

Supplemental Material

p-band engineering in artificial electronic lattices

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In this Supplemental Material, we provide additional background on the experimental and theoretical observation of *p*-like orbitals for the 2D electron gas patterned by CO adatoms on Cu(111), thus generating the artificial lattices as discussed in the main text of the manuscript. We show the details of the Lieb lattice designs that were demonstrated in the main text. In addition, we present the band structure for the different designs of the Lieb lattices as shown in the text, and provide more insight in the *s*- and *p*-like character of the wave functions by theoretically investigating the sign of the wave function.

DESIGNS OF THE REALIZED LATTICES

In Figs. S1-S3, we show the details of the design in a schematic of the lattice and show the entire lattice as realized in the STM. The Lieb lattice is presented in Fig. S1, the symmetric Lieb-like lattice with enlarged unit cell in Fig. S2, and the asymmetric Lieb-like lattice in Fig. S3.

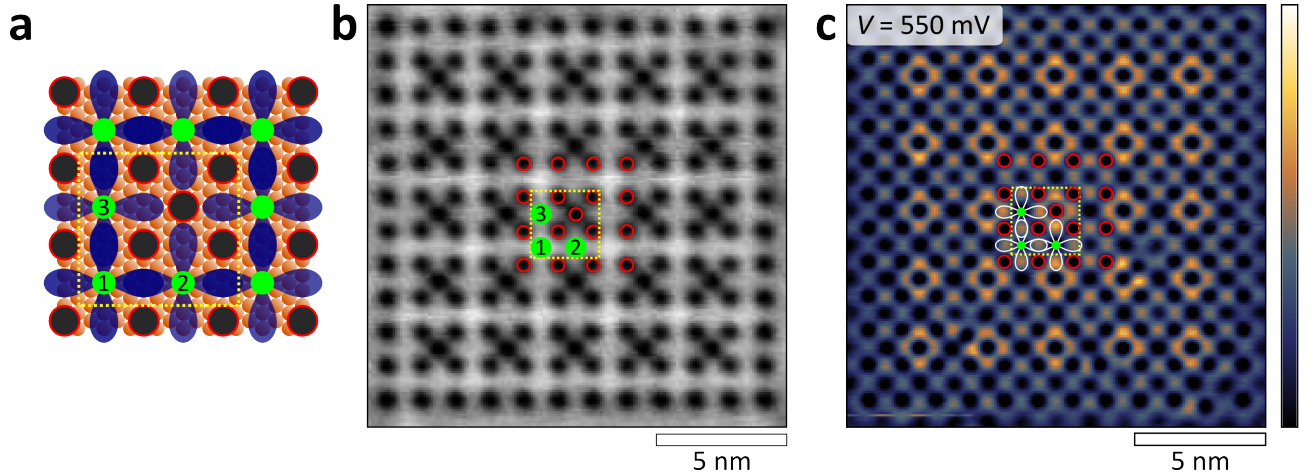


FIG. S1. (a) Schematic of a plaquette of a Lieb lattice with unit-cell size $6\sqrt{3}a \times 10a \approx 2.66 \text{ nm} \times 2.56 \text{ nm}$, where $a = 0.256 \text{ nm}$ is the Cu(111) nearest-neighbor distance. The unit cell (yellow dashed box) contains 3 artificial-atom sites (green). The sites are generated by the shown configuration of CO molecules (black circles with red contour) on a Cu(111) surface. The *p*-like orbitals at each site are indicated in blue. (b) Constant-current STM image of the realized 5×5 Lieb lattice. The CO molecules (red circles) and three artificial-atom sites (green) are indicated in one unit cell (yellow). Imaging parameters: $V = 50 \text{ mV}$, $I = 1 \text{ nA}$. (c) Differential-conductance map acquired at $V = 550 \text{ mV}$. *p*-like orbitals can be observed, as indicated by the white contours for one unit cell. The map was acquired at $+110 \text{ pm}$ with respect to the setpoint $I_{\text{set}} = 1 \text{ nA}$, $V_{\text{set}} = 50 \text{ mV}$, with a bias modulation $V_{\text{rms}} = 20 \text{ mV}$.

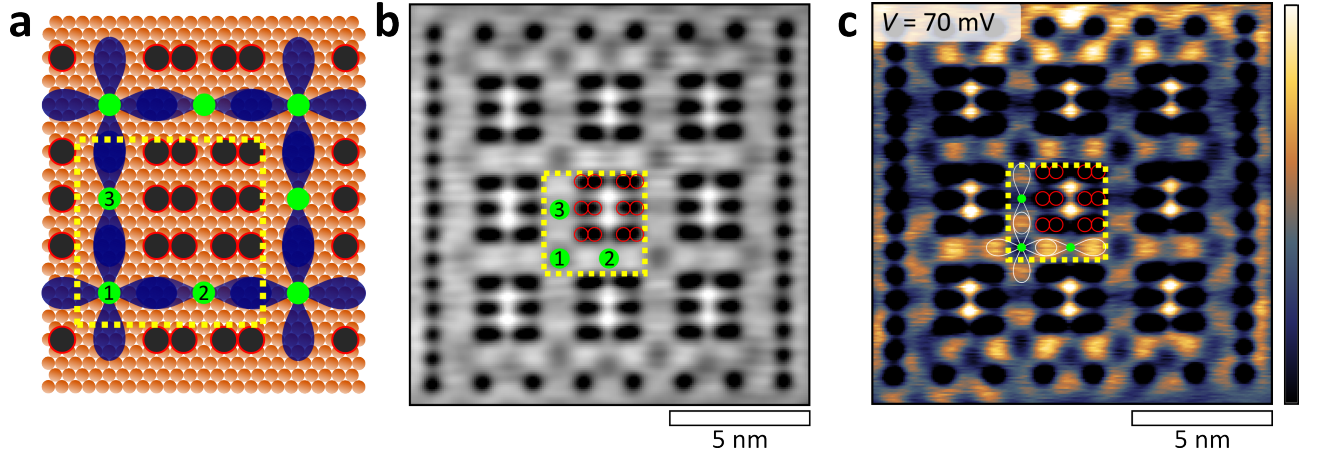


FIG. S2. (a) Schematic of a plaquette of a large symmetric Lieb-like lattice with unit-cell size $14a \times 8\sqrt{3}a \approx 3.58 \text{ nm} \times 3.55 \text{ nm}$. In comparison to Fig. S1, the unit cell (yellow box) is larger. At the edge sites 2 and 3, only the p_x -like and p_y -like orbitals, respectively, have been indicated. Due to the added CO molecules in this design, the p_y -like (p_x -like) orbital at site 2 (3) has been shifted to a significantly higher energy. (b) Constant-current STM image of the realized 3×3 symmetric Lieb-like lattice. Imaging parameters: $I = 0.1 \text{ nA}$, $V = 100 \text{ mV}$. (c) Differential-conductance map acquired at $V = 70 \text{ mV}$. The map was acquired after stabilization at $I_{\text{set}} = 1 \text{ nA}$, $V_{\text{set}} = 70 \text{ mV}$, with a bias modulation $V_{\text{rms}} = 10 \text{ mV}$.

