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Real-space subfemtosecond imaging of quantum electronic coherences in molecules

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Tracking electron motion in molecules is the key to understanding and controlling chemical transformations. Contemporary techniques in attosecond science are able to generate and trace the consequences of this motion in real time, but not in real space. Scanning tunnelling microscopy, on the other hand, can locally probe the valence electron density in molecules, but cannot alone provide dynamical information at this ultrafast timescale. Here we show that, by combining scanning tunnelling microscopy and attosecond technologies, quantum electronic coherences induced in molecules by <6-fs-long carrier-envelope-phase-stable near-infrared laser pulses can be directly visualized at ångström-scale spatial and subfemtosecond temporal resolutions. We demonstrate concurrent real-space and -time imaging of coherences involving the valence orbitals of perylenetetracarboxylic dianhydride molecules, and full control over the population of the involved orbitals. This approach opens the way to the unambiguous observation and manipulation of electron dynamics in complex molecular systems.

Chemical transformations in molecules are a consequence of valence electron motion and its eventual coupling to nuclear motion^{1–4}. Many experiments have shown that it is possible to generate and track the temporal evolution of a coherent superposition of quantum states of valence electrons at attosecond timescales, albeit only non-locally^{5–8}. Consequently, so far the local time-evolution of the electron density can only be inferred by reconstruction from the (often elusive) features appearing in electron, ion, absorption or emission spectra^{9–12}.

Light-matter interactions at molecular scales allow electronic motion to be probed at its natural length^{13–16} (ångström scale) and timescales¹⁷ (100 as to few femtoseconds). Lightwave-driven scanning tunnelling microscopy (STM) can now generate and track extremely fast tunnelling currents^{17–27}, as well as coherently control electron tunnelling on an approximately 200 as timescale¹⁷. Yet, the ultimate goal, to watch electrons in action in real-space and -time, remains unrealized^{5,28,29}. Here we combine carrier-envelope-phase (CEP)-stable few-cycle (duration <6 fs) laser pulses with a scanning tunnelling microscope to break this fundamental barrier, and to follow coherences between molecular orbitals concurrently with ångström-scale spatial and subfemtosecond temporal resolutions, thus going well beyond the previously established space-time limits³⁰ and bypassing any kind of reconstruction.

Ultrafast photon-induced electron tunnelling

In our experiments, orthogonally polarized near-infrared laser pulses with slightly different carrier frequencies (Fig. 1a) are focused at the apex of a tungsten nanotip in tunnel contact with molecular layers of perylenetetracarboxylic dianhydride (PTCDA) molecules grown on top of a Au(111) surface. The polarization axes of the two laser pulses formed an angle of 45° with respect to the tip-axis. This configuration ensures that the non collinear polarizations of the pulses overlap with each other through their component along the nanotip axis, as well as along the molecular axis (parallel to the Au(111) surface); this overlap leads to homodyne beating

between the polarization components (Fig. 1b and Supplementary Sections 1 and 2)^{31,32}.

The correlation of the laser-induced tunnelling current at the STM junction as a function of the delay between the two laser pulses is shown in Fig. 1c. At zero delay between the two laser pulses, the polarization induced along the nanotip axis resembles the one induced by a single laser pulse at the tunnel junction (Supplementary Sections 2 and 7). This induced polarization along the tip-axis can be assumed to be instantaneous³³. We note that, for the wavelength ($\lambda \approx 810$ nm) and intensities ($\sim 1 \times 10^{12}$ W cm⁻²) of the laser pulses used in this work, only photon-driven tunnelling is possible¹⁷ (Keldysh parameter, $\gamma > 1$), not field-driven tunnelling, which is only possible at higher pulse intensities¹⁷.

The variation of the laser-induced tunnelling current when the polarizations of the two laser pulses are rotated with respect to the tip-axis is shown in Fig. 1d. A quasi-uniform laser-induced tunnelling current is measured for all polarizations of the pulses. In the case of homodyne interference between the two pulses, we measure the difference of the laser-induced tunnelling current induced by them. This result shows that the far-field orthogonality of the laser pulses is preserved in the near field of the tungsten nanotip (Supplementary Section 2.1).

The variation of the laser-induced tunnelling current with the d.c. bias when the tungsten nanotip is placed on top of a PTCDA molecule on Au(111) is shown in Fig. 1e; a differential conductance ($dI_{d.c.}/dV$) plot is also shown. Here we have used a single laser pulse as described above. The laser-induced tunnelling current exhibits marked features at -1.8 V and $+1.4$ V, which are the resonances for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PTCDA molecules on Au(111), respectively, and at -0.3 V, which corresponds to the Coulomb-shifted Au(111) surface state. This implies that when we elevate the electronic states of the molecules (that is, the HOMO at -1.8 V, LUMO at 1.4 V and the surface state of Au(111) at -0.3 V), the laser-induced tunnelling current primarily arises from the

