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Formation of an Organic/Metal Interface State from a Shockley Resonance

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ABSTRACT: The emergence of an organic/metal interface state is studied for the interface between 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) and Ag(100) by means of time- and angle-resolved two-photon photoemission and density functional theory. The interface state is located in the projected band gap of Ag(100), 2.3 eV above the Fermi level, and has an electron lifetime in the 10 fs range. The interface state has no direct counterpart on the clean Ag(100) surface, which only exhibits a broad resonance at ≈1 eV lower energy. Our results thus show that organic overlayers are able to shift such a resonance substantially and even qualitatively change its character to a distinct electronic state at the interface.
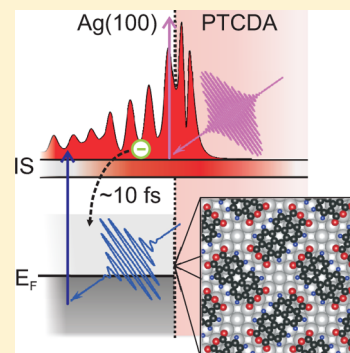
SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

The investigation of well-ordered organic thin films on single crystal metal substrates by means of time- and angle-resolved two-photon photoemission (2PPE) makes it possible to access the fundamental physical processes involved in charge carrier dynamics at organic/metal contacts.[1−4] Such contacts are generally not ohmic but exhibit a tunnelling behavior. For that reason, the lifetime of electronic excitations at the interface and the wave function overlap between metal and molecular derived states decisively influence the efficiency of carrier transport and thus the performance of devices with organic/metal contacts. An important additional factor is the possible existence of new electronic states at the interface.[5] Such interface-specific states can emerge not only as a result of the chemical interaction between molecular layers and the metal surface.[6,7] Analogous to the Shockley states of clean metal surfaces, already the abrupt change of symmetry at the interface can lead to solutions of the Schrödinger equation with a large amplitude at the interface and a probability density that decays rapidly in both materials.[8]

Previous 2PPE and density functional studies clearly showed that the origin of an unoccupied state at the interface between PTCDA and Ag(111) was of that Shockley-type.[8−10] With the adsorption of the PTCDA molecules, the initially occupied Shockley state of clean Ag(111) shifts about 0.6 eV to higher energies. It hybridizes with molecular states and forms an unoccupied interface state with a strong metallic character. Similar interface states have subsequently been found at other organic/metal interfaces.[11−16] Recent work has identified the adsorption height of the molecules and the surface density of the carbon rings as crucial factors for the energy position of the states.[15,16]

In this Letter, we address the question of whether the existence of an occupied Shockley surface state located in the projected band gap of the metal substrate is a necessary prerequisite for the formation of this type of organic/metal interface state. As a model system we use PTCDA/Ag(100). Compared to Ag(111) the projected band gap of Ag(100) is shifted to higher energies. Clean Ag(100) neither supports an occupied Shockley state nor unoccupied states in the band gap other than image-potential states.[17] Nevertheless, in the presence of a PTCDA overlayer, we can clearly identify an organic/metal interface state located within the projected band gap of the metal substrate with 2PPE experiments. Density functional calculations indicate that the interface state emerges from the so-called Shockley resonance at ≈1.3 eV above the Fermi level, which is degenerate with the lower sp-band of Ag(100) and has a large width of ≈1.2 eV.[18]

PTCDA forms long-range ordered monolayers on Ag(100).[19] The adsorption height is slightly smaller than on Ag(111), which points to a stronger adsorbate−surface interaction.[20−23] Our results indicate that this strong organic/metal interaction shifts the Shockley resonance by almost 1 eV to higher energy and thereby into the projected band gap. As a consequence, the electrons excited into this state stay localized at the interface until they decay inelastically by electron hole-pair decay on a 10 fs time scale.

