Supplemental Material for Observation of Highly Dispersive Bands in Pure Thin Film C$_{60}$

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(Dated: December 20, 2018)
FIG. S1. LEED images of monolayer C$_{60}$ (brown) on bulk Bi$_2$Se$_3$ (green) at (a) 34 eV and (b) 15 eV. Dotted gray lines are guides to the eye showing perfect azimuthal alignment between the C$_{60}$ thin film and substrate Bi$_2$Se$_3$.

I. SUPPLEMENTAL DISCUSSION

A. Sample Preparation

High quality thin film C$_{60}$ samples were obtained by first cleaving a bulk Bi$_2$Se$_3$ substrate in situ under ultra-high vacuum ($\sim 10^{-10}$ Torr) to reveal a clean surface and depositing 5 nm of C$_{60}$ (approximately 5 layers) using an effusion cell loaded with high purity (99.9%) C$_{60}$ powder directed at the substrate. During the deposition (at $\sim 1 \times 10^{-9}$ Torr), the sample was heated to 100-200°C to facilitate the arrangement of large crystalline domains through increased C$_{60}$ mobility. Sample thickness and quality were confirmed by a quartz crystal oscillator thickness monitor and low-energy electron diffraction (LEED) measurements.

We are able to achieve epitaxial C$_{60}$ growth on Bi$_2$Se$_3$. This is most clearly evidenced by our test sample of monolayer C$_{60}$ on bulk Bi$_2$Se$_3$. As the C$_{60}$ film is quite thin in this case (approx. 1 nm), we are able to simultaneously resolve the diffraction spots of the C$_{60}$ overlayer (brown) and the substrate Bi$_2$Se$_3$ (green) as shown in the 34 eV LEED image in Fig. S1(a). The dotted gray lines are guides to the eye which show the excellent alignment
between the thin film and substrate. In the 15 eV LEED image shown in panel (b), the $C_{60}$ diffraction spots are easier to see as they appear stronger and again show the same alignment as in the higher energy LEED image.

$Bi_2Se_3$ has a layered structure allowing for a clean, flat surface after in situ UHV cleaving. By comparing lattice constants, we find that $\sim 7$ times the nearest neighbor distance between Se atoms on the $Bi_2Se_3$ surface is $\sim 3$ times the nearest neighbor distance between $C_{60}$ molecules (equivalent to the single layer lattice constant). Thus, a 3.4% compression on the close-packed $C_{60}$ lattice is imposed as shown in Fig. S2. Additionally, the $Bi_2Se_3$ surface layer has a hexagonal lattice, in accord with the $C_{60}$ single layer hexagonal lattice.

B. Photon Energy Dependence

The average intensity from each band cluster in $C_{60}$ is highly photon energy dependent. Most of the data presented in the main text was taken using 45 eV photons where the HOMO band cluster has about twice the average intensity as the HOMO-1 band cluster as can be seen in Fig. S3 (solid black line). This is the opposite of what we see in the density of states (DOS, yellow line, calculated for a single $C_{60}$ layer) where the peak DOS for the HOMO is roughly half of that for the HOMO-1. This is, however, not indicative of a general disagreement between the theory and experiment due to the strong photon energy dependent
FIG. S3. Momentum-integrated ARPES data for 45 eV (solid black line) and 38 eV (dashed black line) incident photon energy on a C$_{60}$ film. Theory calculated density of states are presented in yellow.

FIG. S4. Dependence of the energy of bulk C$_{60}$ in the $P\bar{6}3$ and $F\bar{m}3$ structures on lattice constant using both (a) PBE and (b) PBE+vdW functionals.

intensity effects in C$_{60}$. For example, at 38 eV (dashed black line) incident photon energy we recover nearly the exact same ratio of HOMO to HOMO-1 intensity as we find in the calculated DOS.

