

Supporting Information

Molecular plasmonic cavities

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Table of Contents:

Figure S1. Frequency dependent SNOM for multiple C₆₀ islands.	S3
Figure S2. Calculation of the loss function with and without C₆₀.	S4
Figure S3. Fitting simulated data to experimental data.	S5
Figure S4. Finite-element simulation of freely propagating SPPs.	S6
Figure S5. DFT calculations on model C₆₀/graphene heterostructures.	S7
Figure S6. Characterization of C₆₀ islands.	S9
Supplementary Methods	S10
References	S12

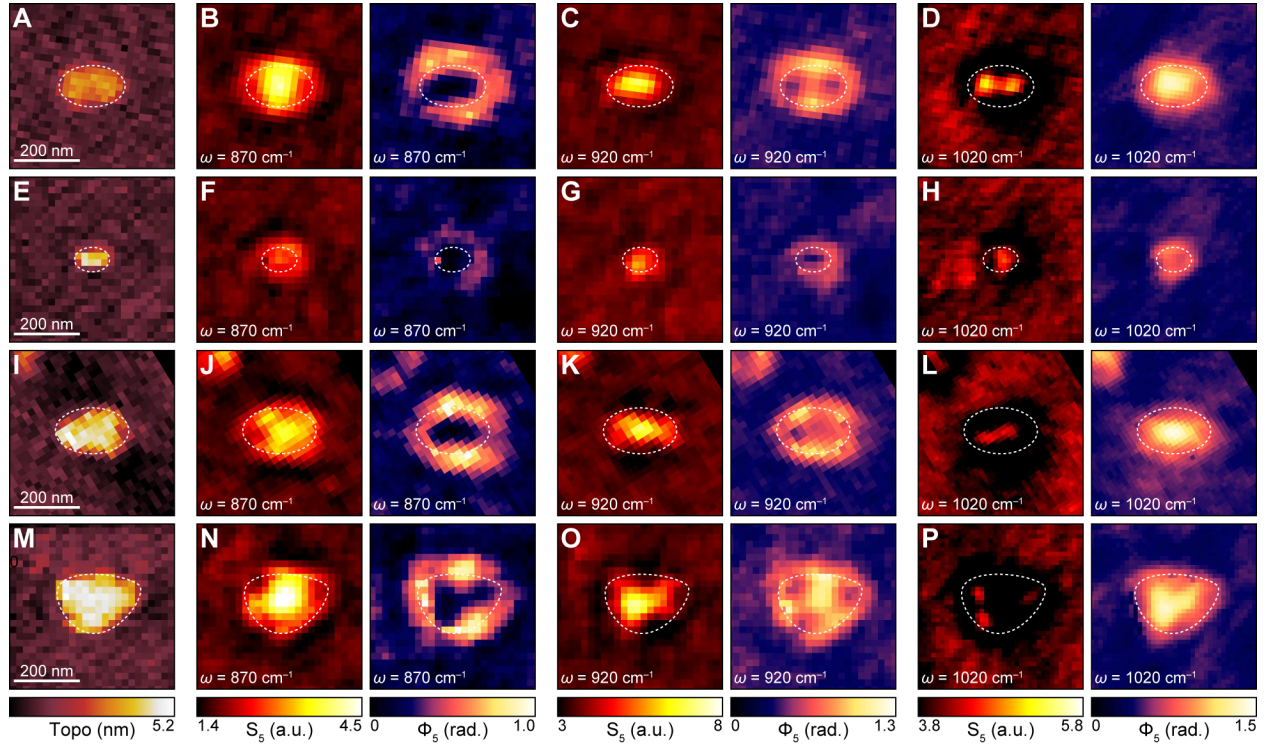


Figure S1. Frequency dependent SNOM for multiple C_{60} islands. (A) Topographic map of the elliptical C_{60} island discussed in the main text and the associated (B) near-field amplitude S_5 and phase Φ_5 at $\omega = 870 \text{ cm}^{-1}$, (C) 920 cm^{-1} and (D) 1020 cm^{-1} showing the frequency-dependence of the two-fold symmetric nodal pattern associated with confined SPPs. (E – H) Same as (A – D) for a smaller C_{60} island. (I – L) Same as (A – D) for another elliptical C_{60} island comparable to that shown in (A). (M – P) Same as (A – D) for a triangular C_{60} island showing an SPP nodal pattern with approximate three-fold symmetry. The boundaries of the C_{60} islands in each data set are indicated with the white dashed line.

