Supplementary Information:

Revealing the Local Electronic Structure of a Single-layer Covalent Organic Framework through Electronic Decoupling

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a BP-COF/Au(111)
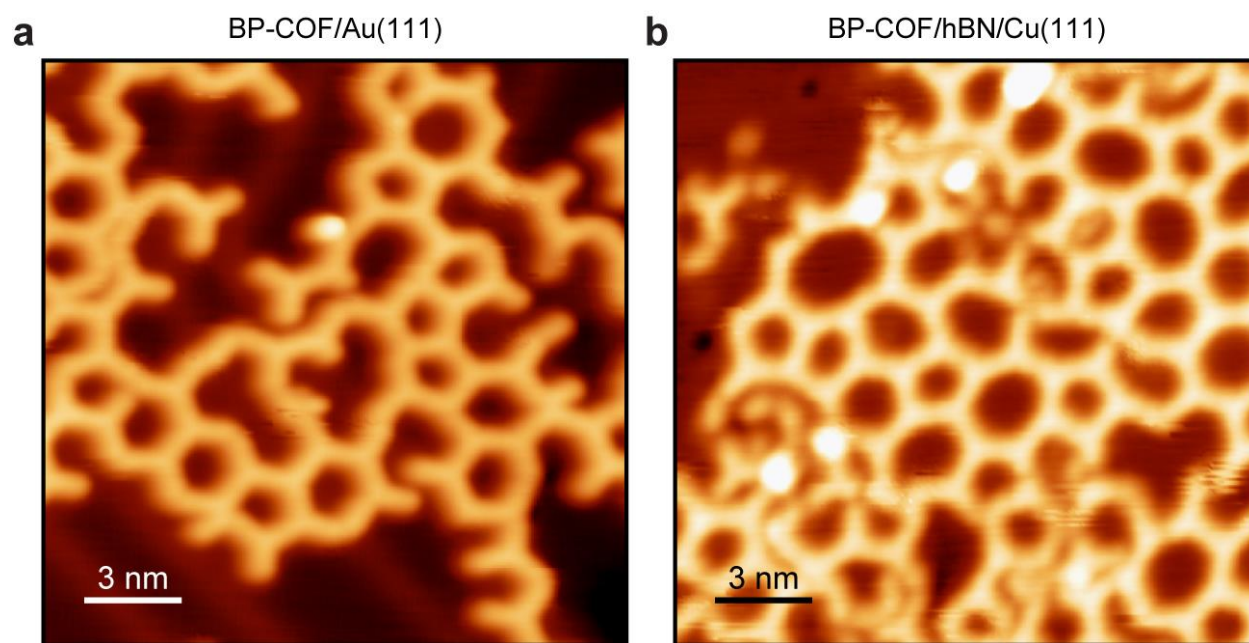
b BP-COF/hBN/Cu(111)

3 nm

3 nm

Figure S1. STM Topography of BP-COF on Au(111) and hBN/Cu(111). Typical STM topographic images of BP-COF grown on (a) Au(111) (V_s = 1.50 V, I_t = 20 pA) and (b) hBN/Cu(111) (V_s = 1.50 V, I_t = 40 pA).