The single-color UV 2PPE spectra of clean and PTCDA covered Ag(100), recorded at normal emission ($\vartheta = 0°$), are displayed in Figure 1a. The energy is given as the energy of the
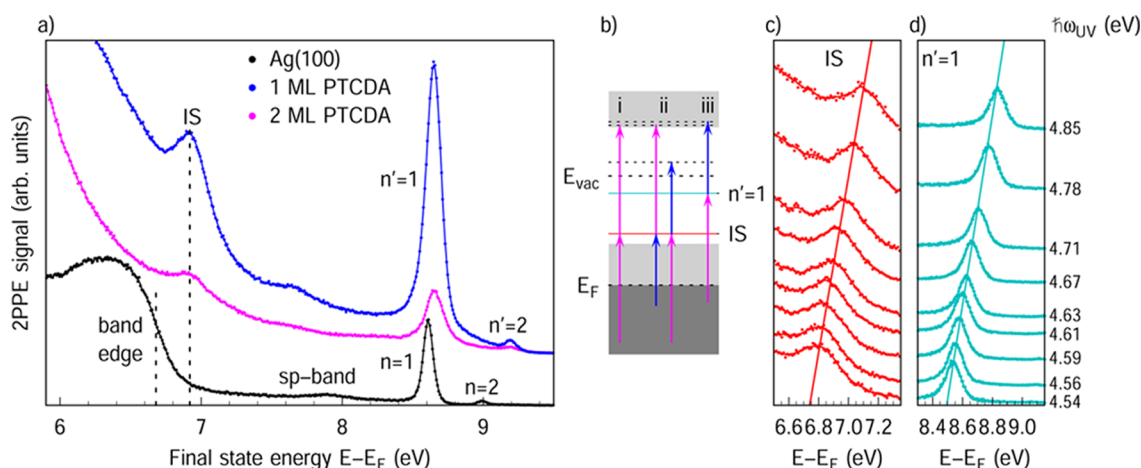
Figure 1. (a) 2PPE spectra of Ag(100) and PTCDA/Ag(100) recorded at normal emission ($\vartheta = 0°$) with UV pulses. The spectrum of clean Ag(100) is scaled. (b) Excitation scheme for (IS) and ($n' = 1$) using only UV (*i*) and blue+UV (*ii + iii*). (c,d) UV 2PPE spectra of (IS) and ($n' = 1$) with varying photon energies. The lines mark the expected peak positions for a linear dependency on the UV photon energy.

photoemitted electrons with respect to the substrate Fermi level E_F (final state energy). For clean Ag(100), three distinct signals are observed at final state energies above 7.4 eV. The two peaks on the high energy side of the spectrum are the first and second image-potential states ($n = 1,2$). The third signal does not originate from an electronic surface state, but from an excitation between Ag-bulk bands due to a direct nonresonant two-photon transition from the lower to the upper *sp*-band.[24,25] In addition, a broad signal from unoccupied states is observed below 6.68 eV. The large intensity indicates a contribution from the Shockley resonance due to a stronger overlap with final free electron states. However, due to its large intrinsic line width, an unambiguous identification of the resonance is not possible on the basis of the 2PPE data.

After adsorption of 1 ML PTCDA, the three isolated peaks above 7.4 eV can still be clearly observed, albeit at slightly different energies. The most striking feature, however, is the occurrence of a new signal (IS) at 6.92 eV. The intensity of this state decreases substantially when the PTCDA coverage is increased to 2 ML, whereas the energetic position is unchanged. This indicates that (IS) is located at the interface between the substrate and the first monolayer.

In order to demonstrate that (IS) originates from an unoccupied electronic state, 2PPE spectra have been recorded for different UV photon energies. The peak position of (IS) shifts linearly as a function of UV photon energy (cf. Figure 1c) with a slope of 1.01 ± 0.10. Additionally, the UV energy dependency of the unoccupied ($n'=1$) is shown in Figure 1d for comparison. The linear slope reveals that, for both states, the emission takes place by absorption of one UV photon. Thus, it can be concluded that (IS) is an unoccupied state at intermediate energy $E_{IS} = 2.25 \pm 0.03$ eV. The corresponding 2PPE process is illustrated in Figure 1b*i*. The lower *sp*-band edge is located at 2.02 ± 0.10 eV for clean Ag(100) at normal emission. The signal (IS) is therefore situated in the band gap.