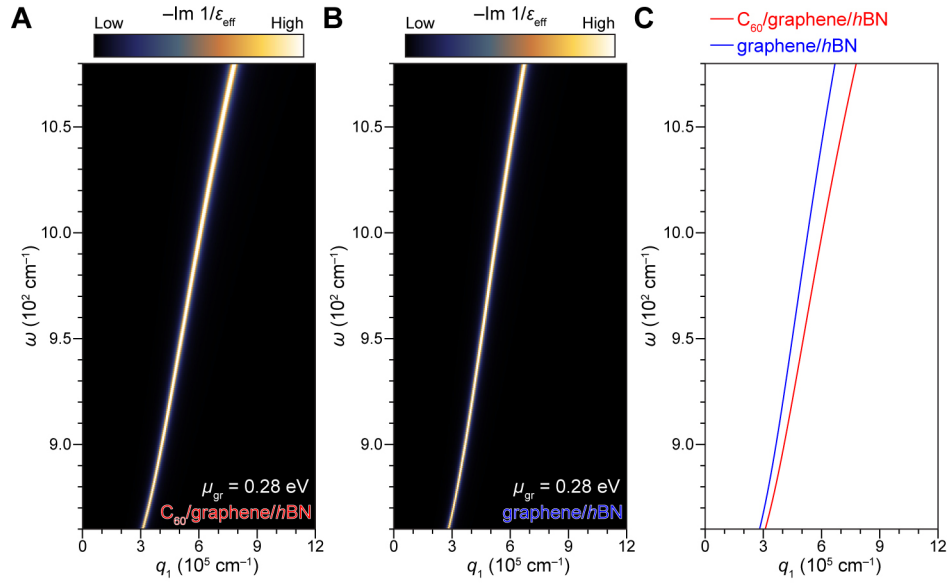


Figure S2. Calculation of the loss function with and without C_{60} . (A) Calculation of the loss function $\text{Im } -1/\epsilon_{\text{eff}}$ of the experimental stack consisting of 3 nm $\text{C}_{60}/\text{graphene}/50 \text{ nm } h\text{BN}/\text{SiO}_2$. Maxima in the loss function trace the SPP dispersion. (B) Same as (A) but for $\text{graphene}/50 \text{ nm } h\text{BN}/\text{SiO}_2$ (i.e., without the C_{60} layer). (C) Plots of the SPP dispersion with (red curve) and without (blue curve) the C_{60} layer extracted from maxima in panels (A) and (B). Computation of the loss function for the experimental stack was conducted by extracting the effective epsilon for a multilayer stack as described previously^{1,2} using reported optical parameters for $h\text{BN}$,³ C_{60} ,⁴ and SiO_2 .⁵