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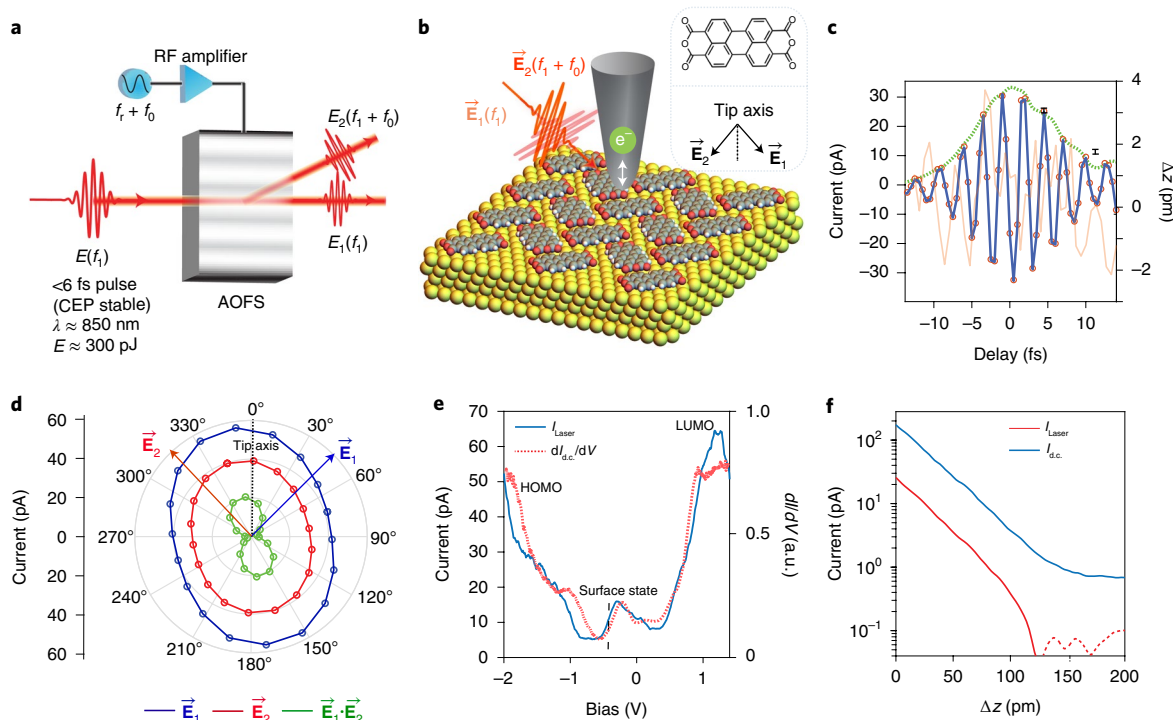


Fig. 1 | Ultrafast photon-induced electron tunnelling. **a**, Laser pulses with a very small offset in their carrier frequencies (<1 kHz) are generated by selecting the zeroth-order ($\mathbf{E}_1$) and first-order ($\mathbf{E}_2$) diffracted beam of laser pulses traversing through an acousto-optic frequency shifter (AOFS). **b**, A schematic of the experimental set-up is shown: a pair of orthogonally polarized CEP-stable near-infrared laser pulses at slightly different carrier frequencies— f_1 (for $\mathbf{E}_1$) and $f_1 + f_0$ (for $\mathbf{E}_2$)—are focused at the apex of tungsten nanotip in tunnel contact with a monolayer of PTCDA molecules on top of a Au(111) surface. The top of the inset shows the molecular structure of a PTCDA molecule and the bottom shows the polarization axes of the two ultrashort pulses with respect to the axis of the nanotip. **c**, Nonlinear cross-correlation of the laser-induced tunnelling current measured on a clean Au(111) surface by orthogonally polarized laser pulses ($\mathbf{E}_1(f_1)$ and $\mathbf{E}_2(f_1 + f_0)$) at the STM junction. The variation in the position of the z-piezo in tunnel contact (Δz , orange curve, right axis) during the cross-correlation measurement is shown. The bias and set-current at the STM (constant-current mode) junction are -1 V and 200 pA, respectively. The error bar indicates the standard deviation of the mean value from five consecutive measurements. The envelope of the cross-correlation trace is shown by the dashed green curve. **d**, Measured variation of the photon-induced tunnelling current as a function of rotating polarization of the laser pulses with respect to the tip-axis (0° , dashed black line) for $\mathbf{E}_1$, $\mathbf{E}_2$ and a homodyne beating signal between them. **e**, Variation of the laser-induced tunnelling current measured on a PTCDA molecule over a Au(111) surface as a function of the bias ($I_{\text{Laser}}-V$ curve). **f**, Comparison of the variation of the laser-induced tunnelling current and the d.c. tunnelling current as a function of the (increasing) tunnel gap width ($I-\Delta z$ curve). The $I-\Delta z$ curve was measured on a Au(111) surface with a d.c. bias of 1 V and a set-point current of 200 pA. The dashed portion of the red curve indicates the noise floor.

aligned level. The laser-induced tunnelling current is proportional to the local density of states (LDOS) of the initial state and to the square of the transition moment matrix element determining the strength of the dipole coupling between the initial and the excited states^{31,34} (Supplementary Section 6).