With increasing emission angles, the signal (IS) shifts to higher energies (cf. Figure 2a). The dispersion of (IS) is shown in Figure 2b along the Ag(100) $\overline{\Gamma X}$ direction. For $k_\| < 0.35$ Å^{-1}, (IS) exhibits a parabolic dispersion. In order to extract the effective mass a free-electron like parabola $E(k_\|) = \hbar^2 k_\|^2 / 2m_{eff} + E_0$ was fitted to the data around the $\overline{\Gamma}$-point, resulting in an effective mass of $m_{eff}^{IS} = (0.61 \pm 0.10)m_e$. The small value for m_{eff} is an indication that electrons excited
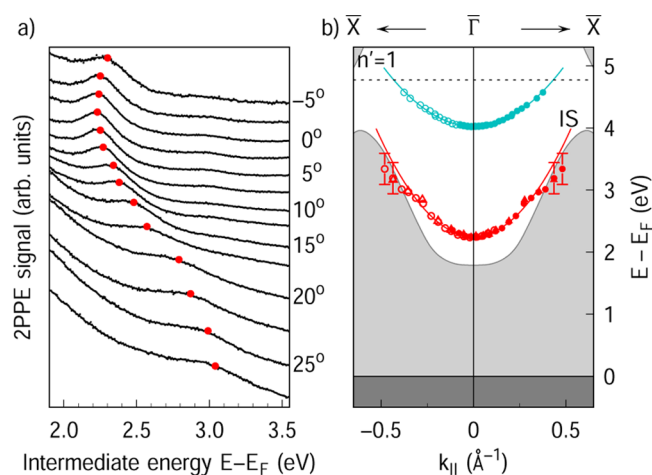

Figure 2. (a) 2PPE spectra measured at different emission angles for 1 ML PTCDA/Ag(100) using only UV. The red dots mark the peak maxima. (b) Dispersion of (IS) and ($n' = 1$) plotted in the projected band structure. Occupied (unoccupied) bulk bands are shaded dark-gray (light-gray). For (IS), two different data sets are shown to emphasize the reproducibility (dots and triangles).

into (IS) are delocalized parallel to the surface. Notably, m_{eff} is reminiscent of an *sp*-band electron and hence a strong indication for the main origin of (IS) as a metal state. At larger parallel momentum ($k_\| \geq 0.35$ Å^{-1}), a deviation from parabolic behavior is observed. The line width broadens significantly, and the band becomes less dispersive.

In order to investigate the electron dynamics, time-resolved two-color 2PPE experiments were performed by recording the emission intensity as a function of pump−probe delay. The energetic position of (IS) permits the use of blue and UV photons. The respective 2PPE processes are depicted in Figure 1b*ii* and result in different final state energies. The signal (IS) can be populated using blue photons $\hbar\omega_{blue}$, and the excited electrons are photoemitted by absorption of $\hbar\omega_{UV}$ photons. This leads to a final state energy almost equal to the signal of the ($n'=1$) image-potential state of PTCDA/Ag(100), which is investigated using the reversed pulse sequence (cf. Figure 3b*iii*). The 2PPE signal of the ($n'=1$) is considerably more intense and therefore dominates in the corresponding pump−probe trace shown in Figure 3a. Positive delay times correspond to the UV
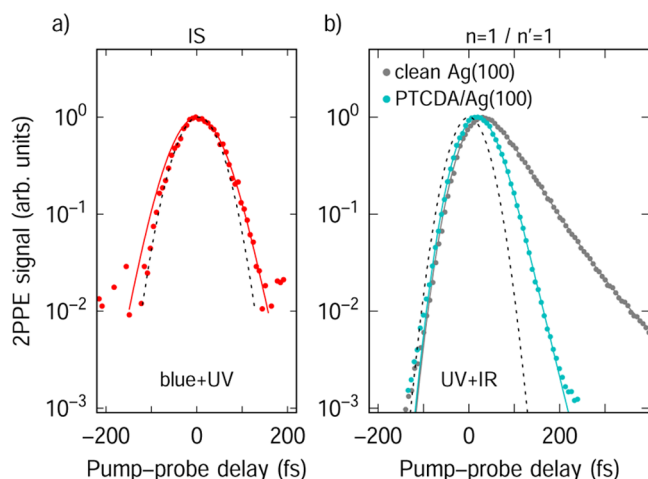
a)   IS   b)   n=1 / n'=1