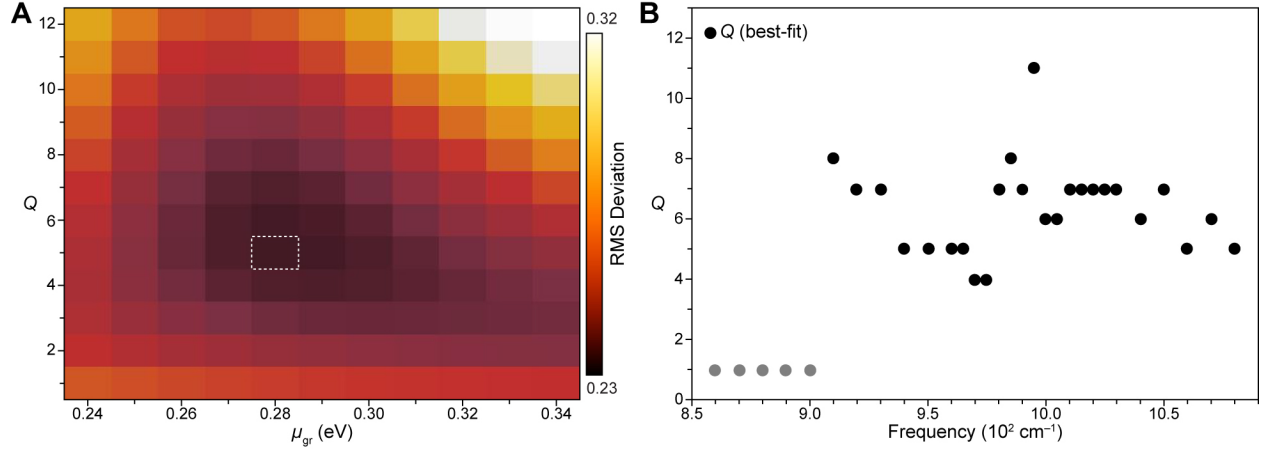


Figure S3. Fitting simulated data to experimental data. (A) Map of the RMS deviation between the experimental ω -dependent linecuts (Fig. 3, left panels) and the associated simulated linecuts (Fig. 3, right panels) for different values of Q and μ_{gr} used for the simulated data. The goodness-of-fit depends on both Q and μ_{gr} , with a minimum RMS deviation observed at $Q = 5$ and $\mu_{gr} = 0.28$ eV (see white dashed outline). (B) The best-fit Q extracted at each ω using $\mu_{gr} = 0.28$ eV as the chemical potential. Integer values of Q are considered in our simulation for $Q = 1$ – 12 , with the value that minimizes the RMS deviation from experiment being taken to be the best-fit value. Semi-transparent points taken for $\omega = 860 - 900$ cm $^{-1}$ indicate a best-fit Q that lies on the threshold of the considered Q values (i.e., do not necessarily represent a local minimum in the RMS deviation).