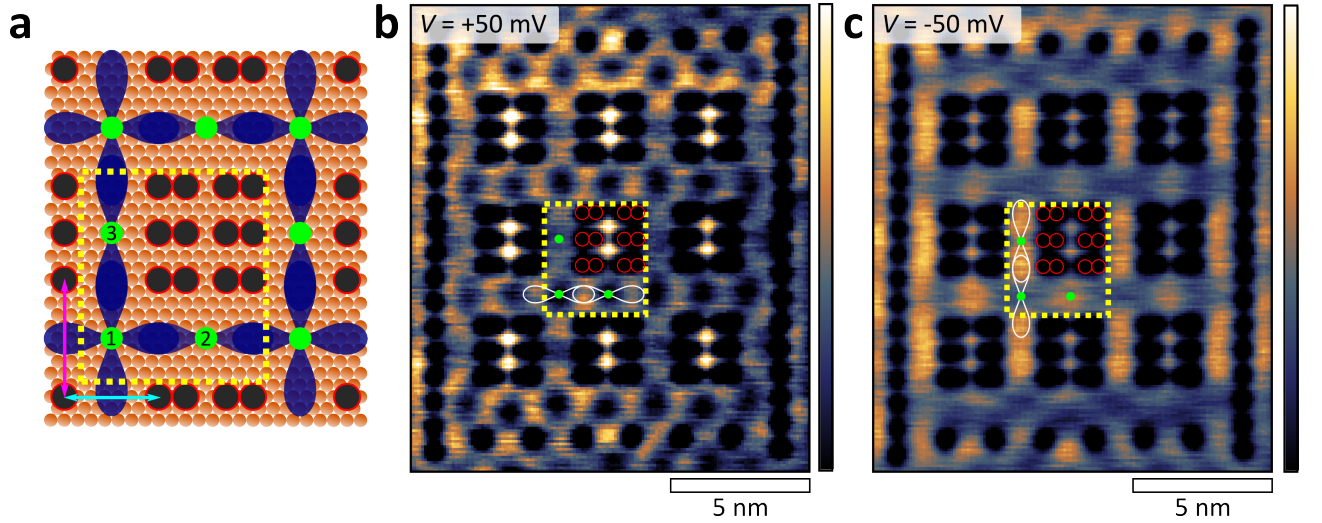


FIG. S3. (a) Schematic of a plaquette of an asymmetric Lieb-like lattice with unit-cell size $14a \times 9\sqrt{3}a \approx 3.58 \text{ nm} \times 3.99 \text{ nm}$. The distance between site 1 and 3 was increased by $0.5\sqrt{3}a$ compared to S2, resulting in more space in the y -direction (pink) than in the x -direction (light blue). (b-c) Differential-conductance map acquired above an asymmetric Lieb-like lattice at $V = +50 \text{ mV}$ and $V = -50 \text{ mV}$, respectively. The maps were acquired after stabilization at $I_{\text{set}} = 1 \text{ nA}$, $V_{\text{set}} = +50 \text{ mV}$ and -50 mV , with a bias modulation $V_{\text{rms}} = 5 \text{ mV}$.

MUFFIN-TIN CALCULATIONS

For the muffin-tin calculations, we consider the 2D electron gas formed by the surface-state electrons of the Cu(111) and model the CO molecules as disks with a repulsive potential [S1–S5]. We numerically solve the Schrödinger equation for this system:

$$(-\hbar^2/(2m_e^*)\nabla^2 + V_{\text{CO}})\psi = E\psi.$$

In this equation, V_{CO} is the disk-shaped repulsive potential due to the CO molecules, and has an effective radius of 0.3 nm and a height of 0.9 eV. The effective electron mass is $m_e^* = 0.42m_e$, where m_e is the bare electron mass [S6]. Furthermore, we use a broadening $\Gamma = 80$ meV to account for the limited lifetime of the surface-state electrons [S1, S2].

Lieb lattice

We first present the muffin-tin results for the Lieb lattice considered in Fig. 1 in the main text and Fig. S1 in the SM. The muffin-tin calculations of the s -like LDOS maps and their analysis can be found in Ref. [S2]. Here, we will focus on the p -like bands.

In Fig. S4a, the LDOS as a function of energy is displayed for the blue, red, and green positions indicated in the inset. The inset shows a zoom-in of the lattice. Corner, edge and bridge sites are indicated in blue, red and green, respectively. CO molecules are indicated in black. The muffin-tin spectra (left panel) were calculated for the finite-size Lieb lattice with 5×5 unit cells. The experimental spectrum at each position (right panel) is the average dI/dV signal as a function of the bias voltage, normalized by the average dI/dV spectrum on the bare Cu(111) following the procedure in Ref. [S1]. The experimental spectra are in good agreement with the calculated spectra. The low-energy part of the spectra ($-300 < E < +300$ meV) is due to s -like bands, as discussed in Ref. [S2]. For $E > 300$ meV, the spectra between the sites (green) exhibit a peak around $E \approx 570$ mV (green vertical line), while the on-site spectra (blue, red) remain mostly flat. This corresponds to the nodal character of the p -like orbitals, which is characterized by a node in the center of the sites and enhanced intensity between the sites. This is visualized in the experimental LDOS map in Fig. 1a and the calculated LDOS maps at the representative energies $E = 300$ meV, $E = 400$ meV and 600 meV in Fig. S4b.