Figure 3. 2PPE spectra as a function of time delay recorded at the peak maxima of (a) (IS) and (b) ($n=1/n'=1$). The photon combination UV+blue was used for (a) and UV+IR for (b). A positive delay corresponds to the UV pulses arriving first. The dotted lines represent the cross correlation. The solid line in (a) corresponds to fixed lifetimes of $\tau_{IS} = -18$ fs and $\tau_{n'=1} = 20$ fs, and the solid lines in (b) depict best fits using a rate equation model to describe the decay.

pulses arriving on the sample first. The exponential signal decay $\propto \exp{-t/\tau}$ for these delays originates from the lifetime τ of electrons excited into the ($n'=1$). Considering the reversed excitation scheme, one would expect the exponential decay of electrons excited into the (IS) for negative delays. However, though a small deviation of the recorded data points from the cross correlation (dashed line) can be observed, it is not as apparent as for positive delays (cf. Figure 3a). Due to the dominating ($n'=1$) signal, the overall signal-to-noise (S/N) ratio of the pump–probe trace is not sufficient to extract both lifetimes simultaneously by fitting a rate equation model to the data. However, it is possible to state an upper limit for the inelastic lifetime of (IS) by comparing the data to a rate equation simulation with fixed lifetimes of both excited states. Using $\tau_{n'=1} = 20$ fs, an upper limit for (IS) of $\tau_{IS} \leq 18$ fs can be given. Alternatively, electrons can be excited into (IS) using UV photons $\hbar\omega_{UV}$, and the transient population is probed by blue photons $\hbar\omega_{blue}$. However, this excitation scheme leads to a lower final state energy, and the (IS) signal is masked by major one-color 2PPE contributions including the trailing edge of the secondary cutoff and the excitation of hot electrons. Time-resolved measurements therefore also suffer from a minor (S/N) ratio and only permit the conformation of the aforementioned upper limit. A lower boundary for the inelastic lifetime of (IS) can be given from the line width Γ_{IS} in the (UV+UV) spectra (Figure 1a), which leads to $\tau_{IS} = \hbar/\Gamma_{IS} \geq 3$ fs. Taken as a whole, the lifetime of electrons excited into (IS) therefore can be narrowed down to 3 fs $\leq \tau_{IS} \leq 18$ fs.

In our 2PPE experiments, we observe an unoccupied, PTCDA-induced electronic state (IS) that is strongly dispersive and located at the interface between the first monolayer and the substrate. Energetically, the interface state lies within the projected band gap around the $\bar{\Gamma}$-point. The ultrashort lifetime indicates a considerable overlap of the interface state wave function with the metal. The strong similarities to our observations for the interface state formation with adsorption of PTCDA and NTCDA on Ag(111)[8,15] suggest an analogue formation mechanism. Since no occupied Shockley state exists on Ag(100), we interpret this Shockley-type interface state