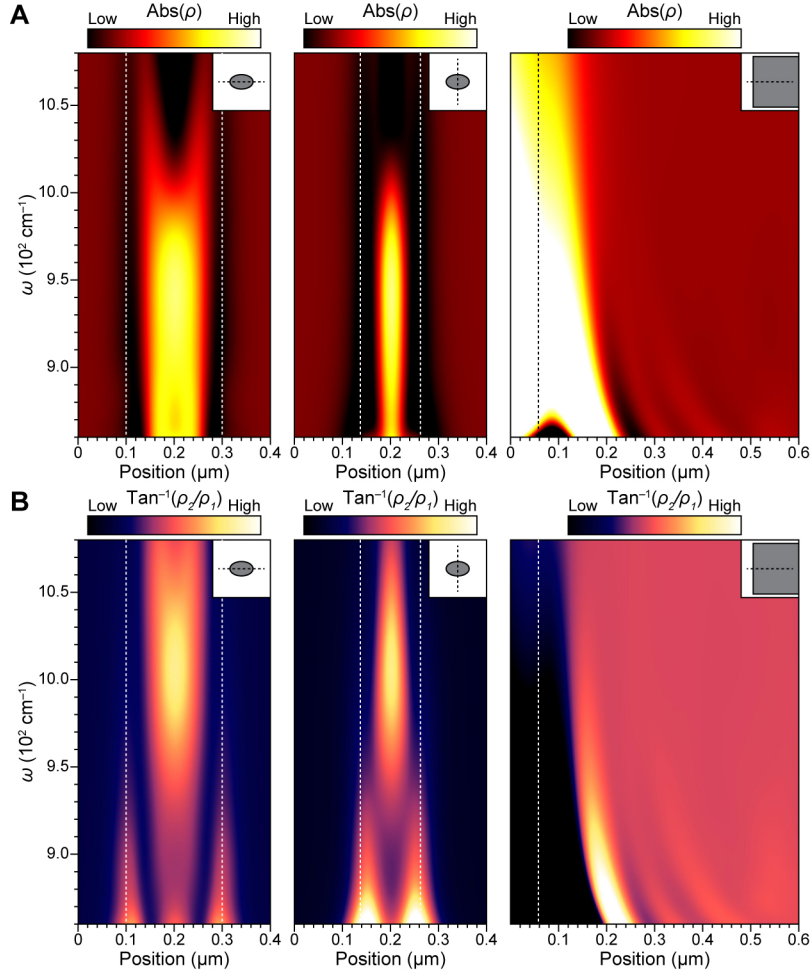


Figure S4. Finite-element simulation of freely propagating SPPs. (A) Frequency-dependence of the SPP line profiles of $\text{Abs}(\rho)$ for the major axis (right panel) and minor axis (middle panel) of the elliptical cavity discussed in the main manuscript along with those of freely propagating SPPs (right panel) (see insets). The dashed vertical lines indicate the boundaries of the region with non-zero conductivity. For all images the graphene chemical potential $\mu_{gr} = 0.28$ eV with $Q = 5$. (B) Same as (A) but for the model near-field phase.