We now solve the Schrödinger equation on a single unit cell with periodic boundary conditions to calculate the band structure, the DOS, and the wavefunctions in the lattice. Note that the energies can differ (slightly) between calculations with and without periodic boundary conditions due to finite-size effects. The band structure (Fig. S4c, also given in Fig. 1c in the main text) shows the s -like bands (green) and the higher bands (blue) along the high-symmetry directions in the Brillouin zone. p -like bands are predicted for energies from $E \approx 300$ meV, corresponding to the calculated LDOS maps shown in Fig. S4b. The geometry of the realized Lieb lattice is slightly asymmetric, with unit-cell size 2.66 nm $\times$ 2.56 nm. This asymmetry leads to a small symmetry breaking between the X and the Y point, but as can be inferred from Fig. S4c, the band structure remains similar in the Γ -X and Γ -Y direction.

Including a broadening of $\Gamma = 80$ meV, we calculate the DOS (Fig. S4d). In the DOS, we can distinguish different peaks belonging to different wave functions. Due to the broadening, some of these wave functions have an overlap in certain energy ranges (e.g. for $E = 0 - 400$ meV).

While experimentally only the probability density $|\Psi(x, y)|^2$ of the electrons can be observed, the muffin-tin model provides insight in the wavefunction Ψ including its sign. In Fig. S4e, we show the wavefunction in a unit cell at the energies corresponding to the peaks in the DOS. The CO molecules in the unit cell are indicated by black circles with a red contour. The wave functions are displayed with their sign, where yellow is positive and blue/grey is negative. We can interpret the first three wave functions as being derived from s -like orbitals. At $E = -300$ meV, the wave function can be thought of as s -like orbitals at each site added with the same sign, resulting in a non-vanishing contribution in-between sites. This is equivalent to a bonding combination of atomic orbitals. At $E = 103$ meV, the wave function has a positive amplitude on site 3 and negative amplitude at site 2, while site 1 has vanishing amplitude. This corresponds to the well-known flat band. At $E = 216$ meV, the amplitude of the wave function changes sign between sites, *i.e.* the wavefunction has a node in between sites, corresponding to an antibonding combination of s -like orbitals. The next orbitals are derived from p -like states. At $E = 293$ (319) meV, we observe a bonding p_{π} -like interaction in the y (x)-direction. The corresponding antibonding states are found at $E = 690$ meV and $E = 669$ meV, respectively. The anti-bonding combinations of p_{σ} -like orbitals are expected to lie at higher energies, corresponding to a larger hopping amplitude in the tight binding model (see Sec. III). However, at higher energies, the orbital character is more difficult to determine due to the limited repulsive (effective) potential of 0.9 eV imposed by the CO molecules, hybridization effects and undesired contributions of the wave function between CO molecules.

