Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information: Rotational Superstructure in van der Waals Heterostructure of Self-Assembled C_{60} Monolayer on the WSe_2 Surface

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van der Waals *ab initio* methods

The calculations reported here are based on *ab initio* density functional theory (DFT) using the SIESTA method[1] and the VASP code.[2,3] The generalized gradient approximation[4] along with the DRSLL functional,[5] which includes van der Waals (vdW) dispersion forces, were used in both methods, together with a double-zeta polarized basis set in SIESTA, and a

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[¶] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, USA well-converged plane-wave cutoff of 500 eV in VASP. Projected augmented wave method (PAW)[6,7] for the latter, and norm-conserving (NC) Troullier-Martins pseudopotentials[8] for the former, have been used in the description of the bonding environment for W, Se and C. The shape of the natural atomic orbitals (NAOs) was automatically determined by the algorithms described in Solet et al.[1] The cutoff radii of the different orbitals were obtained using an energy shift of 50 meV, which proved to be sufficiently accurate to describe the geometries and the energetics. Atomic coordinates were allowed to relax until the forces on the ions were less than 0.01 eV/Å under the conjugate gradient algorithm. To model the experimental system, we created large supercells containing up to 348 atoms to simulate the interface between different C_{60} molecular configurations with the WSe_2 surface. We optimized the C_{60}/WSe_2 supercell using a 3×3 arrangement where the mismatch between different lattice constants is smaller than $\sim$0.10%. C_{60} molecules are repeated periodically with intermolecular distances of 9.89 Å forming a monolayer as observed in the experiments.

To avoid any interactions between supercells in the non-periodic direction, a 22 Å vacuum space was used in all calculations. In addition, a cutoff energy of 120 Ry was used to resolve the real-space grid used to calculate the Hartree and exchange correlation contribution to the total energy. The Brillouin zone was sampled with a 9×9×1 grid under the Monkhorst-Pack scheme[9] to perform relaxations with and without van der Waals interactions. Energetics and electronic band structure were calculated using a converged 22×22×1 k-sampling for the unit cell of C_{60}/WSe_2. In addition to this we used a Fermi-Dirac distribution with an electronic temperature of $k_{BT} = 20$ meV to resolve the electronic structure. Ab initio molecular dynamics simulations using Nose thermostat were performed at 355 K taking into account vdW interactions forces. A time-step of 1.0 fs was used in the integration of the dynamical equation, which were propagates up to 10.5 ps. The initial velocities at $t = 0$ are assigned according to the equilibrium Maxwell-Boltzmann distribution at a given temperature of 355 K unless otherwise specified.