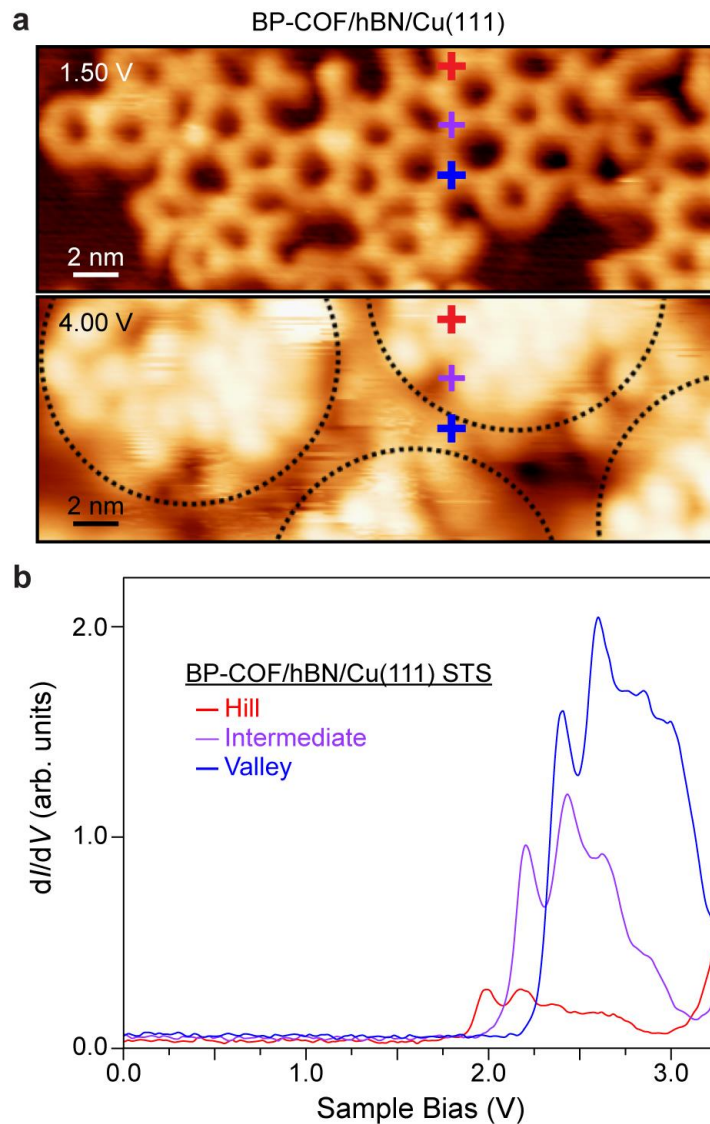
Figure S2. Dependence of BP-COF STS on hBN/Cu(111) Moiré pattern. (a) Top panel: STM topographic image of BP-COF straddling multiple sites on the hBN/Cu(111) Moiré pattern (V_s = 1.50 V, I_t = 10 pA). Bottom panel: The same area observed with a sample bias of 4 V reveals the underlying Moiré superstructure. Dotted black lines are used as a guide to the eye to denote the "Hill" (red crosshair), "Valley" (blue crosshair), and "Intermediate" (purple crosshair) regions of the Moiré pattern. (b) dI/dV point spectra collected at the BP-COF locations shown in (a). Spectroscopy parameters: V_{ac} = 10 mV, f = 581 Hz.
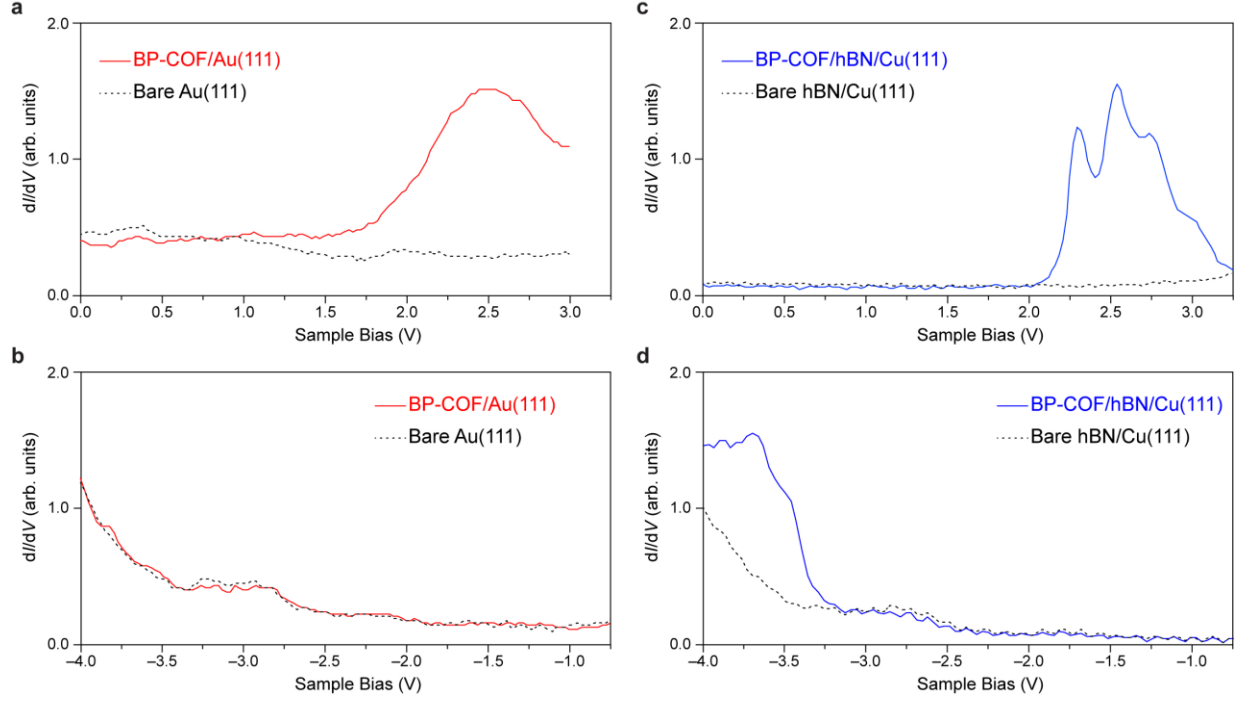
Figure S3. Background dI/dV point spectra for Fig. 2 in the main text. dI/dV spectra obtained on BP-COF/Au(111) (red curve) and bare Au(111) (dotted black curve) for (a) unoccupied states and (b) occupied states. dI/dV spectra obtained on BP-COF/hBN/Cu(111) (blue curve) and bare hBN/Cu(111) (dotted black curve) for (c) unoccupied and (d) occupied states. Spectroscopy parameters: V_{ac} = 10 mV, f = 581 Hz.