The variation of the laser-induced tunnelling current and the d.c. tunnelling current with the tunnel gap width ($I-\Delta z$ curves) is shown in Fig. 1f. The d.c. and photon-induced tunnelling have the same exponential dependence on the tunnelling gap width.

Ultrashort laser-driven imaging of molecular orbitals

A single photon of ~ 1.5 eV from the laser pulse resonantly couples the HOMO (and LUMO) of PTCDA with the Au(111) surface state; thus, with controlled alignment of the electronic levels of the molecule with respect to the Fermi level of the nanotip, a laser pulse can either induce a transition from the HOMO to the surface state (Fig. 2a) or from the surface state to the LUMO (Fig. 2b). By tuning the bias voltage at the tunnel junction one can control the initial state from which the laser-induced transition takes place (Supplementary Figs. 17 and 18).

We consider first the case of zero delay between the two laser pulses (hereafter referred to as a single-pulse experiment). In this

case we note that the electric-field components of the two pulses cancel each other in the surface plane due to the specific geometric arrangement of the two laser pulses (Fig. 1b), so that the only active electric-field component is that along the tip-axis (this is no longer true for non-zero delay between the pulses). Transfer of population from the lower to the upper level commences as soon as this single pulse reaches the sample. Figure 2c shows the calculated temporal evolution of the populations in the surface and LUMO states resonantly coupled by our 6-fs-long laser pulse obtained from standard two-level Rabi formulas (Supplementary Section 7). At the end of the laser pulse, most of the electronic population remains in the lower state, thus excluding the possibility that a single 6 fs pulse induces Rabi oscillations between those states. This is the consequence of the fact that, for the peak electric field (E_p) of the laser pulse used in the experiment and the small value of the dipole coupling between the two levels (μ) the Rabi period ($2\pi\hbar/(\mu E_p)$; where $\hbar$ is Planck's constant) is much longer than the pulse duration. We note that the transition dipole moment along the tip-axis is small due to the nearly perfect planar arrangement of the Au(111) atoms and the PTCDA layer. We exclude any further exchange of population between the two states when the pulse is over due to the extremely short tunnelling times¹⁷ (<0.5 fs). Therefore, in a