C. Theory Calculations

Density Functional Theory (DFT) calculations were performed using the projector augmented wave (PAW) method in the Vienna ab initio Simulation Package (VASP)$^{1,2}$ code.
The Bi (6s, 6p), Se (4s, 4p), and C (2s, 2p) electrons were treated as valence electrons, and their wavefunctions expanded in plane waves to an energy cutoff of 550 eV. $\Gamma$-centered $k$-point grids of 2x2x1 were used for the Bi$_2$Se$_3$/C$_{60}$ calculations, while Monkhorst-Pack $k$-point grids of 4x4x4 were used for the bulk C$_{60}$ crystal calculations for the Brillouin zone sampling. The calculations were performed both with and without spin-orbit coupling (SOC) as indicated. We carried out full structural relaxations of the internal coordinates and the cell shape and size until the Hellmann-Feynman forces were below 10 meV/Å and the stresses were below 0.01 kbar for each structure studied. For our calculations we used the Perdew-Burke-Ernzerhof functionals (PBE) with the DFT-D3 semi-empirical approximation to incorporate van der Waals interactions.

While calculating the full experimental Bi$_2$Se$_3$/C$_{60}$ structure is computationally intractable using first-principles calculations, considering a representative superstructure of one C$_{60}$ ball on one quintuple layer of Bi$_2$Se$_3$ gives us an approximation of the electronic interaction between the C$_{60}$ thin film and Bi$_2$Se$_3$. Our lattice parameters were fixed to the optimized bulk Bi$_2$Se$_3$ values. The distance between the C$_{60}$ buckyballs considered in this calculation (14.33 Å) differs from the value extracted from the experiment. Although this impedes a one-to-one comparison between the measured dispersion of the C$_{60}$ bands and the theoretical results for this structure, it allows a qualitative comparison with the experiment and provides clear information about the degree of hybridization between the C$_{60}$ layers and the Bi$_2$Se$_3$ substrate. As explained in the main text, we found little evidence of hybridization between the C$_{60}$ and Bi$_2$Se$_3$ and hence ultimately use our band structure calculations of a single C$_{60}$ layer to compare with our experimental data.

For our bulk C$_{60}$ calculations, two different possible orientations of the C$_{60}$ molecules with respect to each other were considered: $P\bar{6}3$ and $F\bar{m}3$. The results for the cell optimization for both of these structures are shown in Fig. S4. We found $P\bar{6}3$ to be the C$_{60}$ ground state crystal structure, with an energy of 1.9 eV and 0.2 eV lower than the $F\bar{m}3$ structure using PBE and PBE+vdW functionals respectively. Our calculated lattice parameters of 14.09 Å using PBE and 13.98 Å using PBE+vdW are both close to the experimental value of 14.1 Å for C$_{60}$ in a fcc crystal.

We calculated the energy differences for Bi-terminated and Se-terminated substrates for a variety of C$_{60}$ distances from the substrate, considering both pentagon-down and hexagon-down geometries with the results shown in Fig. S5. We found that the Se-termination is
almost 1.4 eV per Se atom lower in energy than the Bi-termination using van der Waals corrected DFT\textsuperscript{4}, while they were essentially degenerate when van der Waals corrections were not included.

For the Se-terminated surface, we calculated more precisely the optimum distance of the C\textsubscript{60} from the surface, as shown in the main text Fig. 1(c). The hexagon-down geometry is lower in energy than the pentagon-down case by 32 meV per C\textsubscript{60} with an optimal distance of 3.15 Å with PBE+vdW, but at 4.05 Å for PBE. Furthermore, we find a slight (few meV) preference for the hexagon to align along the hexagonal directions set by the Se atoms. The lower energy for the alignment of a C\textsubscript{60} hexagon face towards a Se atom, as compared with a pentagon face, imposes a constraint on the orientation of the C\textsubscript{60} molecules on the Bi\textsubscript{2}Se\textsubscript{3}, which may favor some long range order proven beneficial for ARPES experiments.

\textbf{D. Constant Energy Map Periodicity}

While we do see certain strong matrix elements effects in our constant energy maps as discussed in the main text, these effects do not preclude the presence of a highly periodic band structure. For example, by using in-plane polarized light, these matrix elements effects are minimized and we can clearly see a highly periodic band structure as shown in Fig. S6.