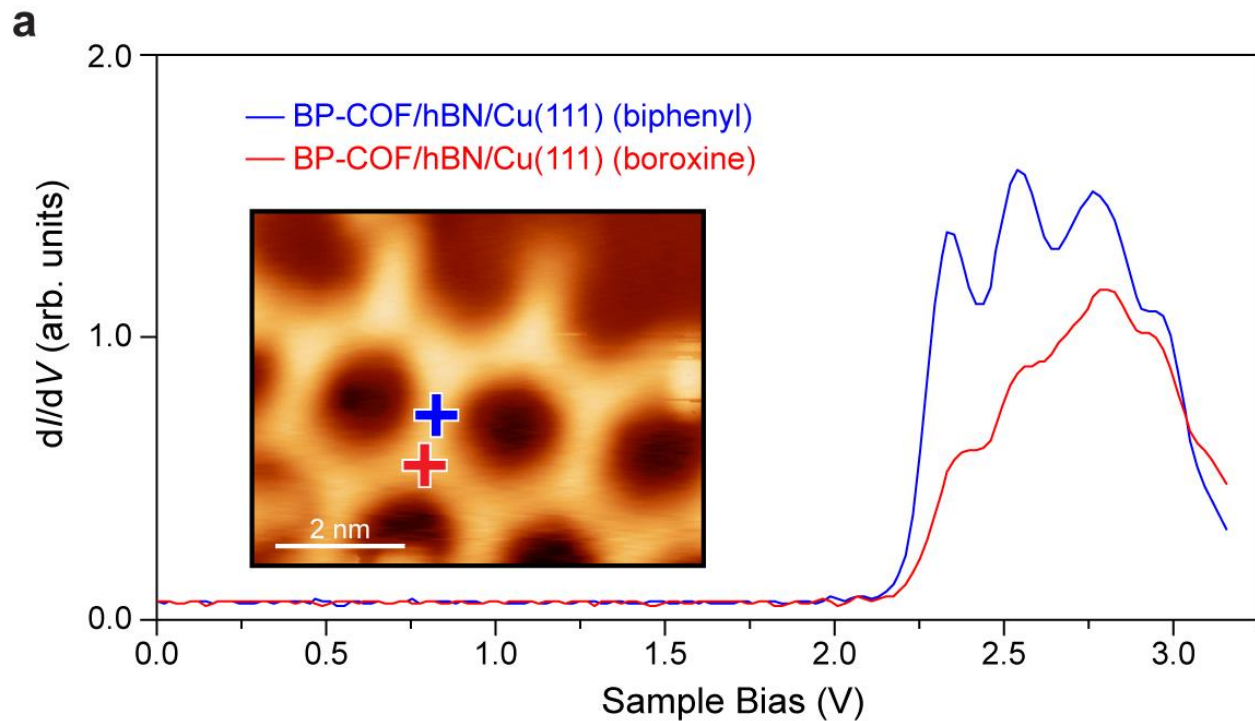
Figure S4. Position-dependence of dI/dV point spectroscopy conducted on BP-COF. Inset:

Topographic image of a multi-pore BP-COF structure (V_s = 1.50 V, I_t = 20 pA). dI/dV intensity

was measured over the biphenyl (blue curve) and boroxine (red curve) as indicated by the

crosses in the inset. While the peak positions are the same for both spectra, their relative intensity

changes depending on the position of the tip. Spectroscopy parameters: V_{ac} = 10 mV, f = 581 Hz.