Simulated STM Images: All Configurations

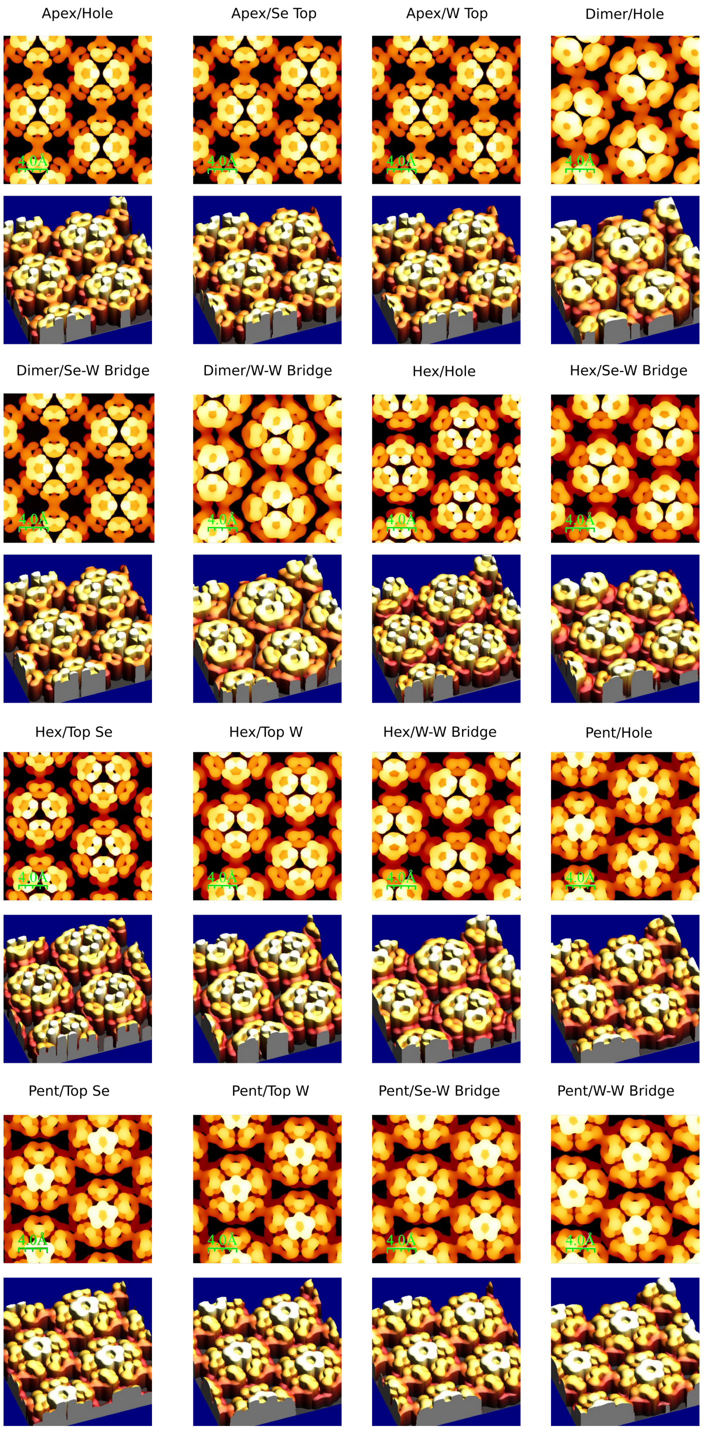

Figure S1: Simulated STM images using *ab initio* vdW methods for all calculated configurations between C_{60} and WSe_2. The first and second rows at each configuration correspond to 2D and 3D views, respectively. The states selected are at the bottom of the conduction band of C_{60}/WSe_2. The scale bar in each panel is set to 4 Å.