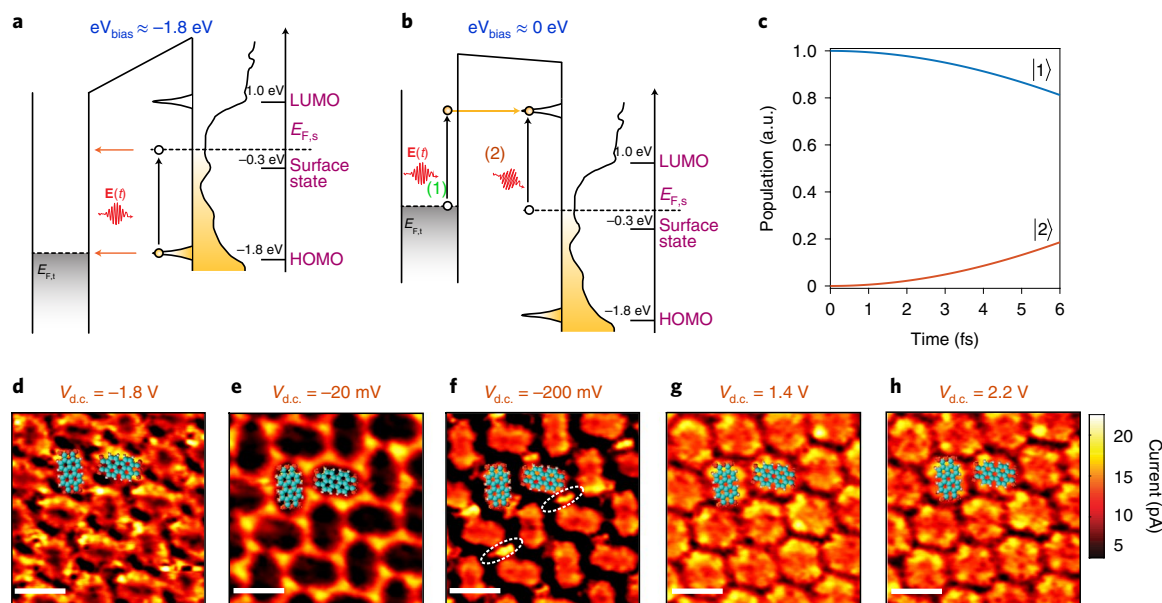


Fig. 2 | Ultrashort laser-driven imaging of molecular orbitals. **a,b**, Illustration of the laser-induced transitions at the tunnel junction. $E(t)$ is the electric field at the tunnel junction. **a**, At a bias where the HOMO of PTCDA molecules rises close to the Fermi level of the tungsten nanotip ($E_{F,t}$), photons of the laser pulse can dipole couple the HOMO of the PTCDA molecule with the surface state of Au(111). **b**, When the Fermi levels of the tungsten nanotip and the Au(111) surface ($E_{F,s}$) are closely spaced, impinging photons can dipole couple either $E_{F,t}$ with the LUMO of the PTCDA molecule (1) or the surface state of Au(111) with the LUMO of the PTCDA molecule (2). **c**, Numerical simulation showing the temporal evolution of the population of the electronic states ($|1\rangle$ and $|2\rangle$)—which are separated by 1.5 eV—on exposure to a resonant 6 fs laser pulse of 1×10^{12} W cm $^{-2}$ intensity, for a transition dipole moment of 0.15 a.u. along the nanotip axis direction (Supplementary Sections 1 and 8). **d–h** Spatially resolved topographic scans of a single-pulse-driven tunnelling current in a monolayer of PTCDA molecules on top of Au(111) at various biases at the STM junction, -1.8 V (**d**), -20 mV (**e**), -200 mV (**f**), 1.4 V (**g**) and 2.2 V (**h**). Steady-state STM imaging was performed in the constant-current mode with a set-point value of $I_{d.c.} = 200$ pA. White dashed ellipses in **f** are to guide the eyes of the reader to the intensity of the tunnelling current present in between the molecules. Scale bars, 1 nm. The reproducibility of data in **d–h** was confirmed in eight individual measurements.

single-pulse experiment, tunnelling from the sample to the tungsten tip will essentially carry spatial information about the lower electronic state. Spatially resolved topographic scans of the single-pulse induced tunnelling current at various biases at the tunnel junction are shown in Fig. 2d–h.

When the HOMO of the PTCDA molecules is aligned with the Fermi level of the tungsten nanotip, the laser-driven tunnelling current images the spatial profile of the HOMO orbitals (Fig. 2d). When it is the Au(111) surface state that is aligned with the Fermi level, the majority of the laser-driven tunnelling current arises from the surface state, so that the intensity of the current is much higher on the metallic surface than on the molecules (Fig. 2e). At a bias where not one, but two dipole transitions are possible (for example, one transition from the surface state to the LUMO and another from the Fermi level of the tip to the LUMO; processes (1) and (2) in Fig. 2b), the spatial profile of the laser-induced tunnelling current exhibits large intensities on both the molecule and the Au(111) surface (Fig. 2f). When the Fermi level of the tungsten nanotip is lifted above the LUMO of the molecule, the dominant process should be a transition from the Fermi level of the tip to an empty state of the molecules below the tunnel barrier. In this case, the spatial distribution of the current should not, in principle, carry any information on the electronic levels of the molecule; however, at a bias of 1.4 V, the spatial distribution of the laser-induced tunnelling current resembles the distribution of the LUMO of the PTCDA molecules, as shown in Fig. 2g. This is due to the elastic tunnelling of electrons from the nanotip to the molecule (or to the Au(111) surface state) prior to the interaction with the laser pulse. Based on the above arguments, the laser-driven imaging of the surface state and the LUMO has to be symmetric around a range of biases at the tunnel

junction, from -200 mV to $+200$ mV, due to the fact that we access the same initial and final states (Supplementary Figs. 9–11).

Space-time resolved imaging of electronic coherences in molecules

To visualize coherent interference involving two dipole-coupled states of the PTCDA/Au(111) system, we varied the delay between the two orthogonally polarized laser pulses (hereafter called pulses 1 and 2; Fig. 3b) and performed space-resolved topographic scans of the laser-induced tunnelling current. For the laser parameters used in this work and the specific electronic states involved in the process, the optimum conditions to induce and trace such dynamics correspond to the case in which pulses 1 and 2 overlap in time. Otherwise we do not observe any coherent interference between electronic states owing to the extremely fast decoherence times (broad linewidths) of the involved electronic states in the present study. The populations for the upper (u) and lower (l) states—as a function of delay τ between pulses 1 and 2, at a time T , after the beginning of the interaction with the two pulses—are approximately given by (Supplementary Section 7):

$$\begin{aligned} \rho_l(T) &= \cos^2 \left[\frac{\varepsilon T}{\hbar} \left\{ \left| \mu_{lu}^{\parallel} \right|^2 \sin^2 \left(\frac{\omega_{ul}\tau}{2} \right) + \left| \mu_{lu}^{\perp} \right|^2 \cos^2 \left(\frac{\omega_{ul}\tau}{2} \right) \right\}^{1/2} \right] e^{-\Gamma\tau/\hbar} \\ \rho_u(T) &= \sin^2 \left[\frac{\varepsilon T}{\hbar} \left\{ \left| \mu_{lu}^{\parallel} \right|^2 \sin^2 \left(\frac{\omega_{ul}\tau}{2} \right) + \left| \mu_{lu}^{\perp} \right|^2 \cos^2 \left(\frac{\omega_{ul}\tau}{2} \right) \right\}^{1/2} \right] e^{-\Gamma\tau/\hbar} \end{aligned} \quad (1)$$

