C₆₀ fullerides are uniquely flexible molecular materials that exhibit a rich variety of behaviour, including superconductivity and magnetism in bulk compounds, novel electronic and orientational phases in thin films and quantum transport in a single-C₆₀ transistor. The complexity of fulleride properties stems from the existence of many competing interactions, such as electron–electron correlations, electron–vibration coupling and intermolecular hopping. The exact role of each interaction is controversial owing to the difficulty of experimentally isolating the effects of a single interaction in the intricate fulleride materials. Here, we report a unique level of control of the material properties of K₃C₆₀ ultrathin films through well-controlled atomic layer indexing and accurate doping concentrations. Using scanning tunnelling microscope techniques, we observe a series of electronic and structural phase transitions as the fullerides evolve from two-dimensional monolayers to quasi-three-dimensional multilayers in the early stages of layer-by-layer growth. These results demonstrate the systematic evolution of fulleride electronic structure and molecular ordering with variable K₃C₆₀ film layer index, and provide essential information for the development of new molecular structures and devices.

The ability to tune competing interactions in the fullerenes arises from advances in our ability to grow well-controlled heterogeneous molecular films. Here, we describe measurements on potassium-doped C₆₀ (K₃C₆₀) ultrathin films having variable thickness from one to three layers (layer index i = 1, 2, and 3) for three specific doping concentrations (x = 3, 4, and 5). Figure 1a shows a scanning tunnelling microscope (STM) topograph of a representative K₃C₆₀ multilayer on Au(111), where the colour scale highlights the plateau structure. Narrow slivers of C₆₀-free voids containing only K atoms (brown) exist between continuous patches of K₃C₆₀. Islands of second- (blue) and third-layer (red) K₃C₆₀ can be seen residing on top of the first K₃C₆₀ layer (green). The average layer thickness is ∼9.9 Å, greater than the 8 Å spacing found in undoped C₆₀ films.

We begin by describing our results for a multilayer of the x = 3 metallic system. Layer-dependent electronic structure in K₃C₆₀ can be seen in Fig. 2a, which shows spatially averaged dI/dV spectra measured at three different layer levels. Within each layer, the spectrum is highly uniform with no sign of spatial inhomogeneity such as that found in the surface of bulk fullerenes. The first layer dI/dV exhibits a wide peak at the Fermi energy (E_F), reflecting the large electronic density of states (DOS) of a metallic, half-filled lowest-unoccupied-molecular-level (LUMO)–derived band in K₃C₆₀. In contrast, the second-layer spectrum shows a sharp dip at E_F, indicating an emergence of an energy gap that tends to split the band into two halves. A similar gap-like feature persists in the third layer. The width of the gap-like feature (measured between adjacent local maxima) is ∼0.2 eV, a much larger value than the superconducting gap 2Δ_s ∼ 6 meV found in bulk K₃C₆₀ (ref. 14). The spectra at energies far above E_F, on the other hand, are nearly identical in all three layers. As these higher-energy features (especially the position of the LUMO+1 resonance) are very sensitive to the intrinsic doping level of K₃C₆₀ (ref. 15), this implies that there is no significant difference of K content across the layers.

The spatial arrangement of C₆₀ molecules also changes markedly with layer index. The first layer of K₃C₆₀ (Fig. 2c) exhibits a complex √3 × √3 superstructure of bright molecules having different orientation from their dimmed nearest neighbours. In the second layer (Fig. 2d), however, C₆₀ molecules form a very simple hexagonal lattice (lattice constant a ∼ 10.5 Å) with long-range orientational ordering. The tri-star-like topography of each molecule suggests that C₆₀ in the second layer is oriented with a...
The insulating $x = 4$ multilayer system exhibits a similar trend. Figure 3a shows $dI/dV$ spectra measured on a $K_4C_{60}$ plateau structure where the number of layers is varied from $i = 1$ to 3. First-layer spectra ($i = 1$) exhibit an insulating energy gap $\Delta \sim 0.2$ eV that is induced by molecular Jahn-Teller distortion. As the layer index increases from $i = 1$ to 3, the energy gap opens continuously (by layer 3, the gap has well-defined edges and a flat bottom). The gap amplitudes observed here are estimated to be $\Delta \sim 0.6$ eV and 0.8 eV for layers 2 and 3 respectively. As seen in the metallic $x = 3$ system, the geometric structure of the insulating $x = 4$ system simplifies as the layer index is increased. Complex 'cross-phase' orientational ordering observed in the $K_4C_{60}$ first layer evolves to a much simpler hexagonal lattice (Fig. 3d) for higher layers. Layers 2 and 3 for the $x = 4$ film exhibit featureless $C_{60}$ molecules with little discernible orientational ordering.