resulting from the upshifted Ag(100) Shockley resonance due to the interaction of the PTCDA molecules with the Ag(100) surface. Assuming the Shockley resonance on clean Ag(100) is located at $E_{SR} - E_F = 1.3$ eV,[18] the interaction of the molecules with the surface induces an energetic shift of $\Delta E \approx 0.95$ eV. Thus, the larger bonding strength and lower adsorption height of PTCDA on Ag(100)[21] lead to an even larger energy shift in comparison to Ag(111) ($\Delta E \approx 0.57$ eV[15]). This is in agreement with our findings for Shockley-type interface states.[15] The interfacial interaction is very substantial and causes the Shockley resonance to be shifted into the projected band gap of the substrate. This reduces the coupling to the lower sp-band and therefore drastically reduces the intrinsic line width. Although the formation of the interface state is a more complex phenomenon, the shift of a surface resonance into the projected band gap and the concurrent decoupling from bulk states is not unique for organic adlayers, but has been observed for other types of interfaces before.[26,27] Presumably, the reduced coupling is also the reason that, in contrast to the resonance of Ag(100), the interface state can be identified in the 2PPE spectra.

The interpretation of the 2PPE results can be further substantiated by time-resolved experiments on the first image-potential state. With the emergence of the interface state for PTCDA covered Ag(100), we observe a strong decrease in the inelastic lifetime of the first image-potential state ($n'=1$) (cf. Figure 3b). For clean Ag(100), the fit of a rate equation model to the data results in a lifetime of $\tau_{n=1} = 59 \pm 2$ fs in good agreement with previous studies.[17] The lifetime of the first PTCDA induced image-potential state $\tau_{n'=1} = 20 \pm 3$ fs is considerably shorter in comparison to Ag(100). On noble metal (111) surfaces, the unoccupied part of the Shockley surface state lies within the projected band gap and states an effective decay channel for electrons in the higher lying image-potential states.[28] The main reason for this is the strong overlap between the Shockley state and the image-potential state in the surface region. In the case of Ag(100), PTCDA induces a shift of the resonance into the band gap, which increases the probability density in the interface region. The overlap with the first image-potential state is therefore stronger, thus decreasing its inelastic lifetime.

In order to verify the interpretation of our experimental findings, we carried out DFT calculations. Calculations for clean Ag(100) performed with too few atomic layers of silver, e.g., nine layers, deceptively suggest the Shockley resonance appears as one discrete band, similar to Shockley states. When the number of atomic layers is strongly increased, it becomes apparent that all bands between E_F and the band edge have an increased probability density in the surface region, but none can be considered a true surface state. Exemplarily, Figure 4a displays a band at $E - E_F = 1.31$ eV for a 60 atomic layer slab. The inset shows the probability density in the surface region.[29] The maximum surface probability density is located at $E_{SR} - E_F \approx 1.3$ eV, in good agreement with previous studies.[18] However, as stated before, the Shockley resonance is intrinsically very broad. This changes drastically when PTCDA is adsorbed. In this case, a Shockley-type surface state is observed (cf. Figure 4b), situated at $E_{IS} - E_F = 1.93$ eV at $\bar{\Gamma}$. This electronic state is very similar to other Shockley-type interface states on Ag(111),[10,16] but with an even higher probability density in the vicinity of PTCDA and a bulk penetration of around $p = 60\%$. Note that accurate quantitative agreement with the experiments cannot be
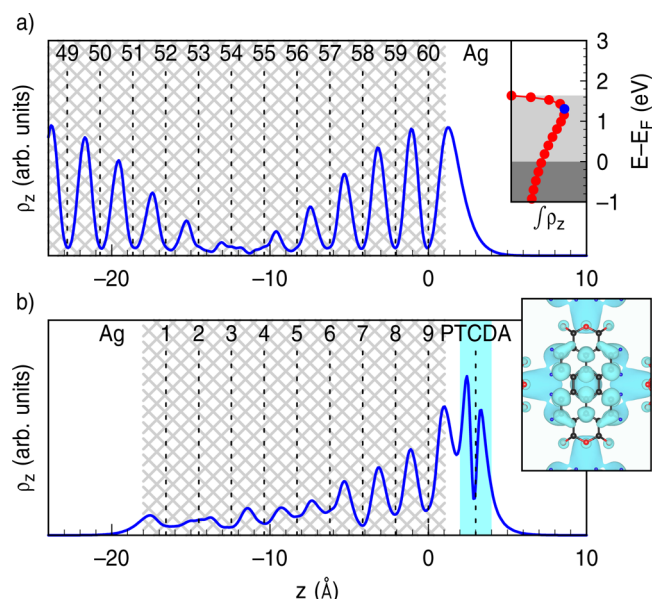
Figure 4. DFT calculations for (a) clean Ag(100) employing 60 atomic layers and (b) PTCDA/Ag(100) consisting of nine silver layers. (a) Probability density ρ_z perpendicular to the surface for a band at $E - E_F = 1.31$ eV. The inset shows the distribution of the surface probability density for all bands in the vicinity of the expected Shockley resonance position. (b) Probability density ρ_z of the interface state. The bulk region is hatched in light-gray. The inset depicts the probability density of the interface state band parallel to the surface at the $\bar{\Gamma}$-point for one PTCDA molecule of the surface unit cell.