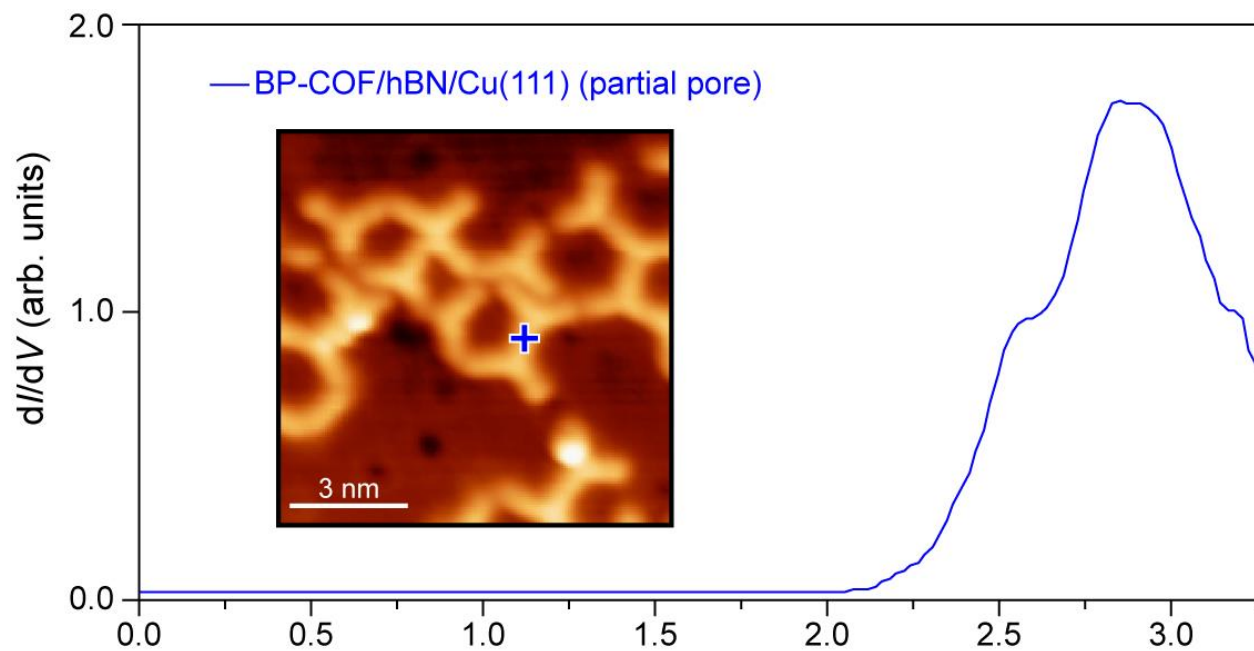
Figure S5. dI/dV point spectroscopy on BP-COF partial pore structure. Inset: Topographic image of a BP-COF partial pore structure ($V_s =$ 1.50 V, $I_t =$ 15 pA). The blue curve indicates the dI/dV intensity measured in the location of the blue cross shown in the inset . Spectroscopy parameters: $V_{ac} =$ 10 mV, $f =$ 581 Hz.
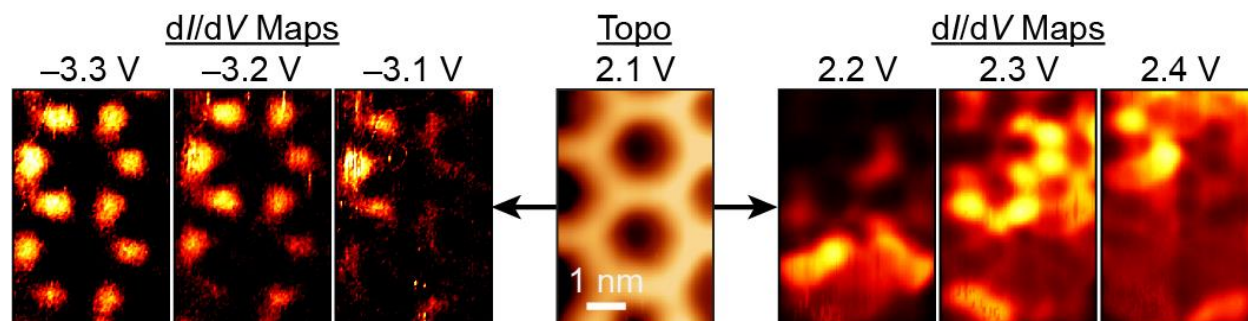
Figure S6. Constant current dI/dV maps of BP-COF/hBN/Cu(111) conducted at occupied and unoccupied band energies. States are down-shifted in energy on the lower half of the COF image due to the position of the COF relative to the underlying Moiré pattern. dI/dV map parameters: I_t = 50 pA, V_{ac} = 20 mV, f = 581 Hz. Middle panel shows an STM topograph of BP-COF/hBN/Cu(111) (I_t = 50 pA, V_S = 2.1 V).