As doping is increased to $x = 5$, $K_5C_{60}$ multilayers show re-entrant metallicity for layer 1 (ref. 10) and an evolution to insulating behaviour by layer 3. At this doping, the upper Jahn-Teller band is only partially filled and the first-layer spectrum (Fig. 4a) exhibits a finite (although suppressed) electronic DOS at $E_F$. Suppression of the DOS at $E_F$ deepens significantly in the second layer, and broadens to a pronounced energy gap $\Delta \sim 0.4$ eV by the third layer. As with the $x = 3$ and $x = 4$ doping levels, complex structural ordering in the first layer of $K_5C_{60}$ (that is, the highly ordered $2 \times 2$ superstructure seen in Fig. 4c) evolves into a much simpler hexagonal ordering in higher layers (Fig. 4d).

Taken collectively, these results clearly show that, for a fixed doping level, increasing film thickness suppresses metallicity and

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**Figure 2** Electronic and structural properties of a $K_4C_{60}$ multilayer. a, Spatially averaged $dI/dV$ spectra measured at three different layer heights of $K_4C_{60}$. The first-layer spectrum has a peak at $E_F$, whereas the second- and third-layer spectra show a sharp dip having a width of $\sim 0.2$ eV. b, Schematic diagram showing the effect of $U$ on the electronic structure of $K_4C_{60}$. A small $U_{J}\bar{T}$ in the first layer (left) has negligible effect on the band structure, but a larger $U_{J}\bar{T}$ in higher layers (right) causes a dip around $E_F$. c, $K_4C_{60}$ first-layer image (taken with $V = 0.6$ V and $I = 20$ pA) shows a $\sqrt{3} \times \sqrt{3}$ superstructure. Each red circle represents one $C_{60}$ molecule. d, Topograph of the second layer ($V = 1$ V and $I = 5$ pA) shows a simple hexagonal lattice.

**Figure 3** Electronic and structural properties of a $K_4C_{60}$ multilayer. a, $dI/dV$ spectra of the Jahn–Teller (JT)-insulating $K_4C_{60}$ measured at three different layer heights. The observed gap $\Delta$ increases from 0.2 eV in layer 1 to 0.6 eV and 0.8 eV in layers 2 and 3 owing to the enhancement of $U_{J}\bar{T}$. b, Schematic band structure of $K_4C_{60}$. Larger $U_{J}\bar{T}$ in layer 3 (right) leads to a much wider gap than that in layer 1 (left). c, Topograph of $K_4C_{60}$ layer 1 ($V = -0.2$ V and $I = 5$ pA) shows a ‘cross’-like orientational ordering. d, $K_4C_{60}$ layer 2 exhibits a simple hexagonal lattice structure with little orientational ordering (image taken with $V = -1$ V and $I = 10$ pA).

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Our K₂C₆₀ multilayers, screening originates from three distinct sources: the metal substrate, surrounding polarizable molecules and itinerant charge carriers.