\hspace{1cm}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{energy_plot}
\caption{Energy per 120 atoms versus distance of the C\textsubscript{60} buckyball from the substrate surface for both Se- and Bi-termination and both hexagon or pentagon face of the buckyball oriented towards the substrate.}
\end{figure}
FIG. S6. Constant energy map taken at -2.9 eV (within the HOMO-1) using in-plane polarized light, i.e. linear vertical (LV) polarization. Periodicity of the band structure is clearly observed for a wide range of momenta across higher-order Brillouin zones.

E. Bandwidth Comparison

The C$_{60}$ dispersion bandwidths of the HOMO and HOMO-1 band manifolds, revealed for the first time by this ARPES study, are a different quantity than the full-width half-maximum (FWHM) spectral bandwidths quantified from angle-integrated photoemission or theoretical k-integrated density of states (DOS). The dispersion bandwidths reflect the near-neighbor (NN) periodic wave function interactions in the thin film, whereas the larger FWHM bandwidths additionally include line-broadenings intrinsic to a single isolated C$_{60}$ molecule. The theoretical density of states calculations for a single molecule on Bi$_2$Se$_3$ (i.e. 14.33 Å NN distance), a single hexagonal layer (with 10 Å NN distance), and bulk C$_{60}$ displayed in Fig. 2 (main text), are replotted in Fig. S7(a) to illustrate this point. The isolated molecule spectrum has a very narrow 0.22 eV DOS bandwidth reflective of no band dispersions, whereas the single layer and bulk C$_{60}$ DOS bandwidths are progressively larger. The theoretical HOMO DOS bandwidth has a very good match to the 0.54 eV FWHM spectral bandwidth of the experimental angle-integrated 45 eV valence spectrum, and whose value agrees well with the sum of the 0.22 eV isolated molecule bandwidth and the 0.33 eV experimental ARPES dispersion bandwidth.

Figure S7(b) also provides a comparison of the 45 eV HOMO-1 and HOMO valence spectrum to three representative C$_{60}$ photoemission spectra from the literature$^{5-7}$ measured at $\approx$ 23 eV. Here we observe that the ordered C$_{60}$/Bi$_2$Se$_3$ spectrum measured at $T=20$ K
FIG. S7. (a) Comparison of the angle-integrated C\textsubscript{60} HOMO-1 and HOMO valence band spectrum acquired at 45 eV to previous literature spectra acquired at 22-23 eV. The literature spectra are energy aligned to the 45 eV HOMO peak and the 45 eV HOMO intensity is separately scaled to match the literature heights. (b) Comparison of the 45 eV valence band spectrum to the C\textsubscript{60} DFT density-of-states spectra from Fig. 2 (main text) calculated for the bulk, single layer, and a single C\textsubscript{60} molecule. The spectra are energy aligned to the bulk theory HOMO peak and the 45 eV HOMO intensity is separately scaled to match the theory heights. See Table S1 for quantitative numbers of FWHM bandwidth values.

has a distinctly narrower FWHM bandwidth and significantly lower background between the molecular orbital peaks than in the literature spectra, all of which were measured at room temperature. (No low temperature measurements of pure C\textsubscript{60} were found in the literature.) Hence the Fig. S7(b) comparison likely represents a combination of phonon broadening as well a orientational disorder broadening. A numerical summary of the HOMO-1 and HOMO experimental and theoretical bandwidths is provided in Table S1.

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TABLE S1. Comparison of experimental and theoretical HOMO-1 and HOMO bandwidths.

<table>
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<th>Reference</th>
<th>System</th>
<th>$h\nu$ (eV)</th>
<th>FWHM (eV)</th>
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<td>Benning’91</td>
<td>C$_{60}$/GaAs(110)</td>
<td>23</td>
<td>0.83 0.66</td>
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<tr>
<td>S. He’07</td>
<td>cleaved C$_{60}$(111)</td>
<td>23</td>
<td>0.8 0.62</td>
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<tr>
<td>Wang’08</td>
<td>C$_{60}$/Si:H(111)</td>
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<td>C$_{60}$/Bi$_2$Se$_3$</td>
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<td>0.72 0.54</td>
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<td>dispersion bandwidth</td>
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<td>(0.52) (0.33)</td>
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<td>DFT single C$_{60}$</td>
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<td>0.22</td>
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<td>DFT bulk C$_{60}$</td>
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(2010).