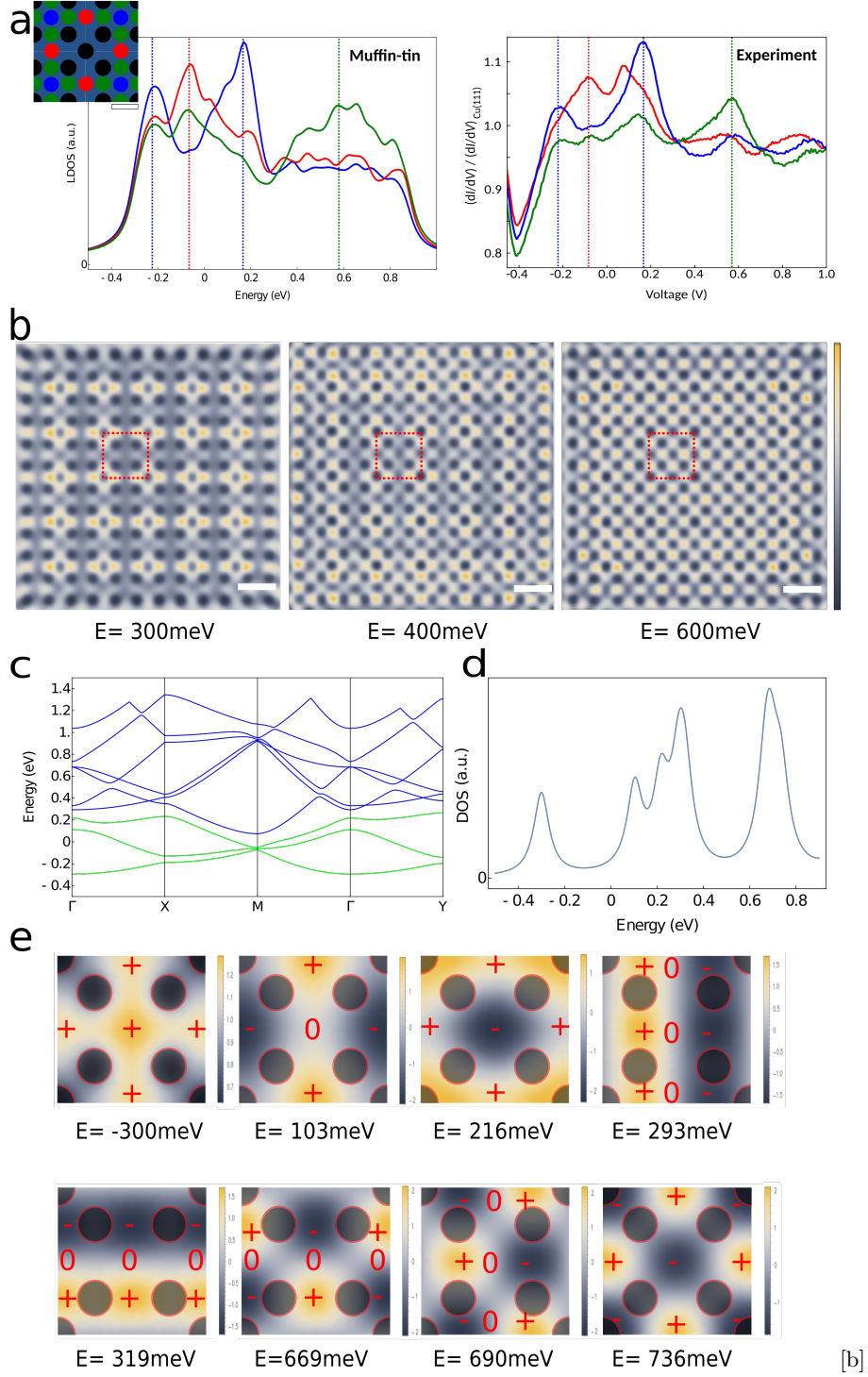


FIG. S4. Muffin-tin description of the Lieb lattice considered in Fig. 1. (a) The LDOS spectra for the Lieb lattice on the blue corner, red edge, and green interstitial positions indicated in the cell in the inset (CO molecules indicated in black; scale bar, 1 nm). The left panel displays the LDOS spectra calculated with the muffin-tin approximation and the right panel shows the normalized experimental dI/dV spectra (stabilization parameters: $I_{\text{set}} = 1$ nA, $V_{\text{set}} = 1$ V; bias modulation $V_{\text{rms}} = 20$ mV). The red and blue spectra correspond to s -like orbitals and the green spectra correspond to a p -like orbital. As a guide to the eye, we included vertical lines to indicate the main peaks in the spectra. (b) Calculated LDOS wave-function maps at different energies ($E = 300$ meV, $E = 400$ meV and $E = 600$ meV) show the p -like character of the wave functions at these energies. Scale bar, 2 nm. (c) Band structure, calculated by muffin-tin periodic lattice calculations. Bands derived from s -like orbitals are depicted in green and bands derived from higher orbitals in blue. See also Ref. [S7] for a description of these orbitals. (d) Corresponding DOS as a function of energy for a unit cell of the Lieb lattice. (e) Contour plots of the wave function for a single unit-cell at different energies (periodic boundary conditions) show the s - and p -like character of the wave-functions. The plus and minus signs indicate the sign of the wave function. At the lowest three energies, we observe states derived from s -like orbitals, next we observe bonding and anti-bonding states derived from p -like orbitals. At even higher energy, more complex patterns are observed.

Symmetric Lieb lattice

Next, we turn our attention to the enlarged symmetric Lieb-like lattice that is described in Fig. 2 in the main text and Fig. S2 in the SM. We increase the size of the unit cell to lower the p -like orbital features to the energy range close to $E = 0$ meV. In Fig. S5a, we show the finite lattice used for the muffin-tin calculated map in the main text (Fig. 2b). The unit cell, containing 12 CO molecules (black), is indicated by the dashed red box, and the positions for spectra are indicated in red and blue (on-site positions) and orange and green (between the sites). Fig. S5b shows the experimental normalized dI/dV spectra (top, thick lines) and the muffin-tin calculations (bottom, thin lines) for the indicated sites. Below $E = 0$ meV, the red and blue spectra show features expected for the s -like orbital bands of the Lieb-like lattice. The green and orange sites exhibit a peak around $E = 50$ meV (green vertical line), whereas the red and blue sites have a minimum, indicating bonding p -like orbital behavior.

Again, we look at the periodic case to interpret the orbitals in the DOS, the band structure, and the wave functions. In Fig. S5c-d, the DOS and the band structure are shifted towards lower energy with respect to the previous Lieb lattice and the Dirac point at M acquired a small gap. Furthermore, the lowest p -like band in the previous case has no longer a global minimum at the M point. As we will see in the tight-binding description of the lattice below, this corresponds to a higher on-site energy for the p_x and p_y orbitals on the corner than on the edge sites, which is a result of more confinement due to the CO molecules. This means that the on-site energy of the orbitals is tunable in these artificial lattices. Despite the small asymmetry in the geometry of the lattice ($3.58 \text{ nm} \times 3.55 \text{ nm}$), the band structures along the Γ -X and Γ -Y directions in the Brillouin zone are almost identical.

This observation also becomes clear in the wave functions of a periodic unit cell, depicted in Fig. S5e. Comparable to the previous lattice, we first observe the bonding s -like configuration ($E = -306$ meV) and wave function generating the flat band ($E = -83$ meV). Next, we observe a bonding combination of p -like orbitals in the x -direction ($E = 30$ meV), an anti-bonding combination of s -like orbitals ($E = 40$ meV) and a bonding combination of p -like orbitals in the y -direction ($E = 42$ meV), all very close in energy. Compared to the finite-size calculations, the energies are slightly lower. Note that, in contrast to the Lieb lattice in Fig. S4, no p_y (p_x)-like orbital is observed at site 2 (3) for the lowest energy states derived from p -like orbitals (compare the wave functions at 293 meV and 30 meV depicted in Fig. S4 and Fig. S5, respectively). This is due to the presence of the additional CO molecules. These features resemble the experiment described in the main text, and show that the wave functions are indeed derived from p -like states.

Asymmetric Lieb lattice

Finally, we describe the asymmetric Lieb-like lattice presented in Fig. 3 in the main text and Fig. S3 in the SM. In the previously presented symmetric Lieb lattice, the states derived from p_x - and p_y -like orbitals were so close in energy (at $E = 30$ meV and $E = 42$ meV, respectively) that they could not be resolved experimentally because of the large broadening. Now, we use the freedom to position the CO molecules to create an anisotropy: we increase the unit cell in only one direction (the y -direction), thereby breaking the four-fold rotational symmetry.

In Fig. S6a, we show the design of the asymmetric Lieb lattice and the positions of the spectra. The size of the elongated unit cell, indicated by the red dashed box, is $3.58 \text{ nm} \times 3.99 \text{ nm}$. Fig. S6b shows the LDOS spectra on the asymmetric lattice. The top thick lines are the experimental normalized dI/dV spectra and the bottom thin lines are the muffin-tin calculated spectra. Note the differences between the green and orange spectra. Clearly, the lifted degeneracy is resolved experimentally.

As for the previous two lattices, we turn to periodic calculations to study the band structure, DOS, and wave functions. The calculated DOS in Fig. S6c and the band structure in Fig. S6d show an overall decrease of the energies, which can be ascribed to the larger size of the elongated unit cells. The broken four-fold rotational symmetry of the lattice is also reflected in the band structure: the X and Y point are no longer identical. This difference can mainly be ascribed to the lower on-site energy of the p_y -orbitals of the elongated sites, as will be described in the next section. As a consequence of the lowered energy of all sites with an additional downshift of the p_y -orbitals of the elongated sites, the top s -band and bottom p -band are very close to each other in the band structure and even touch near the Γ -point.

We show the wavefunctions at different energies in Fig. S6e. The bonding p_σ -like orbital in the y -direction at $E = -62$ meV and the bonding p_σ -like orbital in the x -direction at $E = -30$ meV can be clearly distinguished (note that the energy values are slightly lower than in the finite-size calculations).