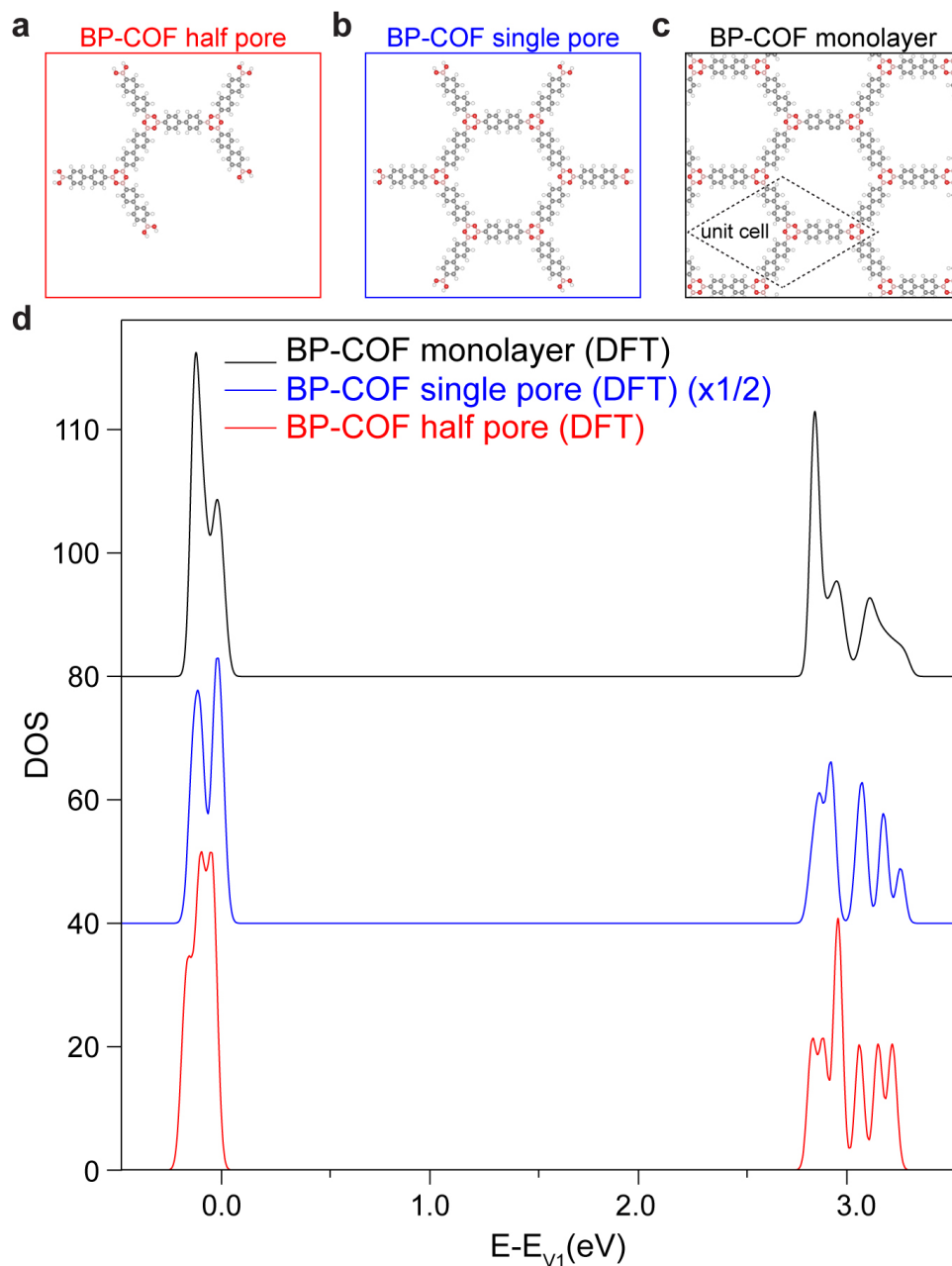
Figure S7. Theoretical electronic structure of finite BP-COF patches. (a) Chemical structure of a partial BP-COF pore. (b) Chemical structure of a fully-formed single pore of BP-COF. (c) Chemical structure of an infinite BP-COF monolayer (the unit cell is indicated by the dashed black line). (d) DFT-calculated DOS for the chemical structures shown in (a) (red curve), (b) (blue curve), and (c) (black curve). The blue (black) curve is offset by 40 states/eV (80 states/eV/unit cell) for clarity.