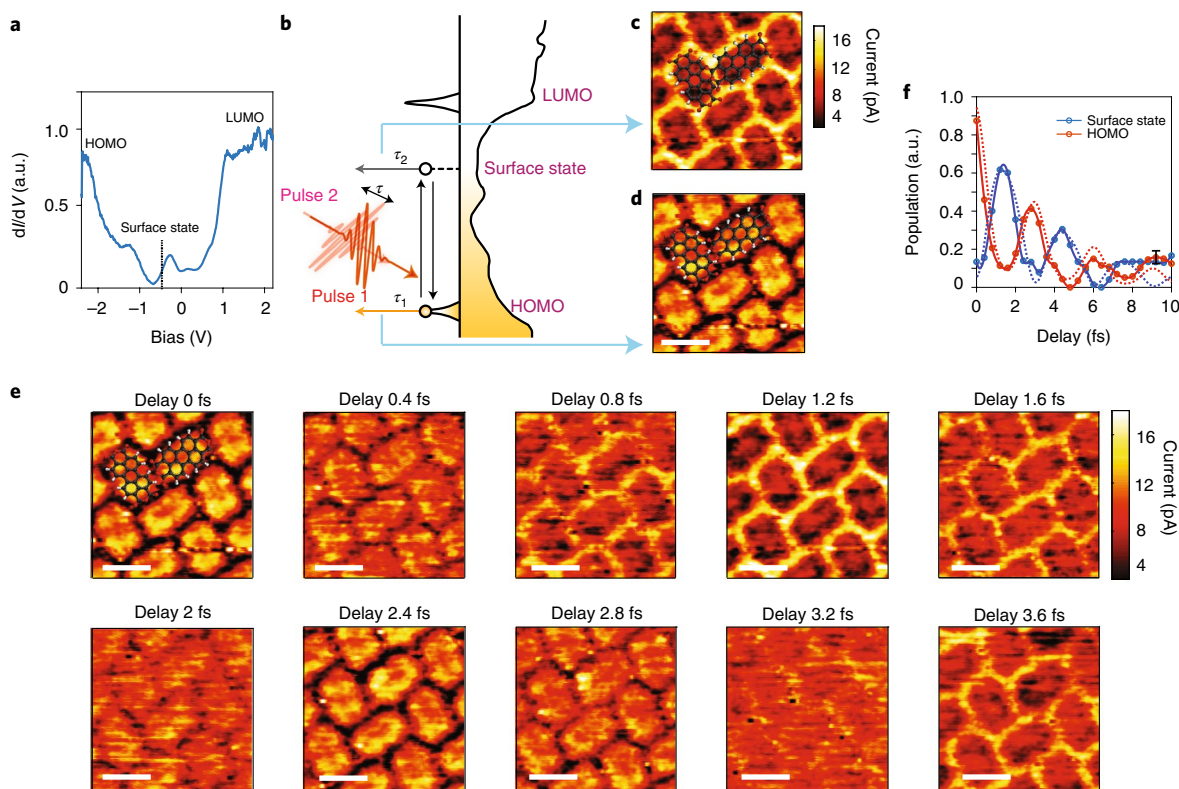


Fig. 3 | Space-time-resolved imaging of quantum coherent interference. **a**, Differential conductance measurement of a PTCDA molecule constituting a monolayer on a Au(111) surface. **b**, Schematic illustration of space-time-resolved probing of the coherent interference between the HOMO of the PTCDA layer and the surface state of Au(111) by delay (τ) control between pulses 1 and 2. **c, d**, Spatially resolved topographic scans of the laser-induced tunnelling current at fixed delays of τ_2 (1.2 fs, surface state; **c**) and τ_1 (0 fs, HOMO; **d**). **e**, Spatially resolved laser-induced tunnelling current as a function of the delay between pulses 1 and 2. Scale bars, 1 nm. The d.c. bias and set-current for the constant-current operation mode of the STM are -1.8 V and 200 pA, respectively. **f**, Temporal evolution of the population in the HOMO and the surface state as a function of the delay between pulses 1 and 2. Solid lines are experimental results and dotted lines are the simulated temporal evolution of the population in the HOMO and the surface state using the two-state analytical model of equation (1). The error bar indicates the s.d. of the experimentally measured data from the simulated population curves (dashed curves). The reproducibility of the data in **c–e** was confirmed in eight individual measurements.

where $\mathcal{E} = E_p/\sqrt{2}$, $\hbar\omega_{ul}$ is the energy difference between the upper and lower states, and Γ is their energy width; $\mu_{lu}^{\parallel}$ and $\mu_{lu}^{\perp}$ are the transition dipole-moment matrix elements between the upper and lower states along the parallel ($\parallel$) and perpendicular ($\perp$) directions with respect to the molecular plane (parallel to the Au(111) surface); $\Gamma = 0.4$ eV for the electronic levels of the PTCDA molecules on top of the Au(111) surface. The effect of Γ is to induce a decay of the electronic coherence induced by the laser pulses. In the case of a single-pulse and $\Gamma = 0$, these formulas are identical to the well-known Rabi equations for a two-level system³⁵.