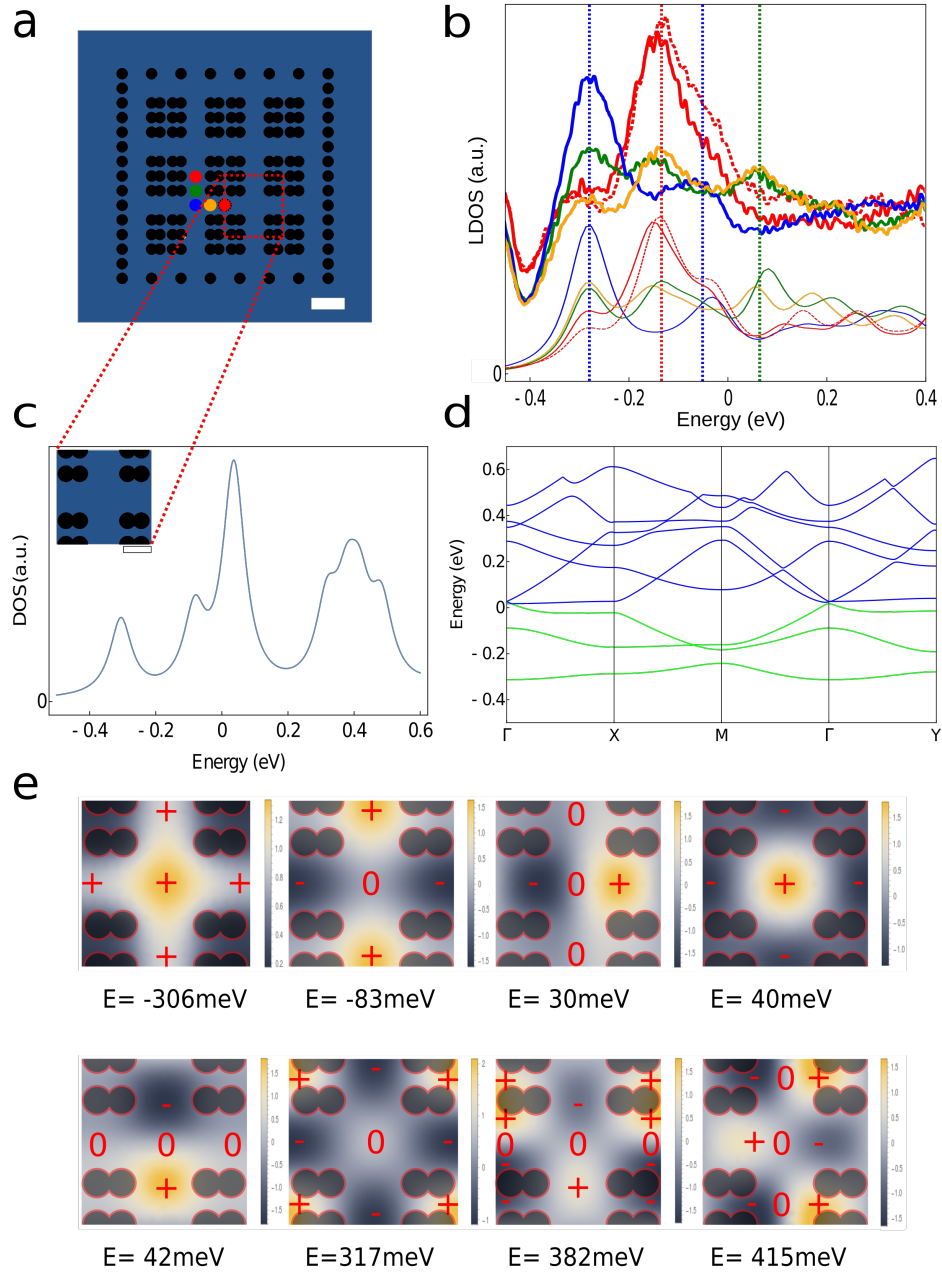


FIG. S5. Muffin-tin description of the large symmetric Lieb-like lattice. (a) The design of the simulated finite-size lattice with colored dots indicating the positions for the spectra. The unit cell is indicated by the red dashed box. Scale bar, 2nm. (b) LDOS at the indicated positions. The top thick lines are the experimental normalized dI/dV spectra and the bottom thin lines are calculated using the muffin-tin model for the finite lattice. The vertical lines indicate the maxima in the STM spectra for the indicated sites. Around $E = 50 \text{ meV}$, the spectra at the green and orange sites exhibit a peak in the LDOS, whereas the red and blue sites show a minimum, which indicates the p -like character. (Stabilization parameters for the experimental spectra: $I_{\text{set}} = 1 \text{ nA}$, $V_{\text{set}} = 600 \text{ mV}$; bias modulation $V_{\text{rms}} = 10 \text{ mV}$.) (c) DOS as a function of energy for the given unit cell (inset; scale bar, 1nm), calculated using periodic lattice calculations. (d) Band structure, in which the bands derived from s -like orbitals are depicted in green and those derived from higher orbitals in blue. The bands are shifted to lower energies with respect to the Lieb lattice considered in the previous figure due to a larger unit cell. (e) Contour plots of the wave function for a single unit-cell at different energies (periodic boundary conditions). The wave functions show the same features as for the previous Lieb lattice, but they have a different energy and therefore overlap with other wave functions. The plus and minus signs again indicate the sign of the wave function at the indicated points and the CO molecules (black circles with red circumference) are included as a guide to the eye. Note that the energies correspond with the peaks shown in the DOS of (b).

