

Electronic Properties of Tetraazaperopyrene Derivatives on Au(111): Energy-Level Alignment and Interfacial Band Formation

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Cite This: *J. Phys. Chem. C* 2021, 125, 19969–19979

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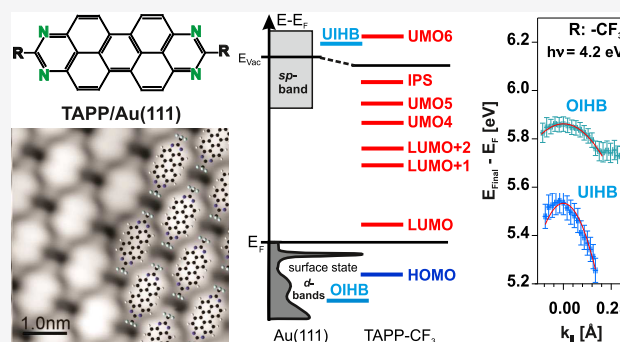
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ABSTRACT: N-heteropolycyclic aromatic compounds are promising organic electron-transporting semiconductors for applications in field-effect transistors. Here, we investigated the electronic properties of 1,3,8,10-tetraazaperopyrene derivatives adsorbed on Au(111) using a complementary experimental approach, namely, scanning tunneling spectroscopy and two-photon photoemission combined with state-of-the-art density functional theory. We find signatures of weak physisorption of the molecular layers, such as the absence of charge transfer, a nearly unperturbed surface state, and an intact herringbone reconstruction underneath the molecular layer. Interestingly, molecular states in the energy region of the *sp*- and *d*-bands of the Au(111) substrate exhibit hole-like dispersive character. We ascribe this band character to hybridization with the delocalized states of the substrate. We suggest that such bands, which leave the molecular frontier orbitals largely unperturbed, are a promising lead for the design of organic–metal interfaces with a low charge injection barrier.



INTRODUCTION

Organic electron-transporting (n-channel) semiconductors are of particular interest for their implementation in field-effect transistors.¹ Replacing carbon atoms by nitrogen atoms in a π -conjugated aromatic molecular backbone typically leads to an energetic stabilization of the frontier orbitals, i.e., the electron affinity (EA) and the ionization potential (IP) increase, while the optical gap size is almost uninfluenced.^{2–5} N-heteropolycyclic aromatic molecules are thus expected to be promising candidates for n-channel semiconductors. Regardless of n- or p-channel semiconducting behavior in a transistor, the energetic positions of the electron affinity level or the ionization potential are the relevant quantities for device performance. The IP can be determined by photoemission spectroscopy (e.g., ultraviolet photoemission spectroscopy (UPS),^{6–9} two-photon photoemission (2PPE)^{10–13}) or scanning tunneling spectroscopy (STS).¹⁴ For the identification of affinity levels, inverse photoemission,^{15,16} 2PPE, or STS can be used. All methods imply that a former unoccupied molecular state is populated with an electron, creating a transient negative ion resonance. The difference between the IP and EA is the transport gap ($IP - EA = E_{\text{transp.}}$), which is different from the optical gap (highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) transition leading to exciton formation).¹⁷ The latter can be determined in surface-adsorbed molecules with

2PPE,^{10–13,18} differential reflectance spectroscopy,^{19–22} or high-resolution electron energy loss spectroscopy.^{18,23–29}

The electronic structure of free (gas phase) molecules is strongly affected in the condensed phase and in particular when the molecules are adsorbed on metal surfaces. The adsorption geometry of the organic compound at the hybrid organic/metal interface has a pronounced influence on the interfacial electronic structure.^{6–9,20,30–38} The interfacial electronic structure, i.e., the wave function mixing (hybridization) between localized molecular electronic states and metal bands, is particularly important for the interfacial charge injection properties and accordingly crucial for the performance of organic field-effect transistors. Hybridization is a necessary prerequisite for interfacial band formation, which can be identified via dispersing states in angle-resolved photoemission experiments. Interfacial band formation has been shown in the case of strong electron acceptors (tetrafluoro-tetracyanoquinodi-methane (F_4TCNQ)/Au(111),^{39,40} 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA)/

Received: May 12, 2021

Revised: August 18, 2021

Published: September 2, 2021



Ag(110),⁴¹ and 1,4,5,8-naphthalenetetracarboxylic-dianhydride (NTCDA)/Ag(111)^{41,42}) and a donor (tetrathiafulvalene (TTF)/Au(111)⁴⁰) adsorbed on noble-metal surfaces. Recently, we demonstrated interfacial band formation for an N-heteropolycyclic molecule, a 1,3,8,10-tetraazaperopyrene derivative (TAPP-CF₃, see Figure 1) adsorbed on Au(111) in the

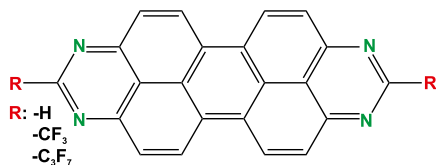


Figure 1. 1,3,8,10-Tetraazaperopyrene (TAPP) derivatives investigated in the present study.

energy regime of occupied and unoccupied electronic states occurred.⁴³ TAPPs belong to the class of N-heteropolycyclic aromatics, which have shown promising results as organic semiconductors in thin-film transistors.^{44,45} The TAPP-H/Cu(111) system has been studied with respect to thermally activated and surface-assisted reactions using scanning tunneling microscopy (STM).^{46,47}

In this study, we used complementary experimental techniques, namely, STS and 2PPE in combination with density functional theory (DFT) to determine the electronic properties of a 1,3,8,10-tetraazaperopyrene derivative (TAPP-CF₃, see Figure 1) adsorbed on Au(111). The adsorption structure of TAPP-CF₃ on Au(111) is analyzed by STM and DFT calculations. 2PPE is applied to study the electronic properties of further TAPP derivatives (TAPP-H and TAPP-C₃F₇, see Figure 1). For all TAPP derivatives, we determined the energetic position of several affinity levels as well as the ionization potential. Hybrid band formation in the energy region of occupied and unoccupied delocalized states is identified via angle-resolved 2PPE.