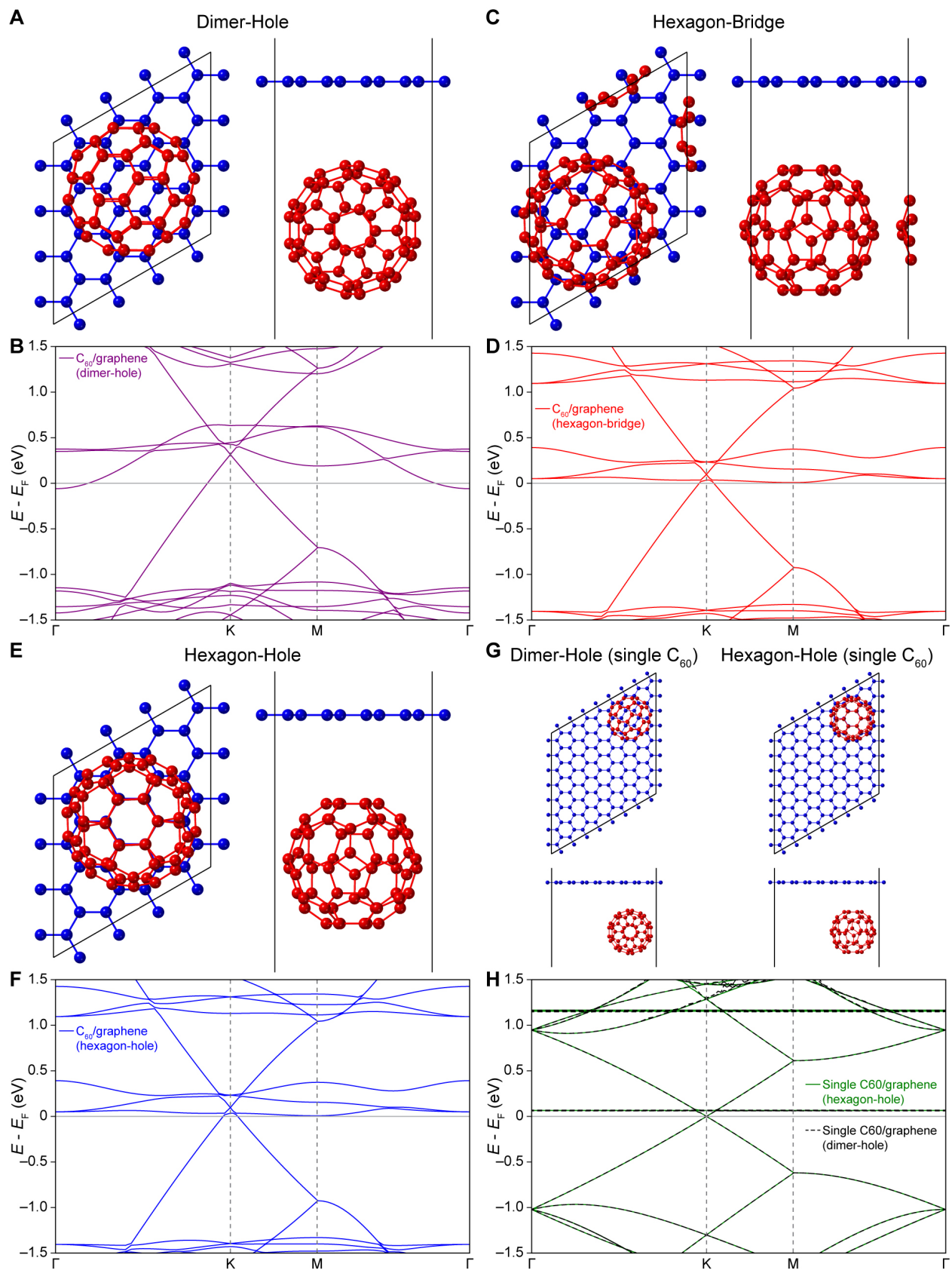


Figure S5. DFT calculations on model C₆₀/graphene heterostructures. (A) DFT supercell and (B) associated band structure for monolayer C₆₀/graphene in the dimer-hole configuration showing a 0.3 eV positive shift in E_{Dirac} . (C, D) Same as (A, B) but for the hexagon-bridge configuration, showing a 0.1 eV positive shift in E_{Dirac} . (E, F) Same as (A, B) but for the hexagon-hole configuration, showing a 0.1 eV positive shift in E_{Dirac} . (G) DFT supercell simulating a single C₆₀ on graphene in the dimer-hole (left panel) and hexagon-hole (right panel) positions. (H) Band structure associated with supercells in (G) for the hexagon-hole (green curves) and dimer-hole (black-dashed curves) configurations showing identical band structures with no shift in E_{Dirac} . In general, the magnitude of the shift in E_{Dirac} (i.e., the amount of charge transfer) increases with the bandwidth of the C₆₀ conduction band (CB), with no shift being observed in the case of a dispersionless CB as seen in panel (H).

