniform. So it is likely that the smaller differences are due to slight polarization dependence. If there was a strong polarization dependence, we would expect a stronger distribution. The outliers are thus likely due to differences in thickness.

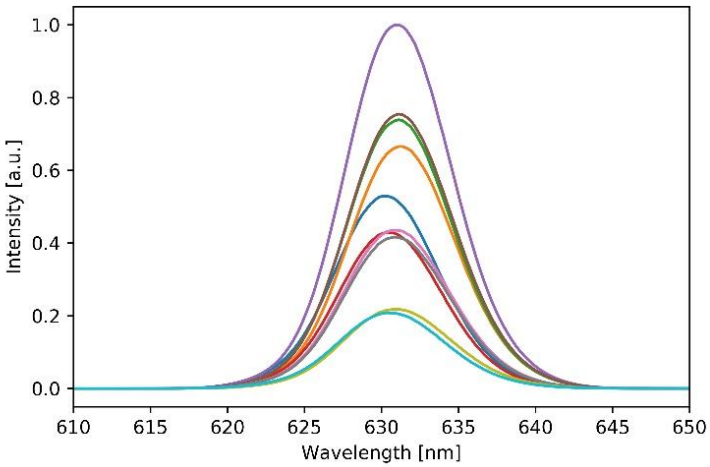

Figure S16 Normalized spectra obtained from C_{60}-Ad films. The spectra have been obtained from films with varying orientation in relation to the excitation beams.

Figure S16 shows all 10 spectra obtained from C_{60}-Ad. AFM measurements here (Figure S13) show a very uniform thickness distribution, so the differences are likely due to a strong polarization dependence.

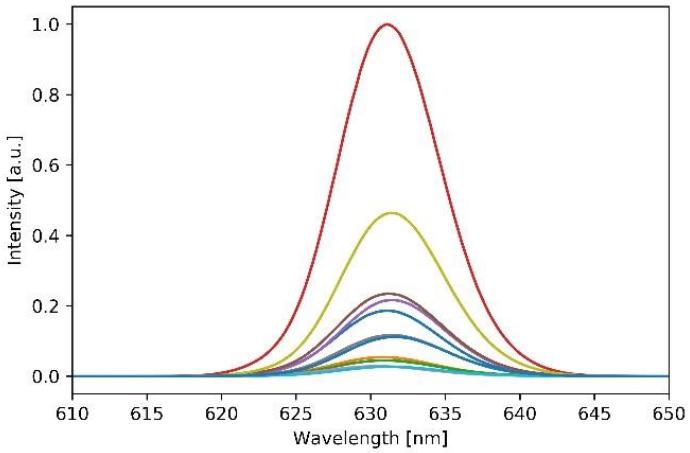

Figure S17 DFWM spectra of C_{60} films at various orientation in relation to the excitation polarization.

Figure S17 shows all 11 spectra obtained from C_{60}. As AFM showed strong variations in thickness (Figure S14), it is difficult here to determine a polarization dependence. However, a previous publication showed no polarization dependence in C_{60} films.[2]

References

[1] Akasaka, T.; Liu, M. T. H.; Niino, Y.; Maeda, Y.; Wakahara, T.; Okamura, M.; Kobayashi, K.; Nagase, S. Photolysis of Diazirines in the Presence of C_{60}: A Chemical Probe for Carbene/Diazomethane Partitioning. *J. Am. Chem. Soc.* **2000**, *122*, 7134-7145

[2] K. Wang, T. G. Zhang, W. P. Lin, S. Z. Liu, G. K. Wong, M. M. Kappes, R. P. H. Chang and J. B. Ketterson, *Appl. Phys. Lett.,* 1998*,* **60**, 810 – 812