The arrangement of the electronic energy levels of one monolayer of PTCDA molecules on top of Au(111), as measured by scanning tunnelling spectroscopy (STS), is shown in Figs. 3a and 1e. According to equation (1), by elevating the HOMO of the PTCDA molecules above the Fermi level of the nanotip, an impinging photon from pulse 1 can coherently couple the HOMO with the surface state and thus induce a transition between them. A second pulse, pulse 2, at a certain delay from pulse 1, can then induce a second transition between the two states. If the electronic density is concentrated in the surface state, it will stimulate the transition back to the HOMO and vice versa, akin to quantum beating between the two states. In this way the electronic density will resemble that of either one of the two states depending on the delay between the two pulses, and electrons will eventually tunnel carrying the spatial information of the state that they tunnel from, as schematically

shown in Fig. 3b. At zero delay (τ_1) between the two pulses, the spatially resolved laser-induced imaging maps the spatial profile of the HOMO (Fig. 3d), whereas at a delay of 1.2 fs (τ_2), the intensity of the tunnelling current maps the Au(111) surface state between the molecules (Fig. 3c). The laser-induced tunnelling current for the latter is much higher than for the former, which is consistent with the single-pulse spatial imaging discussed above (Fig. 2e).

The spatially resolved laser-induced tunnelling current as a function of the delay between pulses 1 and 2 is shown in Fig. 3e. A clear coherent oscillation of the electron density between the HOMO of the PTCDA molecules and the Au(111) surface state can be seen in the space-time snapshots, with an oscillation period of ~ 2.7 fs. Details on the experimental methodology used to record these space-time maps are given in Supplementary Section 5. Integration of the laser-induced tunnelling current from the individual panels in Fig. 3e reveals the population dynamics of electrons between the two states, as shown in Fig. 3f. The coherent interference dynamics predicted by the two-level model given by equation (1)—using an electric-field strength of $\mathcal{E} \approx 0.25$ V Å⁻¹, an electronic decoherence time of ~ 5 fs, and transition dipole-moment matrix elements of 1 a.u. ($\mu_{lu}^{\parallel}$) and 0.2 a.u. ($\mu_{lu}^{\perp}$) along the parallel and perpendicular axis of the PTCDA molecules, respectively—is shown in Fig. 3f. The chosen values for $\mu_{lu}^{\parallel}$ and $\mu_{lu}^{\perp}$ are compatible with those obtained from density functional theory (DFT) simulations (Supplementary Section 8).

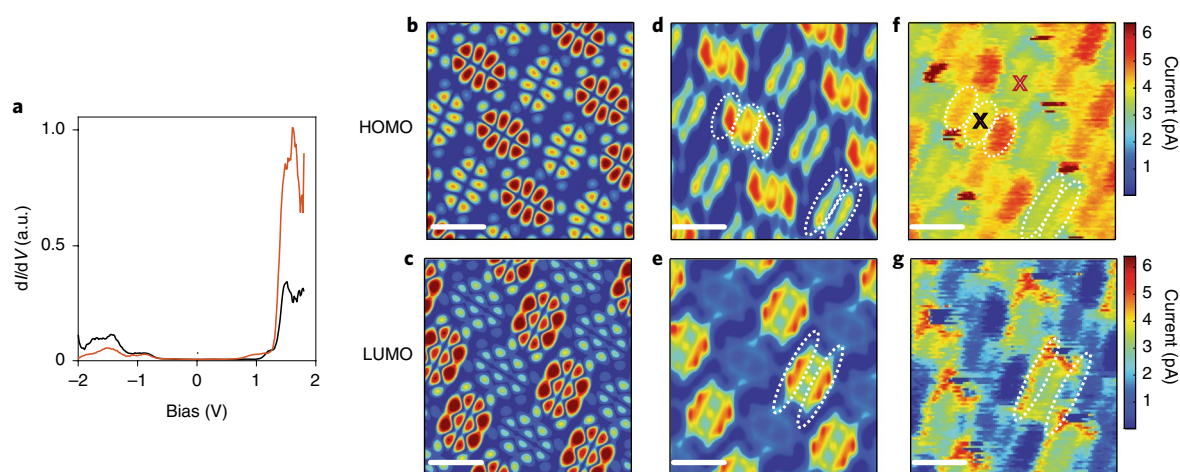


Fig. 4 | Ångström-scale resolution in laser-induced molecular orbital imaging. **a**, Differential conductance (dI/dV) measurements on an individual PTCDA molecule constituting a four-monolayer-thick multilayer assembly on a Au(111) surface. The two curves are measured on PTCDA molecules in adjacent rows. The spatial positions of the nanotip during the measurement are indicated by coloured crosses in **f**. The d.c. bias and set-current before the start of the measurement are -2 V and 50 pA, respectively. **b,c**, Simulated constant-current (50 pA) STM images of the HOMO and LUMO of PTCDA molecules constituting a four-monolayer thick multilayer on top of Au(111), respectively, by utilizing the Tersoff–Hamann approximation (Supplementary Section 8). **d,e**, Simulated STM images obtained by convoluting the images given in **b** and **c** with an s-type wavefunction of the nanotip of the STM with a decay length of 1.8 Å along the vertical direction and 0.8 Å along the horizontal direction. **f,g**, Experimentally measured spatial distribution of the laser-induced tunnelling current for the HOMO (-1.8 V; **f**) and LUMO (1.4 V; **g**) orbitals. Scale bars in all the panels denote a spatial distance of 1 nm. White dashed circles in **d–g** are guides to the eye. Steady-state STM imaging was performed in the constant-current mode at a set-point current of $I_{dc} = 50$ pA. The reproducibility of the data in **f** and **g** was confirmed in five individual measurements.