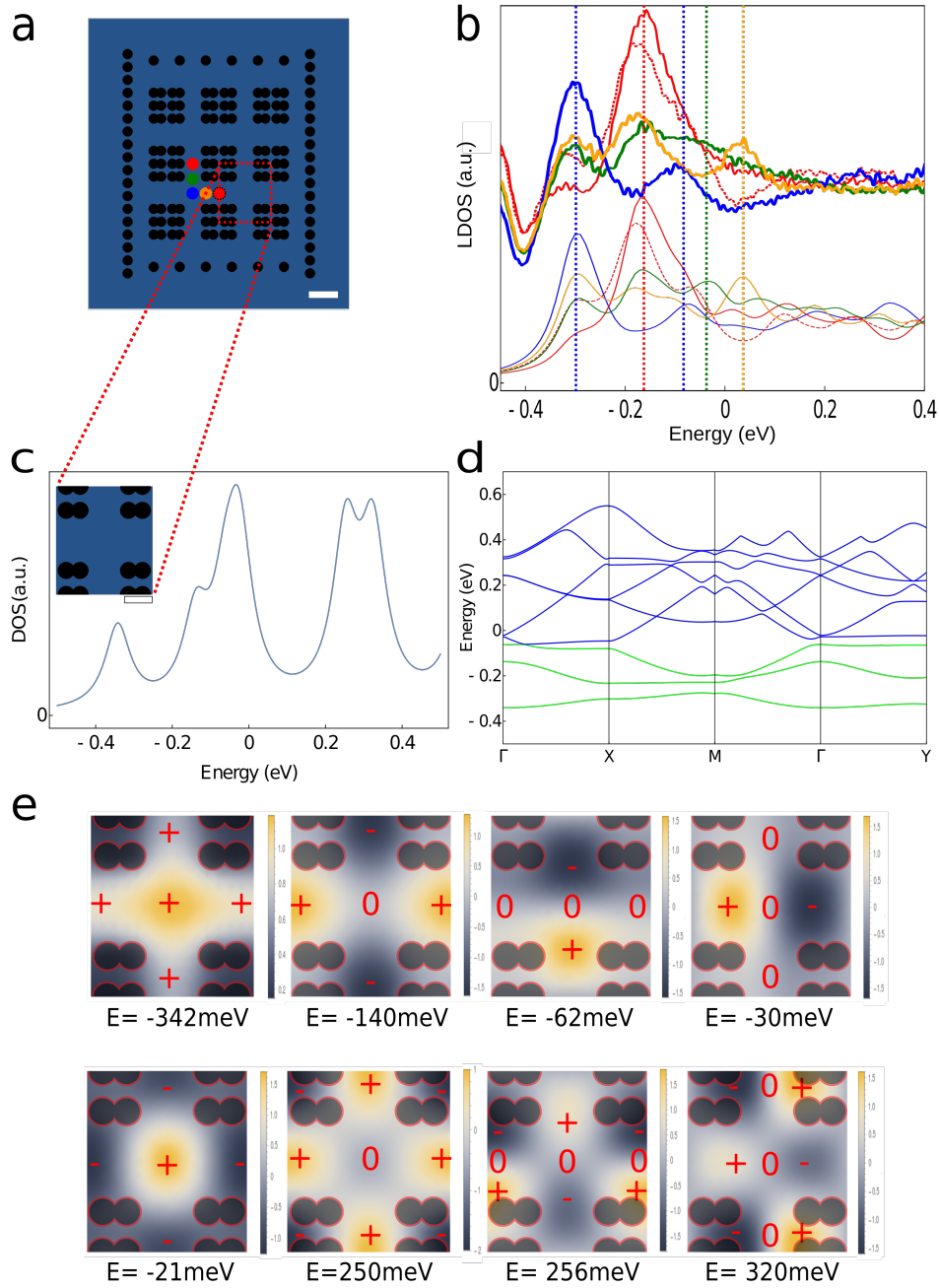


FIG. S6. Muffin-tin description of the asymmetric Lieb lattice. (a) The design of the simulated finite-size lattice with colored dots indicating the positions for the spectra. The asymmetric unit cell is indicated by the red dashed box. Scale bar, 2nm. (b) LDOS at the indicated positions. The top thick lines are the experimental normalized dI/dV spectra and the bottom thin lines are calculated using the muffin-tin model for the finite lattice. The vertical lines indicate the maxima in the STM spectra for the indicated sites. With respect to Fig. S5b, we now observe a split between the green and orange spectra, confirming that the p_y -like orbitals have a lower energy than the p_x -like orbitals. (Stabilization parameters for the experimental spectra: $I_{\text{set}} = 1\text{ nA}$, $V_{\text{set}} = 600\text{ mV}$; bias modulation $V_{\text{rms}} = 10\text{ mV}$.) (c) DOS as a function of energy for the given unit cell (inset; scale bar, 1nm), calculated using periodic boundary conditions. (d) Band structure, in which bands derived from s -like orbitals are depicted in green and those derived from higher orbitals in blue. The bands are shifted to a slightly lower energy compared to the symmetric lattice due to the (asymmetrically) enlarged unit cell. (e) Contour plots of the wave function for a single unit-cell at different energies (periodic boundary conditions). The bonding p_σ -like orbitals in the y - and the x -direction are found at $E = -82\text{ meV}$ and $E = -30\text{ meV}$, respectively. The degeneracy between these orbitals is thus lifted due to the larger distance in the y -direction (note that the energies are slightly higher in the finite lattice than in the periodic case).

TIGHT-BINDING DESCRIPTION OF THE LATTICES

The Lieb lattice

As was shown in Ref. [S7], p -type orbitals can be incorporated in the tight-binding description of the lattices. In the following, we tune the nearest- and next-nearest-neighbour (NN and NNN) hopping, orbital overlap and on-site energies such that we obtain similar results as for the muffin-tin. Note that the parameters used in our muffin-tin calculations (repulsive potential of 0.9 eV and a radius of 0.3 nm) were tailored to fit the experimental results. These values differ strongly from the values used in Ref. [S7].

The tight-binding parameters are reliable for the low-energy sector. At higher energies, it is more difficult to tune the parameters in an appropriate way due to the presence of higher bands. Note that we do not consider these higher orbitals in the remainder of this tight-binding model and focus on the low-lying p -like bands.