expected since the interface state is a highly excited state. Such states can not be described very accurately by standard exchange-correlation functionals. However, the strong upshift is described qualitatively correct and the energy difference between band edge ($E_{edge} = 1.64$ eV) and interface state $E_{IS} - E_{edge} = 0.30$ eV agrees very well with the experimental findings ($E_{IS} - E_{edge} = 0.23$ eV). More accurate calculations (e.g., with the GW approximation) are not yet feasible for the system size at hand.

Around the $\bar{\Gamma}$-point, the interface state is located in the band gap of the substrate. Electrons excited into such states are confined to the interface and can only decay inelastically, the dominating channel at a metal interface being electron–hole-pair decay.[30] Following the argumentation of refs 8 and 15, an estimation of the lifetime of the interface state can be derived from the lifetime of the ($n = 1$) image-potential state. For this estimation, one neglects any surface contribution to the decay and assumes that the screening of the Coulomb interaction at the organic/metal interface is the same as on the metal surface. Then the efficiency of the channel is determined by the wave function overlap with bulk silver states and the available number of final states in the metal (phase space). For Ag(100), the ($n = 1$) is located at $E_{n=1} - E_F = 4.0$ eV and has an inelastic lifetime of $\tau_{n=1} = 59 \pm 2$ fs. The results of our DFT calculations show a very small bulk penetration of 5.3% for this state which is in perfect agreement with a theoretical approach using a model potential.[31] For an electronic state with an increased bulk penetration of 60% that is located at 2.25 eV within the projected band gap, a linear scaling with the bulk penetration and energy difference $E - E_F$ leads to a lifetime of $\tau_{IS} = 9$ fs. This estimate agrees with the experimentally deduced lifetime of 3 fs $\leq \tau_{IS} \leq 18$ fs. The lifetime measurements thus fully support the description of the interface state given above.

Our results reveal a similar formation mechanism of an organic/metal interface state with adsorption of a PTCDA overlayer for the two different silver surfaces Ag(111) and Ag(100). Since the interface state of Ag(111) emerges out of a real surface state while its pendent on Ag(100) is a resonance, one might suspect at first glance that the interface state of PTCDA/Ag(100) has more of a metallic character than that of PTCDA/Ag(111). However, one arrives at a different conclusion after taking the different energy positions into account. In the case of Ag(111), the interface state is energetically located between E_F and the first unoccupied molecular state, whereas it lies significantly above the LUMO+1 for Ag(100). Since the molecular π-states tend to be more delocalized with increasing distance to E_F, the higher interface state position with respect to E_F and the stronger molecule surface interaction both suggest a stronger overlap of the interface state with molecular states in the case of PTCDA/Ag(100). Since the interface states originate from a surface state/resonance of the bare substrate, i.e., purely metallic states before PTCDA adsorption, the enhanced mixing with molecular orbitals leads to a decreased metallic character compared to the clean surface. This expectation is supported by our calculations, which reveal a larger penetration of the interface state into the molecular layer and a stronger mixing with molecular states compared to Ag(111). The electron density distribution of the interface state in the vicinity of the adsorbed PTCDA molecules cannot be assigned reliably to a specific state, but shows strong similarity with the LUMO+3/4 states (cf. Figure 4).