Electronic coherences, which arise from interactions between laser pulses and a monolayer of PTCDA molecules on Au(111), involve both molecular and surface states. We have grown multilayers of PTCDA molecules on top of the Au(111) surface to observe coherences arising purely from the valence electronic states of the molecules. Weak van der Waals coupling between the molecular layers ensures that the upper layer can be sufficiently decoupled from the Au(111) surface³⁶. The differential conductance measurement for the four-monolayer system is shown in Fig. 4a. There is no longer any trace of the surface state and the HOMO–LUMO gap is of the order of around 2.5 – 3.0 eV. This energy gap can be overcome by single-photon transitions involving the blue tail of the pulses, or two-photon transitions^{17,37} involving the pulses's peak frequency. Hence, when a laser pulse interacts with upper-layer PTCDA molecules whose HOMOs (-1.8 V) have been lifted close to the Fermi level of the nanotip, oscillations between HOMO and LUMO are expected, but with a frequency that will be considerably different from that of the one-monolayer case due to a different energy gap. This strategy allows for laser-induced spatial imaging of the frontier molecular orbitals, as shown in Fig. 4f,g. At variance with the one-monolayer case, not all molecules lead to the same laser-induced tunnelling current: half of the molecules, organized in parallel rows, lead to considerably higher currents than the other half. The rows reflecting the HOMOs are accompanied by rows with very low laser-induced tunnelling current in the LUMOs (Fig. 4g). By contrast, when the LUMOs of the latter rows become apparent, the HOMOs in the former rows are nearly invisible (Fig. 4f). As shown by extensive DFT calculations for the four-monolayer PTCDA/Au(111) system, this behaviour is the consequence of the specific vertical stacking of the PTCDA molecules: the delicate balance between intralayer hydrogen bonding and interlayer π – π interactions forces PTCDA molecules in the higher layers to displace horizontally (~ 1 Å) with respect to molecules in the lower layers. This leads to a LDOS where molecules in one of the rows have a higher DOS than those in the adjacent rows (Fig. 4a and Supplementary Section 8). Figure 4b,c shows

simulated STM images resulting from the Tersoff–Hamann approach³⁸. As the calculated images are obtained with infinite spatial resolution, comparison with experiment requires convolution with the wavefunction of the nanotip, which can be modelled by an s-wave with decay lengths of 1.8 and 0.8 Å along the vertical and horizontal directions, respectively. The results shown in Fig. 4d,e are in good agreement with the experimentally measured spatial profiles. It is worth noting that near-infrared laser pulses can achieve ångström-scale resolution, several orders of magnitude below their diffraction limit^{39,40}.

Real space-time images as a function of the delay between pulses 1 and 2 are shown in Fig. 5d. Pronounced oscillation of the electron density between the HOMO and LUMO can be observed. The temporal evolution of the populations in HOMO and LUMO levels as a function of the delay between pulses 1 and 2—obtained by integrating the individual panels in Fig. 5d—is shown in Fig. 5e. Counter-phase oscillations of the HOMO and LUMO populations, with a period of ~ 1.4 fs, can be clearly seen, which is approximately half of the period of the oscillation observed in the one-monolayer case (Fig. 3f) and corresponds to a frequency that matches the energy separation between the HOMOs and the LUMOs in the four-monolayer system. Both the counter-phase character of the oscillations and their frequency are very well reproduced by the two-level formula in which the experimental HOMO–LUMO gap, an electronic decoherence time of ~ 10 fs, an electric-field strength of $\varepsilon \approx 0.25$ V Å⁻¹ and transition dipole moments of 0.8 a.u. ($\mu_{lu}^{\parallel}$) and 0.1 a.u. ($\mu_{lu}^{\perp}$) are used. The values of the transition dipole moment are compatible with those obtained from our DFT calculations. The only components of the transition dipole moments that are notably different from zero lie in the molecular plane. Thus, dipole couplings between molecular states are possible as the polarization axis of the laser pulses is at 45° with respect to the molecular plane (Fig. 1b). At variance with the one-monolayer case, the amplitude of the measured oscillations does not decrease monotonously with the delay between pulses 1 and 2. This is probably due to the competition between one- and two-photon transitions, as well as the