The first two screening mechanisms can be treated in a straightforward manner. As discussed by Hesper et al., the screening of U from a nearby metal can be modelled using an image charge potential as

\[ \delta U_i = e^2/(4\pi\varepsilon_0 2d), \]

where \( d \) is the distance from the centre of a molecule to the metal substrate (Fig. 1b). The screening from nearby polarized molecules can be expressed as

\[ \delta U_\text{eff} = 2\alpha e^2/(4\pi\varepsilon_0 R^2), \]

where \( z \) is the number of nearest neighbours, \( \alpha \) is the molecular polarizability and \( R \) is the intermolecular distance²⁵. The third mechanism, renormalization of \( U \) by itinerant electrons (\( \delta U_\text{it} \)), depends sensitively on the doping concentrations of the fullerides and is a more complex term²⁶–²⁹. The total reduction of \( U \) due to the molecular environment is the sum of the three terms:

\[ \delta U = \delta U_i + \delta U_\text{eff} + \delta U_\text{it}, \]

and \( U_\text{eff} = U_0 - \delta U \) is the final effective Hubbard \( U \). These relations show how the variable layer structure of our K₂C₆₀ ultrathin films can provide a systematic technique to control electron correlations by changing both the distance to the metal substrate (\( d \)) and the number of nearest neighbours (\( z \)).

This is seen most clearly in the insulating K₂C₆₀ multilayers. The K₂C₆₀ monolayer has been demonstrated to be a Jahn–Teller insulator³, where the strong Jahn–Teller effect at filling level \( x = 4 \) splits the degenerate LUMO states of C₆₀ and opens an energy gap at \( E_0 \) (Fig. 3b; ref. 30). Assuming that the Jahn–Teller splitting remains unchanged with varied layer index, the layer dependence of the gap in K₂C₆₀ is accounted for by equations (1) and (2) owing to the absence of itinerant charge carriers (\( \delta U_\text{it} = 0 \)). As the layer index increases from \( i = 1 \) to 3, \( \delta U_\text{eff} \) (substrate screening) decreases from 1.5 eV to 0.3 eV according to equation (1). In contrast, \( z \) increases from 6 in the first layer to 9 for both the second and third layer terraces, causing \( \delta U_\text{eff} \) to increase from 0.6 eV to 0.9 eV via equation (2) (here we use \( \alpha = 90 \AA^3 \), the value for undoped C₆₀)³¹. The total screening (equation (3)) is thus \( \delta U = 2.1, 1.4 \) and 1.2 eV for \( i = 1, 2 \) and 3, respectively, leading to an increase in \( U_\text{eff} \) from 0.9 eV to 1.8 eV as \( i \) increases from 1 to 3. The relative increase of the experimentally observed gap by 0.4 eV (from \( i = 1 \) to 2) and 0.2 eV (from \( i = 2 \) to 3) is in fairly good agreement with the calculated relative increase of \( U_\text{eff} \) by 0.7 eV (from \( i = 1 \) to 2) and 0.2 eV (from \( i = 2 \) to 3). This agreement becomes much better if we use a larger \( \alpha \) value for K₂C₆₀ (a reasonable assumption).

We note that some factors, such as screening from the STM tip, the effect of intermolecular electron hopping on the bandwidth and the interplay between different screening mechanisms are not included in our simple phenomenological model. Nevertheless, the good agreement between the observed experimental trend and the semiquantitative analysis clearly demonstrates that stronger electron correlation in higher layers is responsible for the observed layer-dependent increase of gap in K₂C₆₀.

The behaviour of K₂C₆₀ multilayers is quite different from the insulating K₂C₆₀ case above. The Jahn–Teller effect is much weaker at an uneven filling level \( x = 3 \), leading to a metallic ground state in bulk K₂C₆₀ (refs 21,30). In K₂C₆₀ multilayers, the layer-dependent electronic structure is still caused by layer dependence in \( U \), but here the itinerant electron screening term (\( \delta U_\text{it} \)) becomes
important. Determining the renormalized $U_{\text{eff}}$ for $K_xC_{60}$ is quite controversial. Various theoretical calculations in bulk $K_xC_{60}$ ($x = 12$) produce a combined screening strength $(\delta U_{\|} + \delta U_{\perp})$ that ranges widely from 2.2 to 3.2 eV (refs 1,28). Using a mean value of $(\delta U_{\|} + \delta U_{\perp}) = 2.7 \text{ eV}$, and including substrate screening $(\delta U_{\perp})$ through equation (1), we find that the effective Coulomb interaction becomes $U_{\text{eff}} = U_0 - \delta U = 0.2, 0.5 \text{ and } 0.7 \text{ eV for } i = 1, 2 \text{ and } 3$. For $i = 1$, $U_{\text{eff}}$ is too small compared with the bandwidth $W$ to open a gap, whereas in layers 2 and 3, we expect a small Mott–Hubbard gap to begin opening as $U_{\text{eff}}$ becomes comparable to $W$ (Fig. 2b). This explains the gap-like structure observed in the $K_xC_{60}$ data of Fig. 2a.