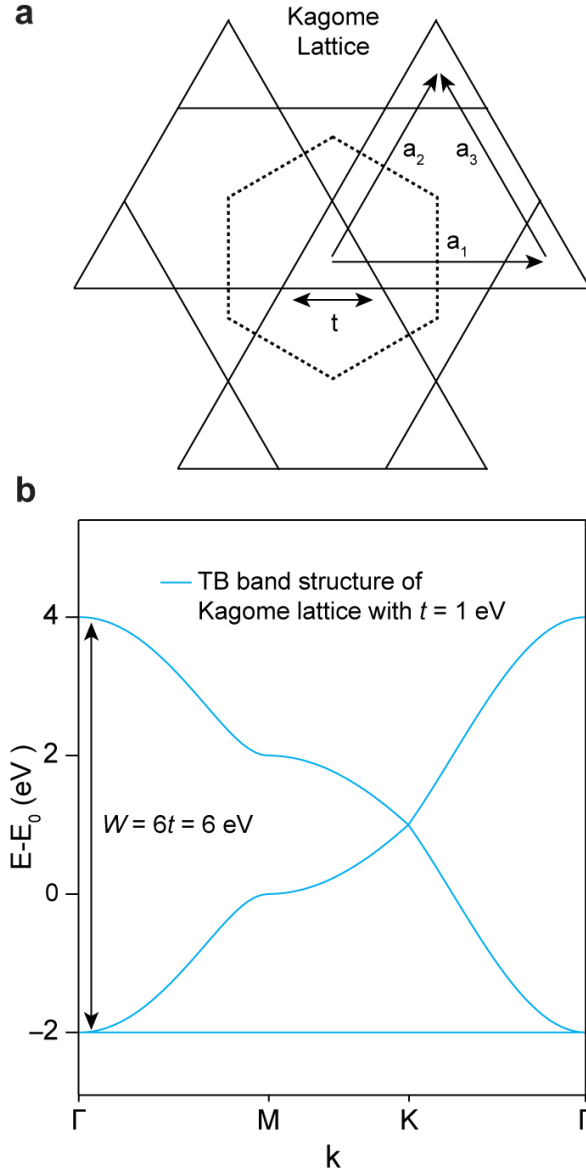
Figure S8. Derivation of Kagome band structure using tight binding. (a) Solid black lines trace a Kagome lattice. The dotted black line outlines the unit cell, with arrows a_1 and a_2 indicating the lattice vectors (a_3 is their difference). All nearest neighbor hopping amplitudes are taken to be equal to t. (b) The tight-binding band structure for a Kagome lattice is given by $\varepsilon_1 = -2t$ and

$$\varepsilon_{2,3} = t\left[1 \pm \sqrt{(4\{\cos^2 k \cdot a_1 + \cos^2 k \cdot a_2 + \cos^2 k \cdot a_3\} - 3)}\right].[1]$$ The light blue line traces the tight-binding Kagome lattice band structure for nearest neighbor hopping amplitude $t = 1$ eV. The resulting bandwidth W is six times the hopping amplitude t, or 6 eV.