By projecting the p -orbitals in a σ - and π -bond, we obtain the periodic Hamiltonian

$$H_k = \begin{pmatrix} H_{ss} & H_{sp} \\ H_{sp}^\dagger & H_{pp} \end{pmatrix}, \quad (S1)$$

where

$$H_{ss} = \begin{pmatrix} e_s & -2tc_{kx} & -2tc_{ky} \\ -2tc_{kx} & e_s & -4t_2c_{kx}c_{ky} \\ -2tc_{ky} & -4t_2c_{kx}c_{ky} & e_s \end{pmatrix}, \quad (S2)$$

$$H_{pp} = \begin{pmatrix} e_{pxA} & 2t_{p\sigma}c_{kx} & -2t_{p\pi}c_{ky} & 0 & 0 & 0 \\ 2t_{p\sigma}c_{kx} & e_{pxB} & 2(t_{p\sigma 2} - t_{p\pi 2})c_{kx}c_{ky} & 0 & 0 & -2(t_{p\pi 2} + t_{p\sigma 2})s_{kx}s_{ky} \\ -2t_{p\pi}c_{ky} & 2(t_{p\sigma 2} - t_{p\pi 2})c_{kx}c_{ky} & e_{pxC} & 0 & -2(t_{p\pi 2} + t_{p\sigma 2})s_{kx}s_{ky} & 0 \\ 0 & 0 & 0 & e_{pyA} & -2t_{p\pi}c_{kx} & 2t_{p\sigma}c_{ky} \\ 0 & 0 & -2(t_{p\pi 2} + t_{p\sigma 2})s_{kx}s_{ky} & -2t_{p\pi}c_{kx} & e_{pyB} & 2(t_{p\sigma 2} - t_{p\pi 2})c_{kx}c_{ky} \\ 0 & -2(t_{p\pi 2} + t_{p\sigma 2})s_{kx}s_{ky} & 0 & 2t_{p\sigma}c_{ky} & 2(t_{p\sigma 2} - t_{p\pi 2})c_{kx}c_{ky} & e_{pyC} \end{pmatrix}, \quad (S3)$$

and

$$H_{sp} = \begin{pmatrix} 0 & -2it_{sp}s_{kx} & 0 & 0 & 0 & -2it_{sp}s_{ky} \\ -2it_{sp}s_{kx} & 0 & -4it_{sp2}c_{ky}s_{kx}/\sqrt{2} & 0 & 0 & -4it_{sp2}c_{kx}s_{ky}/\sqrt{2} \\ 0 & -4it_{sp2}c_{ky}s_{kx}/\sqrt{2} & 0 & -2it_{sp}s_{ky} & -4it_{sp2}c_{kx}s_{ky}/\sqrt{2} & 0 \end{pmatrix}. \quad (S4)$$

Here, we introduced the on-site energies e_s and e_{pij} (where $i \in x, y$ for the orientation of the orbitals and $j \in A, B, C$ for the position), the NN-(NNN-) hopping parameters t (t_2) between s -like orbitals, t_{sp} (t_{sp2}) between s - and p -like orbitals, and $t_{p\sigma}$ ($t_{p\sigma 2}$) and $t_{p\pi}$ ($t_{p\pi 2}$) for the σ and π hopping between p -like orbitals. Furthermore, we introduced the abbreviation $c_{kx(ky)} = \cos[kx/2(ky/2)]$ and $s_{kx(ky)} = \sin[kx/2(ky/2)]$. These hopping parameters and the σ - and π bonds are sketched in Fig. S7. Furthermore, for some matrix elements, the p -orbitals are rotated either parallel or perpendicular to the other s - or p -orbital, such that there is a nonzero hopping amplitude between the orbitals. These rotations result in additional prefactors such as $1/\sqrt{2}$ and $1/2$ in the Hamiltonian and are illustrated in the right side of Fig. S7.

We now calculate the band structure for the Lieb, large symmetric Lieb, and large asymmetric Lieb lattice and compare it with the band structure obtained from the muffin-tin model. For this band-structure calculation, we also make use of the orbital overlap s (for both s and p) between NN-sites. The results are shown in Fig. S8a-c and should be compared with the ones in Figs. S4c, S5d, and S6, respectively. Note that we focus on the lowest-lying p -like bands and try to get an effective description, fitted-by-eye, rather than solving for the entire lattice. Moreover, to get an accurate description for the higher bands, we would need to include higher orbitals in the description as well.

The tight-binding band structures give insight in the different parameters of the lattices, which are in this case mainly determined by the on-site energy. For the large symmetric Lieb lattice (see Fig. S8b), all bands have a

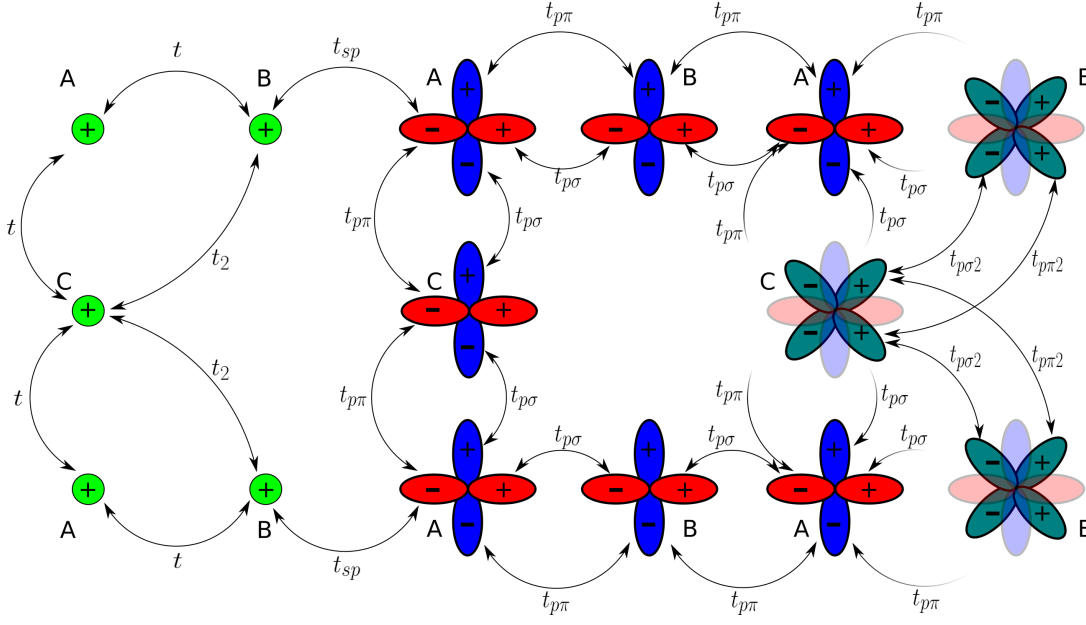


FIG. S7. Schematic picture of the Hamiltonian of the Lieb lattice and the indicated orbitals including the hopping amplitudes. Note that each site has a s (green), p_x (red) and p_y (blue) orbital and all the hoppings indicated in the figure (the image is just a sketch to show the different type of hopping parameters in the model). The p_x and p_y orbitals have a positive (+) and negative (-) part of the wave function that needs to be taken into account accordingly. The hopping t (t_2) represents the s -orbital hopping, t_{sp} (t_{sp2}) the hopping between s - and p -orbitals, $t_{p\sigma}$ ($t_{p\sigma2}$) the hopping for a σ -bond, and $t_{p\pi}$ ($t_{p\pi2}$) the hopping for a π -bond. Note that we need to rotate the p -orbitals for the t_{sp2} (not shown), $t_{p\sigma2}$ and $t_{p\pi2}$ hopping amplitudes by an angle of 45° . The shown rotation (last column for the B-sites, and one column before for the C-site) is arbitrary and can also be chosen in a different way, but at the end, when the signs of the wave function are taken into account accordingly, the rotation does not change the Hamiltonian and the energy of the model.