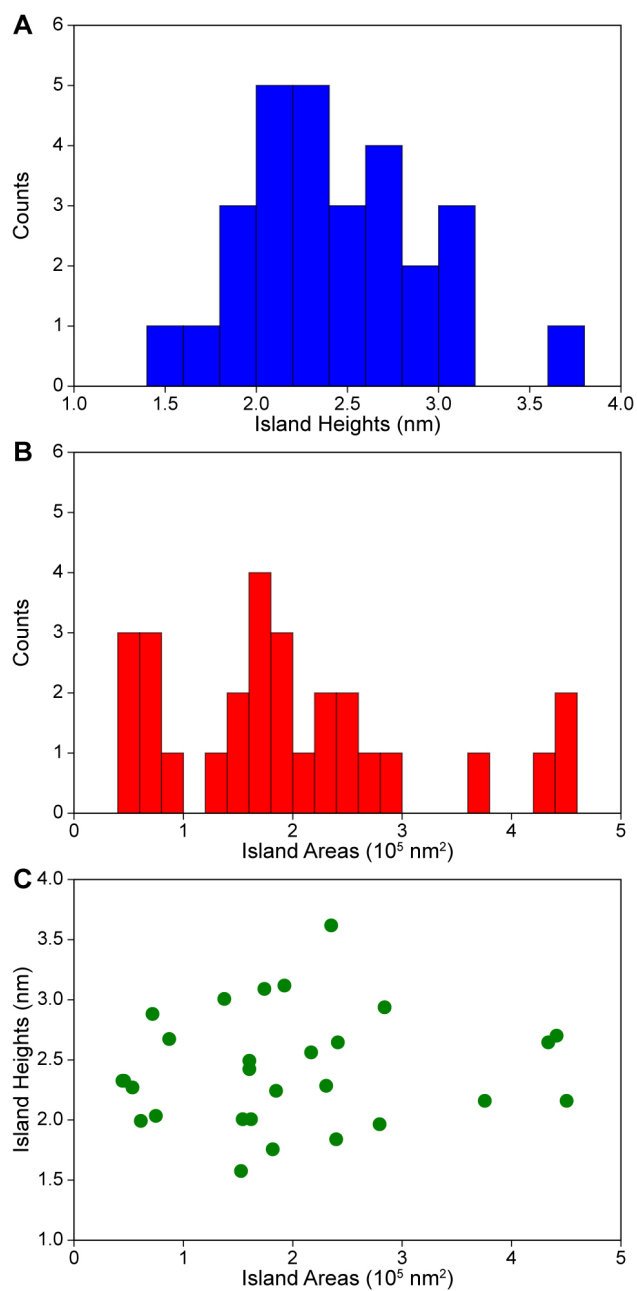


Figure S6. Characterization of C_{60} islands. (A) Histograms of C_{60} island height and (B) area. (C) Dependence of C_{60} island height versus island area, showing negligible dependence ($R^2 = 0.009$).

Supplementary Methods

Device Fabrication

The assembly of graphene/*h*BN heterostructures was carried out using standard dry-stacking methods, as described in previous work.⁶ To ensure a clean graphene surface, a polypropylene carbonate (PPC) film on a polydimethylsiloxane (PDMS) support was used for the stacking process. Compared to the conventional polycarbonate (PC) film typically employed in dry-stacking, PPC can be removed via thermal annealing under vacuum, leading to a cleaner heterostructure with minimal bubble formation, as it eliminates the need for solvent washes to remove the polymer. Additionally, during the fabrication process, the top graphene surface remains untouched by the polymer due to the flipping procedure outlined below.

Graphene and *h*BN flakes were exfoliated onto a Si/SiO₂ wafer using the Scotch tape method.⁷ To pick up the flakes, the PPC film was manually brought into contact with the substrate using a micromanipulator, initially at 40-45°C. The temperature was then gradually increased to 70°C to facilitate the pick-up of the *h*BN flake, as the thermal expansion of PPC allows it to cover the flake. Here, uniformly thick (> 50 nm) *h*BN flakes were chosen to maximize the likelihood of forming a clean interface with graphene. After the flake was covered, the temperature was reduced back to 40-45°C, and the PPC stamp was carefully lifted off. The same procedure was repeated for the graphene flake using the polymer-supported *h*BN flake.

Once the heterostructure was complete, the PPC film was flipped over and placed onto a PDMS support with a hole in the center, leaving the PPC film with the heterostructure exposed. The stamp was brought into contact with a bare Si/SiO₂ wafer and the temperature was gradually increased to 140°C, allowing the PPC film to adhere to the wafer. The film was then removed by vacuum annealing at 350°C for 12 hours, and the stack was cleaned of any residual contaminants using contact mode atomic force microscopy (AFM) (Bruker ICON, OTESPA-R4 tip).

Fullerene Deposition on Heterostructures

Fullerene (Sigma-Aldrich, sublimed, 99.9%) was deposited onto the heterostructures via thermal evaporation using an Angstrom-MB200B evaporator with a base pressure of approximately 10^{-7} – 10^{-6} torr. The substrate was maintained at room temperature during deposition. The deposition rate was controlled at 0.1 Å/s, with a target thickness of 2 Å. These values correspond to the evaporator's lowest sensitivity settings and do not accurately reflect the actual thickness of the deposited fullerene, which was < 5 nm. Following deposition, the samples were annealed in an argon environment at 150°C for 90 minutes, before being imaged using tapping mode AFM (Bruker ICON, OTESPA-R4 tip). Molecular islands present with an apparent height ranging from 1.5 – 3.5 nm likely due to the comingling of monolayer and multilayer regions as observed previously.⁸ There is no obvious dependence of apparent height on the size of molecular islands (Fig. S6).