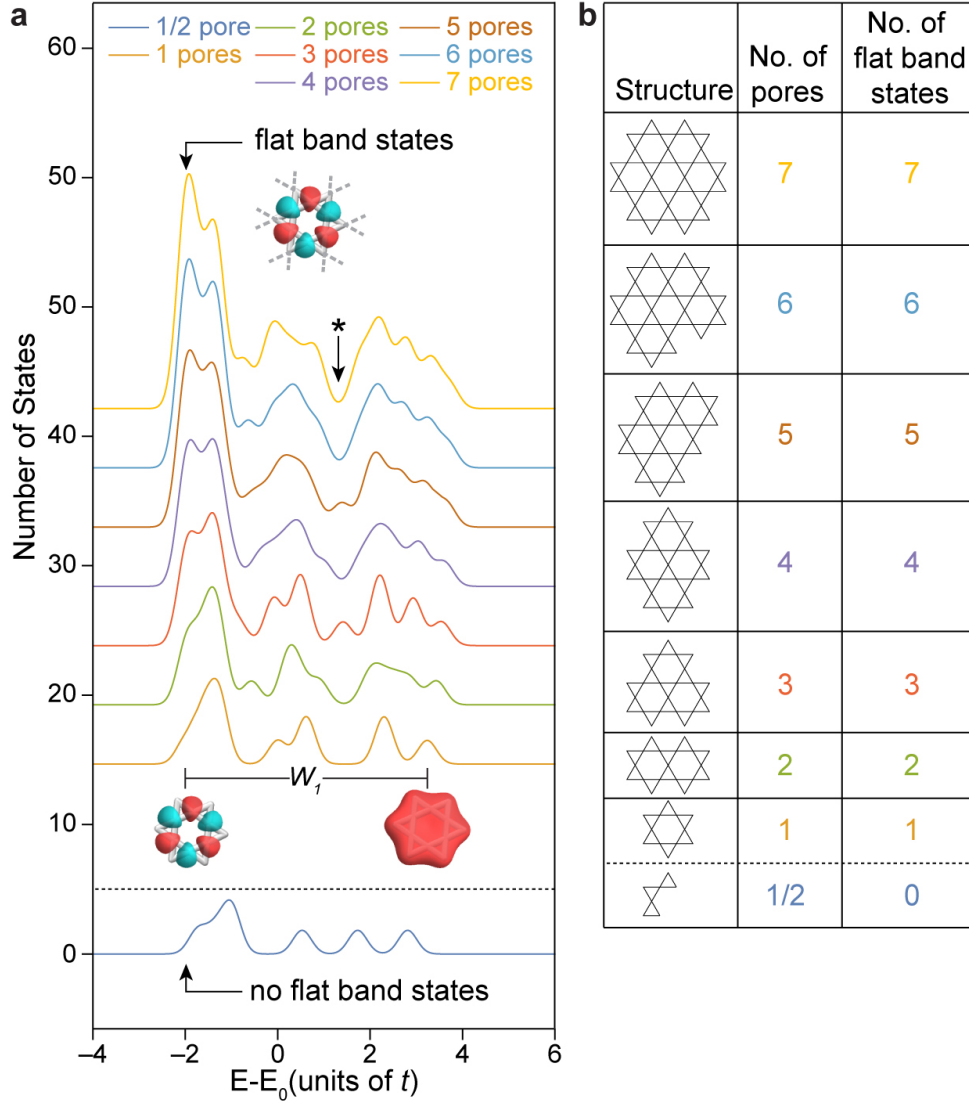
Figure S9. Tight-binding calculation for finite Kagome lattice. (a) Nearest-neighbor tight-binding eigenenergy spectrum for finite Kagome lattice patches possessing 1–7 pores as well as a partial pore as sketched in (b).[2] All nearest neighbor hopping terms are equal to t and an energy broadening of $0.25t$ is chosen to provide better comparison with experiment. For clarity, successive curves are offset vertically. The states labelled "flat band states" possess eigenenergies associated with the Kagome flat band ($-2t$) and the diagram shows a generic flat band state (the wavefunction is colored red and blue, indicating a positive and negative phase, respectively, of the atomic/molecular orbitals residing at each vertex of the Kagome lattice).

Notably, the partial pore is the only finite BP-COF system lacking any flat band states. The states labelled " $*$ " near $+t$ show the location of the BP-COF Dirac point in the 2D limit, where a suppressed density of states is seen flanked by a roughly linear density of states for larger finite systems. W_1 indicates the energy range spanned by the states of a single star-of-David/single-pore structure with the highest and lowest energy states shown. (b) The chemical structure of each finite Kagome patch used for tight binding calculations in (a). The table shows that the number of degenerate flat band states possessing an eigenenergy of $-2t$ is equivalent to the number of pores, and that the partial pore system lacks any such states.