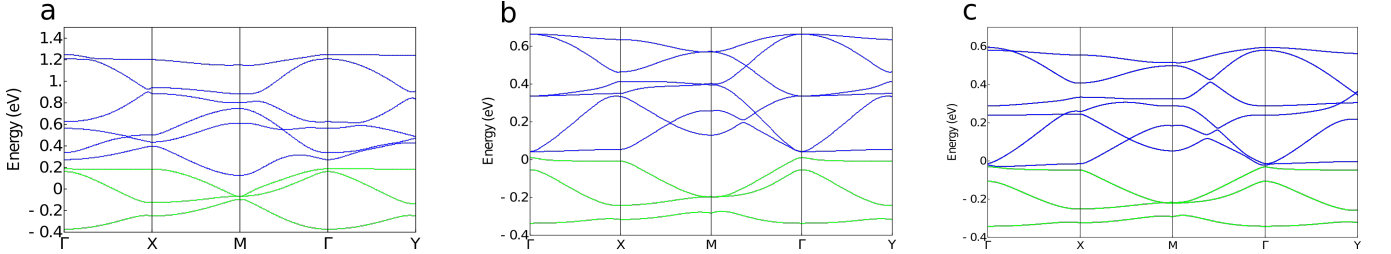


FIG. S8. Band structure from the tight-binding model for the different Lieb lattices. See the muffin-tin band structure in Fig. S4c, Fig. S5d and Fig. S6d for (a), (b) and (c) respectively. (a) The Lieb lattice considered in Ref. [S2], with the following parameters (all in eV, except for the overlap integrals which are dimensionless): $e_{pxA} = 0.89$, $e_{pxB} = 0.89$, $e_{pxC} = 0.53$, $e_{pyA} = 0.81$, $e_{pyB} = 0.45$, $e_{pyC} = 0.89$, $e_s = -0.05$, $s_{\pi\pi} = 0.02$, $s_{sp} = 0.15$, $s_{ss} = 0.2$, $s_{\sigma\sigma} = 0.02$, $t = 0.1$, $t_2 = 0.6 \cdot 0.09$, $t_{p\pi} = 0.07$, $t_{tp\pi2} = 0.065$, $t_{tp\sigma} = 0.2$, $t_{p\sigma2} = 0.09$, $t_{sp} = 0.06$, and $t_{sp2} = 0.06$. Note that the on site energies for e_{pyB} and e_{pxC} are rather low in comparison with the other on site energies. (b) The band structure for the modified Lieb lattice considered in Fig. S5. The parameters are $e_{pxA} = e_{pxB} = e_{pxC} = e_{pyA} = e_{pyB} = e_{pyC} = 0.4$, $e_s = -0.10$, $s_{\pi\pi} = 0.02$, $s_{sp} = 0.15$, $s_{ss} = 0.2$, $s_{\sigma\sigma} = 0.02$, $t = 0.06$, $t_2 = 0.6 \cdot 0.06$, $t_{p\pi} = 0.05$, $t_{tp\pi2} = 0.06$, $t_{tp\sigma} = 0.15$, $t_{p\sigma2} = 0.05$, $t_{sp} = 0.08$, and $t_{sp2} = 0.05$. We notice that the on-site energy is lower for all sites, but especially e_{pyB} and e_{pxC} differ significantly from the previous case and have the same energy as the other on-site p -orbitals. This is because these orbitals are more confined than in the Lieb lattice considered in Ref. [S2]. This supports the findings in the main text. The p -bands are higher in energy than the s -orbitals, in particular at the M point. (c) The band structure for the asymmetric Lieb lattice considered in Fig. S6. The parameters are approximately the same as in (b). Due to more spacing in the y -direction, all on-site energies are slightly lower than before (this can also be seen when comparing energies of similar wavefunctions in Fig. S5e and Fig. S6e). In addition, the on-site p_y energy of site 1 and 2 is lowered with 0.06eV, whereas the one of site 3 remains the same. This lowering of the p_y energy results in more asymmetry between the X and Y point in the Brillouin zone than in the previous band structures.

lower energy compared to the Lieb lattice (see Fig. S8a). This can be described by a reduced on-site energy of all s - and p -like orbitals by approximately 50 meV. Only the on-site energies of the p_x -orbital at the C-site (e_{pxC}) and the p_y -orbital at the B-site (e_{pxB}) are hardly affected, pushing these bands out of the lowered energy window that is considered. A significant change in the band structure due to the relatively higher on-site energies e_{pxC} and e_{pxB} can be recognized in the lowest p -band. For the first Lieb lattice, the lowest- p -band has its minimum at the M -point. The larger symmetric Lieb lattice no longer has this minimum.

The large asymmetric lattice can be fitted with a slightly decreased on-site energy ($\Delta E \approx -40$ meV) for all sites, as all sites become slightly larger due to the elongation. In addition, the p_y -bands of the elongated sites 1 and 2 exhibit an extra shift of -60 meV. This results in the lifted degeneracy of the p_x and p_y band in this lattice. As a result, the top s -band and bottom p -band are very close to each other in the band structure and touch near the Γ -point. Note that site 3 was not elongated, in contrast to site 1 and 2, and the p_y -band of site 3 thus did not exhibit the extra shift. This leads to a slightly modified band structure: if the p_y on-site energy of site 3 would also be decreased by additional -60 meV, the bands would touch at the X-point instead of the Γ -point. We believe, however, that this breaking of the symmetry is too small to reveal any further physical effects, especially in the STM spectra, where broadening plays a significant role.

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