$K_xC_{60}$ is an intermediate case to the extremes of $K_xC_{60}$ and $K_yC_{60}$. Here, the Jahn–Teller effect is weaker than in $K_yC_{60}$, and hence it is not insulating, but the filling-dependent effective bandwidth is narrower than in $K_yC_{60}$, making it less metallic. We thus expect the layer-dependent $U_{\text{eff}}$ for $K_xC_{60}$ to lie between the two extremes. This is indeed the case, as we observe a relatively small suppression of electronic DOS in layer 1 (Fig. 4a), but by layer 3 a well-defined gap $\Delta \sim 0.4 \text{ eV}$ has emerged. This gap is about 0.4 eV smaller than that of the $i = 3$ layer in $K_yC_{60}$, mainly owing to the reduced Jahn–Teller effect and enhanced metallic screening. On the other hand, it is about 0.2 eV larger than the gap observed in the $i = 3$ layer of $K_yC_{60}$, reflecting the narrower bandwidth in $K_yC_{60}$.

The layer-index-dependent change in structural properties seen for all three doping levels as the index increases above $i = 1$ is less a direct result of electronic screening and more likely dominated by intermolecular electron hopping via the overlap of molecular orbitals. The complex structures found in layer 1 of $K_yC_{60}$, $x = 3–5$ (Figs 2c, 3c and 4c) are characteristic of geometric frustration of molecular orientational ordering in a two-dimensional (2D) lattice. As the layer index is increased, further interaction with adjacent $C_{60}$ molecules in the lower layers leads to quasi-3D-like intermolecular interactions. This creates a more isotropic local molecular environment and puts more spatial constraints on molecular orientation, limiting the possibility of exotic molecular ordering. Therefore, the much simpler and more homogeneous spatial structures found in the higher layers of $K_yC_{60}$ (Figs 2d, 3d, and 4d) can be seen as a natural consequence of dimensional crossover from the 2D limit to the quasi-3D bulk regime.

Using accurately fabricated $K_xC_{60}$ ultrathin films, we have demonstrated how electron correlation strength, a key factor in determining the material properties of fullerenes, can be experimentally controlled by varying proximity to a metal substrate, the number of nearest neighbours, and intrinsic doping levels. These results support the notion of tuning molecular electronics via variable layer structure and distance to metal contacts, and open new routes towards engineering novel molecular devices and creating new electronic phases in strongly correlated molecular materials.

METHODS

Our experiments were conducted in a home-built ultrahigh vacuum cryogenic STM with a PtIr tip. $C_{60}$ thin films with desired thickness were made by evaporating $C_{60}$ molecules onto a clean Au(111) surface from a Knudsen cell evaporator. Appropriate amounts of K atoms were dosed onto the films from an alkali metal dissector from SAES Getters. The evaporation rates of the K and $C_{60}$ evaporators were calibrated by depositing them separately onto a clean metal substrate, followed by directly counting the number of K atoms and $C_{60}$ molecules in the STM images. The calculated areal densities of the atoms and molecules were used to determine the ratio $x$ of a $K_xC_{60}$ multilayer. The $K_xC_{60}$ thin films were annealed at 200 °C for 20 min before being cooled to 7 K for STM experiments. Progressive doping was obtained by adding more K atoms onto the existing film followed by re-annealing. We found that in the highly doped samples ($x > 4$), the K content may be decreased by very high temperature annealing; therefore, a lower annealing temperature of ~140 °C was used in this regime to avoid K loss. STM topography was carried out in a constant-current mode, while lock-in detection of the a.c. tunnelling current driven by a 450 Hz, 1–10 mV (rms) signal added to the junction bias (defined as the sample potential referenced to the tip) under open-loop conditions.

References