In conclusion, we have identified an unoccupied interface state (IS) for PTCDA/Ag(100), which results from the interaction of the Shockley resonance of Ag(100) with molecular PTCDA states. The investigations demonstrate that Shockley-type interface states can just as well emerge at organic/metal systems from Shockley resonances. The large bonding strength of PTCDA on Ag(100) causes the Shockley resonance to be shifted into the band gap, which reduces the line width drastically and renders possible the identification in 2PPE experiments in the first place. The upshift in energy leads to an extensive phase space for decay by electron–hole pair creation. In conjunction with the considerable wave function penetration into the metal, this causes the interface state to decay very efficiently. Based on the similar formation mechanism compared to PTCDA/Ag(111) and other inter-faces,[11−16,27] we think that such interface states are a more general phenomenon for a larger class of organic/metal or even semiconductor/metal interfaces. Our results show that the exact properties of the interface states are not only determined by the molecular electronic structure and the interaction at the interface, but sensitively depend on the surface band structure of the substrate.

■ EXPERIMENTAL AND THEORETICAL METHODS

The ultrahigh vacuum chamber (base pressure 5×10^{-11} mbar) and the optical 2PPE setup have been described elsewhere.[32] The measurements were carried out making use of the fundamental (IR), the frequency doubled (blue) and tripled (UV) p-polarized laser pulses of a Ti:Sa-oscillator. The photon energies were $\hbar\omega_{IR} = 1.56$ eV, $\hbar\omega_{blue} = 3.07$ eV and $\hbar\omega_{UV} = 4.64$ eV with pulse durations of $\tau_{IR} = 40$ fs, $\tau_{blue} = 55$ fs and $\tau_{UV} = 70$ fs. The overall energy resolution of the setup was 65 meV with an angular resolution of 1.2°. The Ag(100) surface was prepared by sequences of argon sputtering (3 μA/cm^2, 15 min)

and annealing (60 min, 725 K) cycles. The PTCDA thin films were deposited at a rate of 0.2−0.4 ML/min onto the sample held at 273 K. The film thickness was determined by the attenuation of the Ag_{3d} signal in the X-ray photoelectron (XPS) spectra. The monolayer was checked for long-range order using low-energy electron diffraction (LEED).[19]

The DFT calculations were performed with the VASP[33,34] code that employs periodic boundary conditions and a plane wave basis set. Self-consistent (SC) calculations were performed within the generalized gradient approximation (GGA) using the PBE functional.[35] The projector-augmented wave (PAW) method[36,37] was employed allowing for a kinetic energy cutoff of 340 eV. The Brillouin zone of Ag(100) was sampled by a $12 \times 12 \times 1$ and the PTCDA/Ag(100) supercell by a $3 \times 3 \times 1$ $\bar{\Gamma}$ centered Monkhorst-Pack k-mesh.[38] The electronic SC cycles were carried out until the energy difference between consecutive steps converged to 10^{-5} eV. In order to describe the Shockley resonance adequately, the number of silver layers were varied between 9 and 60 for Ag(100). The calculations for PTCDA/Ag(100) were performed with the structure and adsorption height taken from previous experimental work.[19,21] The $(4\sqrt{2} \times 4\sqrt{2})R45°$ superstructure has an area of 267 Å^2 and consists of two PTCDA molecules. The PTCDA/Ag(100) calculations were performed with nine layers of silver, leading to a cell containing 288 silver atoms and 76 atoms for the molecules. Geometry optimizations with the D3-BJ correction were also performed,[39] but only led to changes within the experimental error for the C and the anhydride O atoms. The adsorption height for the acylic O was slightly reduced by 0.11 Å in agreement with previous theoretical investigations.[21]

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Notes
The authors declare no competing financial interest.

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