Scanning Near-field Optical Microscopy

All s-SNOM measurements were performed on a commercial Neaspec system under ambient conditions using commercial ArrowTM AFM probes with nominal resonant frequencies of $f = 75$ kHz ($k = 2.8$ N/m) or 14 kHz ($k = 0.2$ N/m). We note that $k = 2.8$ N/m AFM tips could cause C₆₀ island degradation after extensive scanning (>10 h), necessitating the use of $k = 0.2$ N/m tips

for multi-day experiments. Two tunable continuous wave quantum cascade lasers produced by Daylight Solutions were used that together cover wavelengths over the range 8.4 – 11.7 μm with nominal laser powers of 5–10 mW. There was no observed dependence of islands stability on incident laser power within this experimental range. The detected signal was demodulated at the fifth harmonic of the tip tapping frequency so as to minimize far-field contributions to the scattered light,⁹ though salient feature of the SPP cavity modes could be observed at the third and fourth harmonics. The fifth harmonic of the near-field scattering amplitude (S_5) and phase (Φ_5) were collected simultaneously using a pseudoheterodyne interferometry technique.

Finite-Element Simulations

The simulated real-space near-field images presented in Figs. 2, 3, and S4 follow the semi-analytical method outlined in detail in the supplementary information of ref. ¹⁰. Here, the near-field scattering signal from a 2D material (e.g., graphene) is approximated to be proportionate to the z -polarization of a polarizable dipole raster-scanned above the plane of the 2D surface. In our simulations, molecular clusters are modelled as elliptical regions possessing some non-zero conductivity as determined by the complex valued wavevector (see eq. 1) surrounded by regions of zero conductivity. In addition, the reflectivity of the 2D substrate is taken to be that of $h\text{BN}$. The real-space line profiles were simulated for all experimental frequencies, with the charge-transfer-dependent SPP wavevector acting as the salient input parameter. The goodness-of-fit between simulation and experiment was determined for a wide range of values for the graphene chemical potential and SPP Q -factor, yielding nominal values of $\mu_{\text{gr}} = 0.28$ eV and $Q = 5$, respectively (See Fig. S3).

Ab-initio Calculations of C₆₀/Graphene Heterostructures

First-principles calculations based on density functional theory (DFT) are performed using the Vienna Ab-initio Simulation Package.¹¹ The projector-augmented wave method and the semilocal Perdew-Burke-Ernzerhof (PBE) functional¹² are employed to describe effects of the core electrons and electron-electron exchange correlation interactions, respectively. For the vdW interactions, we employed the DFT-D3 method with Becke-Johnson damping.^{13,14} The plane-wave basis set has an energy cutoff of 400 eV, and the first Brillouin zone is sampled using a $5 \times 5 \times 1$ Γ -centered $\mathbf{k}$ -mesh. Atomic structures are relaxed until the forces on all ions are below 0.02 eV/ $\text{\AA}$, and the electronic self-consistency convergence threshold is set to 10^{-4} eV. The Fermi-Dirac distribution is employed with Gaussian smearing of 0.02 eV to determine the electronic occupancies near the Fermi level. The dimer/hole, hexagon/hole, and hexagon/bridge stacking configurations of the C₆₀/graphene heterostructures are considered. For the monolayer (single) C₆₀ molecule on graphene, a 4×4 (8×8) graphene supercell is used as the unit cell, and each unit cell contains a single C₆₀ molecule. The graphene lattice constant is relaxed to be 2.467 $\text{\AA}$. To prevent spurious interactions between periodic images, all C₆₀/graphene slab models include a vacuum layer larger than 15 $\text{\AA}$.

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