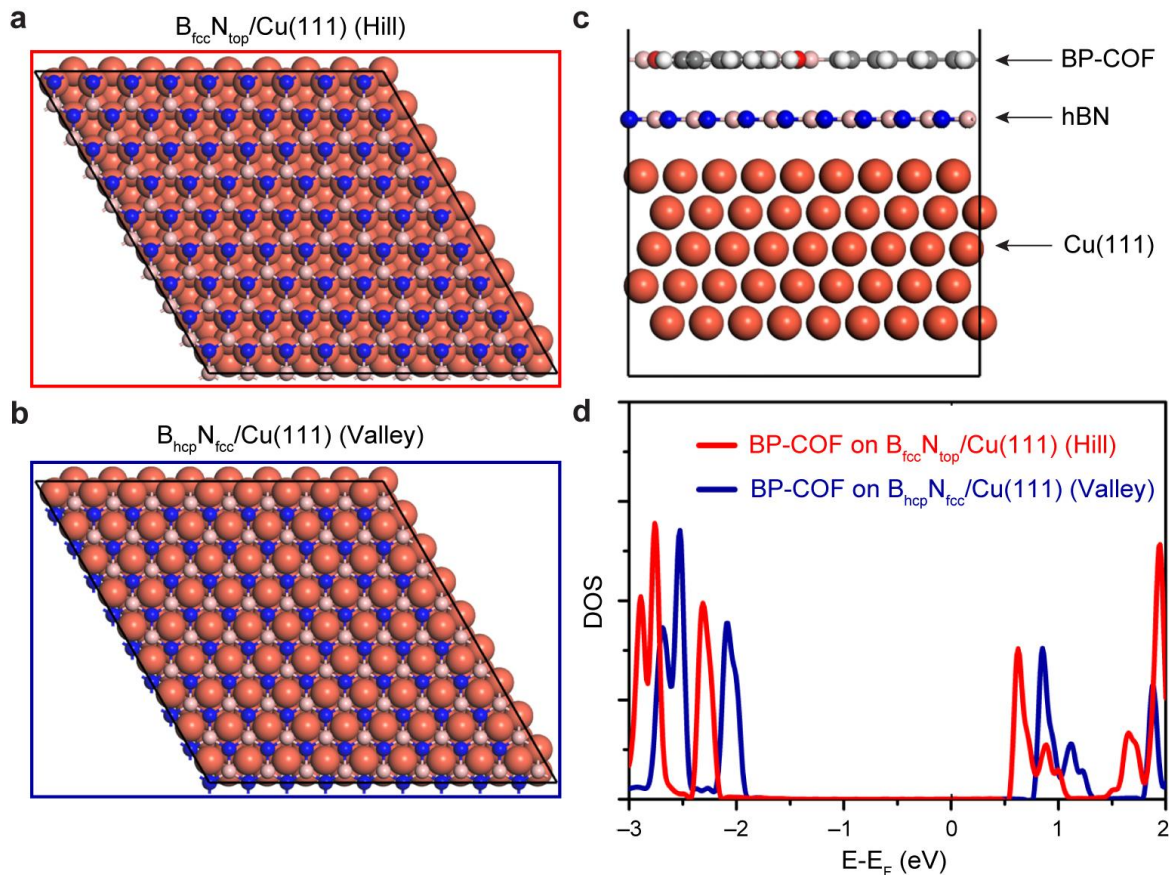
Figure S10. Theoretical dependence of BP-COF electronic structure on hBN/Cu(111) registry. Atomic subscript indicates the registry of the boron and nitrogen atoms with the underlying Cu(111) surface in (a) a "Hill" supercell and in (b) a "Valley" supercell (corresponding to different regions in the experimental Moiré pattern for hBN/Cu(111)). The work functions of the two configurations differ by 0.18 eV, in good agreement with previous calculations.[3] (c) Side view of the supercell used to calculate the electronic structure of BP-COF/hBN/Cu(111). (d) DFT-calculated PDOS for BP-COF supported by hBN/Cu(111) for the two registries shown in (a) ("Hill", red curve) and (b) ("Valley", blue curve), reproduces the Moiré-induced shift in LDOS peaks observed experimentally. DOS peaks in the red and blue curves differ by 0.23 eV, reflecting the modification of the local work function due to the differing registry of hBN with the underlying Cu(111).

References

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