Wavefunctions for C_{60}/WSe_2 Heterostructure

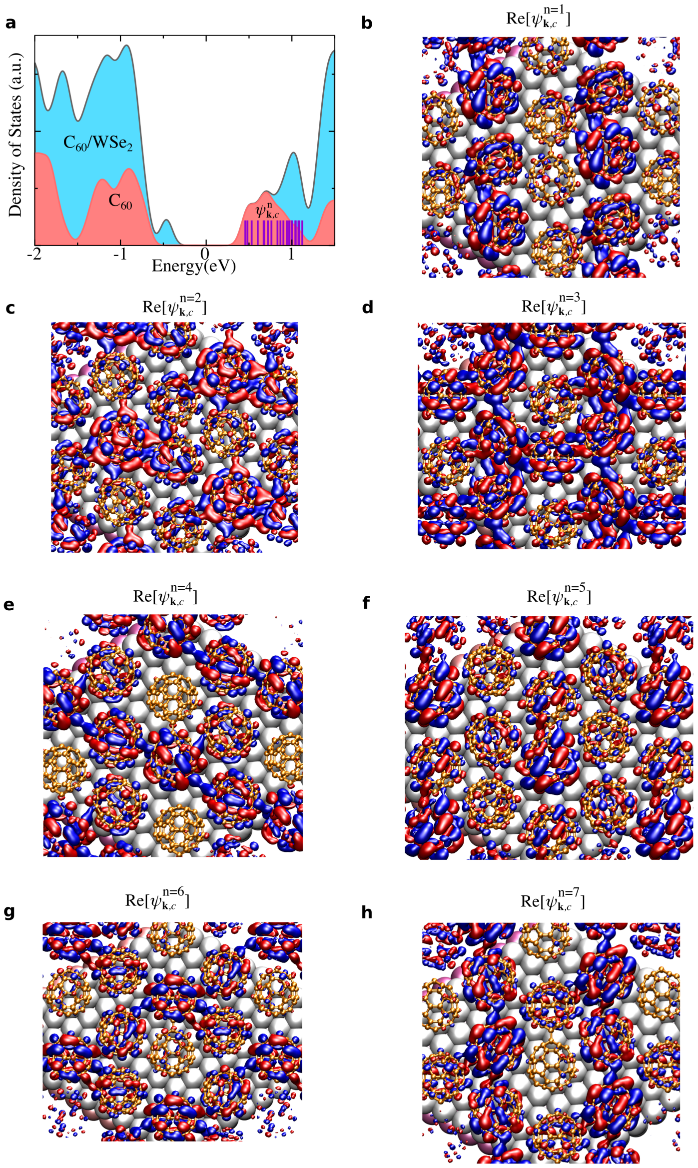

Figure S2: (a) Calculated density of states (DOS) for C_{60}/WSe_2 heterostructures after time-evolved for 10.5 ps at 355 K using *ab initio* molecular dynamics. Four C_{60} molecules are used in the supercell, which reaches a total of 348 atoms with WSe_2. This allows observation of any symmetry breaking in the molecular configuration of the molecules induced either by the WSe_2 surface or the C_{60}–C_{60} intermolecular interactions. DOS projected on C_{60} states are shown in faint red, and corresponding states at the bottom of the conduction band in vertical bars marked as $\psi^{n}_{\mathbf{k},c}$. Fermi level is set to zero. (b)-(h) Isosurfaces for $\mathrm{Re}[\psi^{n}_{\mathbf{k},c}]$ with $n = 1, 2, 3, 4, 5, 6, 7$. The order of the states follow their energetic relative to the Fermi level as displayed in (a), from low to high energies. This sampling of the eigenvalues remarkably shows that the C_{60} molecules are electronically linked to each other, and the basic symmetry involved follows a 2×2 superlattice.

Ab Initio **Molecular Dynamics Simulations at finite temperatures on C_{60}/WSe_2 Heterostructures**

We have explicitly checked the possibility of molecular spinning of C_{60} buckyballs on WSe_2 surface at 355 K and 55 K. We performed *ab initio* molecular dynamics simulations including vdW dispersion forces starting from different initial configurations and temperatures (Movies 1, 2, 3, 4). We have used four C_{60} molecules in the supercell with WSe_2 as any symmetry breaking due to interactions, thermal fluctuations, or structural distortions can be easily identified. Moreover, this corresponds to the unit cell observed in the measurements for the 2×2 superlattice as shown in Figure 2. We observed small degree of rotation of the C_{60} molecules on the WSe_2 surface despite the initial conditions set in the simulations. Most of the rotations take place in the initial 1.0 ps, and the fullerenes do not complete a 2π rotations around the W or Se atoms for the time that the system has evolved, 10.5 ps. Mainly the vibrational and translational degrees of freedom are sensible to the initial geometries and temperatures, which show differences relative to the C_{60} molecules. Moreover, when the molecules assume the most stable molecular configuration on WSe_2, Hexagon/Top Se, they tend to stay close to the initial configuration as smaller variations are observed as function of time (Movie 4). From the energetic point of view, temperatures in the range used in the experiments 55 K–355 K, would correspond to thermal energies up to $\sim$30 meV. This amount is considerably smaller than the binding energy calculated for the initial configuration, 1.086 eV, which suggests that once the molecules assumed this configuration they are trapped at the minimum energy point. Therefore, only when rotations, as high as 0.334 eV (Figure 4**b**), and molecule-molecule interactions, 0.700 eV, take place the C_{60} would have enough energy to scape from this stable position driven by thermal fluctuations. This shows that the strong interplay between molecule–substrate and molecule–molecule interactions actively play a role in the stabilization of the superlattice at finite temperatures.

- Movie 1: vdW molecular dynamics simulation at 355 K using Dimer/Hole configuration as starting point

- Movie 2: vdW molecular dynamics simulation at 55 K using Dimer/Hole configuration as starting point
- Movie 3: vdW molecular dynamics simulation at 55 K using the four most stable configurations as starting point
- Movie 4: vdW molecular dynamics simulation at 55 K using Hexagon/Top Se configuration as starting point

C_{60} molecular spacing

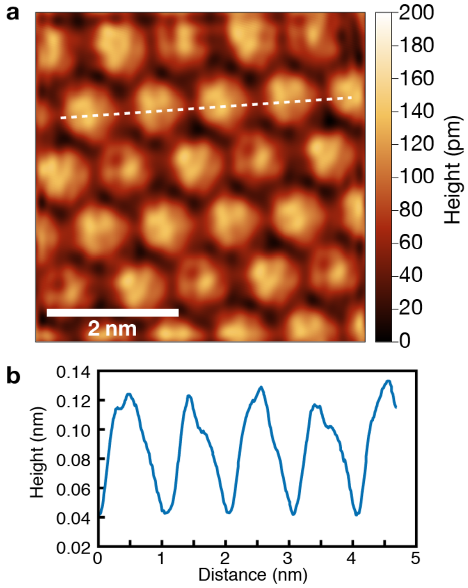

Figure S3: (a) STM image of C_{60} molecules self-assembled on WSe_2 (same image as in Figure 2 of main text). (b) Line profile along dashed line in panel (a) showing molecular spacing.

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