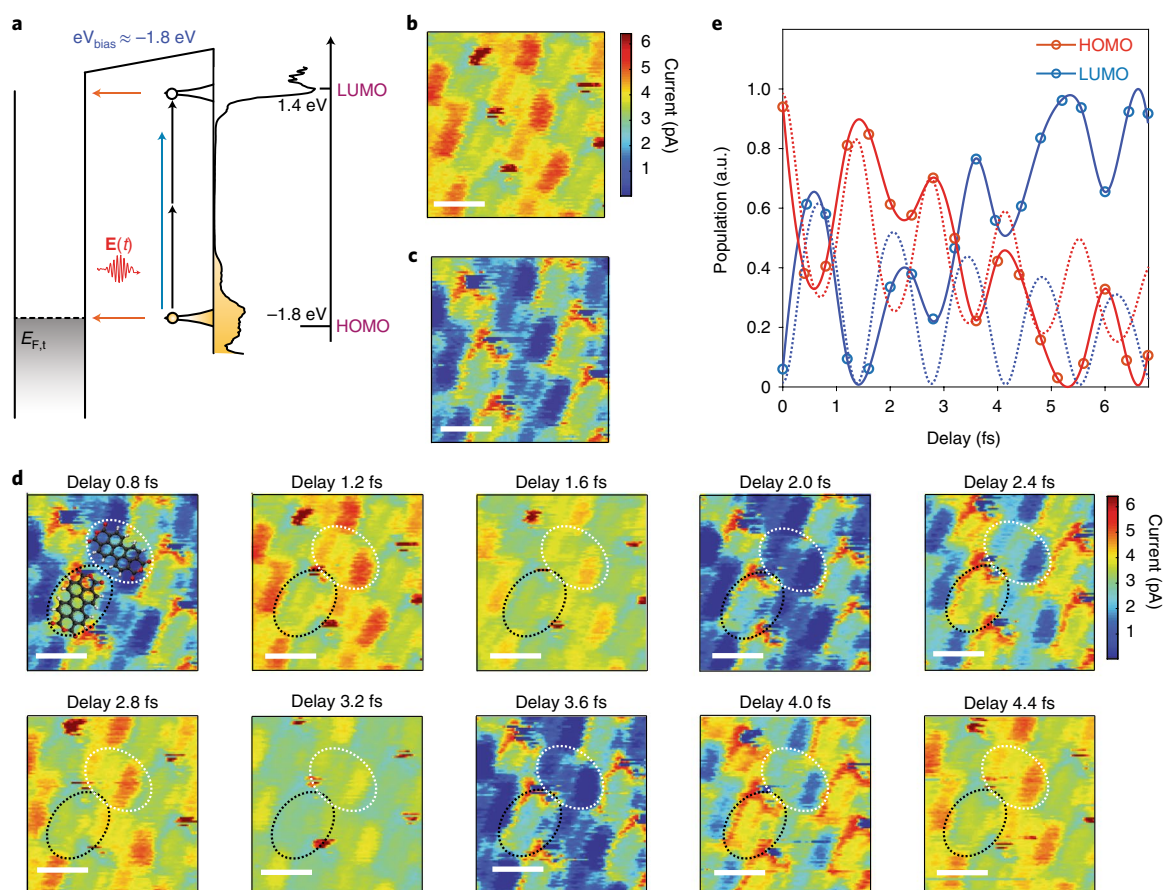


Fig. 5 | Tracking coherent interference of valence electronic states in molecules. **a**, Schematic illustration of the photon-induced transitions in the four-layer experiment. At a bias where the HOMO of a PTCDA molecule rises close to $E_{F,t}$, photons of the laser pulse can dipole couple the HOMO with the LUMO of a PTCDA molecule either by a sequential two-photon transition (black arrows) or by a single-photon transition from the blue tail of the laser pulse (blue arrow). **b,c**, Spatial variation of the ultrafast laser-induced tunnelling current on PTCDA molecules in the four-monolayer coverage for the HOMO (-1.8 V; **b**) and LUMO ($+1.4$ V; **c**). **d**, Real-space and real-time resolved maps of the laser-induced tunnelling current as a function of the delay between pulses 1 and 2. Scale bars, 1 nm. Dashed black and white ellipses in all the panels are drawn to highlight the contrast in the variation of the laser-induced tunnelling current upon change of the delay between pulses 1 and 2 in two individual PTCDA molecules undergoing a HOMO to LUMO oscillation. The d.c. bias and set current for constant-current operation mode of the STM are -1.8 V and 50 pA, respectively. **e**, Temporal oscillation of the population in the HOMO and LUMO states as a function of the delay between pulses 1 and 2. Solid lines are experimental results, whereas dotted lines are the simulated temporal evolution of the population in HOMO and LUMO using the two-state analytical model. The reproducibility of the data in **b–d** was confirmed in five individual measurements.

involvement of more than two electronic levels (multiple HOMOs and LUMOs) in the induced dynamics⁴¹.

The capability to image electronic coherences involving valence electronic states in molecules both at their natural length and natural timescales opens completely new avenues to understand chemical transformations driven by electron transfer; for example, in photosynthetic molecules and other light harvesting molecules^{42–44}, and to the unambiguous observation of electron dynamics in complex molecular systems, two-dimensional materials and superconductors.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41566-021-00929-1>.

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Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

Code availability

The codes used for the two-level and DFT simulations in this study are available from the corresponding author on reasonable request.

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Author contributions

M.G. and K.K. conceived the project and designed the experiments. K.K. supervised the project. M.G., A.M.-J and Y.L. built the experimental set-up, performed the experiments and analysed the experimental data. M.P. and F.M. developed the two-state model and performed the DFT calculations. M.P., M.G. and F.M. analysed the theoretical data. All authors interpreted the results and contributed to the preparation of the manuscript.

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Competing interests

The authors declare no competing interests.

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