METHODS

STS and 2PPE experiments were carried out with two different setups under ultrahigh-vacuum (UHV) conditions. In both cases, a clean Au(111) substrate was prepared by a standard procedure of sputtering–annealing cycles. The TAPP molecules were deposited from an effusion cell held at a temperature of 520 K, while the Au(111) surface was kept at room temperature. For the STM experiments, the deposited coverage was below one monolayer (ML). This provides clean

areas of Au(111) for tip treatment and reference measurements. To prepare a well-defined ML coverage for the 2PPE experiments, a multilayer coverage was deposited and afterward annealed to 500 K. The desorption of the multilayer was monitored by temperature-programmed desorption measurements (see the Supporting Information).

2PPE Experiments. 2PPE measurements enable the quantitative determination of the energetic position of occupied initial and unoccupied intermediate or final electronic states of the adsorbate/substrate system in a pump–probe scheme.^{11,12,23,48–53} Detailed photon-energy-dependent measurements are needed to assign the observed photoemission peaks to occupied or unoccupied states. Dispersion relations of the electronic states can be obtained by variation of the detection angle (α) as $\hbar k_{\parallel} = (2m_e \cdot E_{\text{kin}})^{1/2} \sin \alpha$, where m_e denotes the free electron mass and $k_{\parallel} = 0$ corresponds to electrons detected along the surface normal (i.e., $\alpha = 0$). The tunable femtosecond laser system, which delivers laser pulses over a wide range of photon energies, and the 2PPE setup are described elsewhere.⁵⁴

STM/STS Experiments. STM and STS measurements have been carried out on a submonolayer coverage of TAPP-CF₃ on Au(111) at a temperature of $T = 4.5$ K under UHV conditions. The STM tip was prepared by indentation into the clean Au crystal. Differential conductance (dI/dV) spectra and maps were recorded using a lock-in amplifier at a frequency of $f = 937$ Hz with a modulation amplitude of $V_{\text{RMS}} = 5$ mV. The metallic properties of the tip were checked by recording dI/dV spectra on clean areas of the Au(111) substrate, where only in the energy regime of the occupied Au(111) band structure, the Shockley-type surface state, the sp- and d-bands were detected while the spectrum was featureless otherwise. Additional peaks in the dI/dV spectra can thus be associated with molecular resonances.

DFT Calculations. State-of-the-art DFT calculations of surface-bound molecules were performed with the FHI-aims package⁵⁵ using the PBE exchange–correlation functional together with van der Waals (vdW) corrections based on the TS^{surf} method.⁵⁶ FHI-aims employs numeric atom-centered orbitals. For this work, we used the default tight settings for the basis set, except for the onset of the cutoff potential for the gold basis functions, which was increased to 5 Å to get a more accurate description of the surface dipole. The unit cell was sampled with a 7×7 generalized Monkhorst–Pack grid and a Gaussian smearing of 0.1 eV. The interface was modeled using periodic boundary conditions, using a five-layer slab for the metal and approximately 80 Å of vacuum. To electrostatically

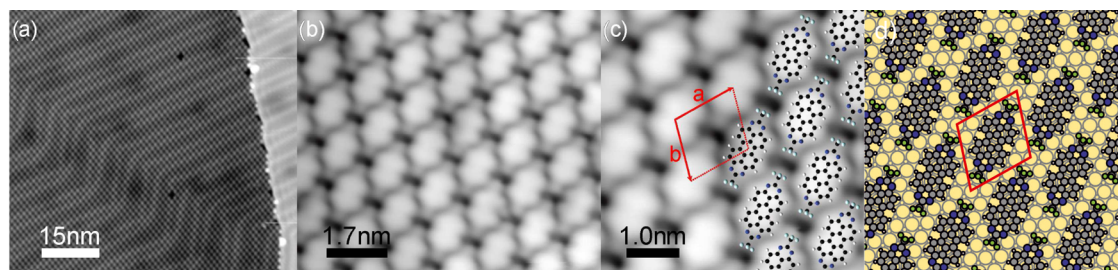


Figure 2. STM topography of a submonolayer coverage TAPP-CF₃ on Au(111). (a) Large-scale image revealing densely packed islands with the size limited by monoatomic steps of the Au(111) surface. $V_{\text{bias}} = 300$ mV, $I_t = 300$ pA. (b) Close-up view of the monolayer showing the individual molecules. $V_{\text{bias}} = -300$ mV, $I_t = 300$ pA. (c) Close-up view of the superimposed structure model and unit cell of the molecules periodic lattice. The unit cell size is $a = 1.23(5)$ nm \times $b = 1.17(5)$ nm with an angle of $104(3)^\circ$ between a and b , resulting in a unit cell area of $1.39(5)$ nm². $V_{\text{bias}} = -300$ mV, $I_t = 300$ pA. (d) Theoretical structure model (see text).

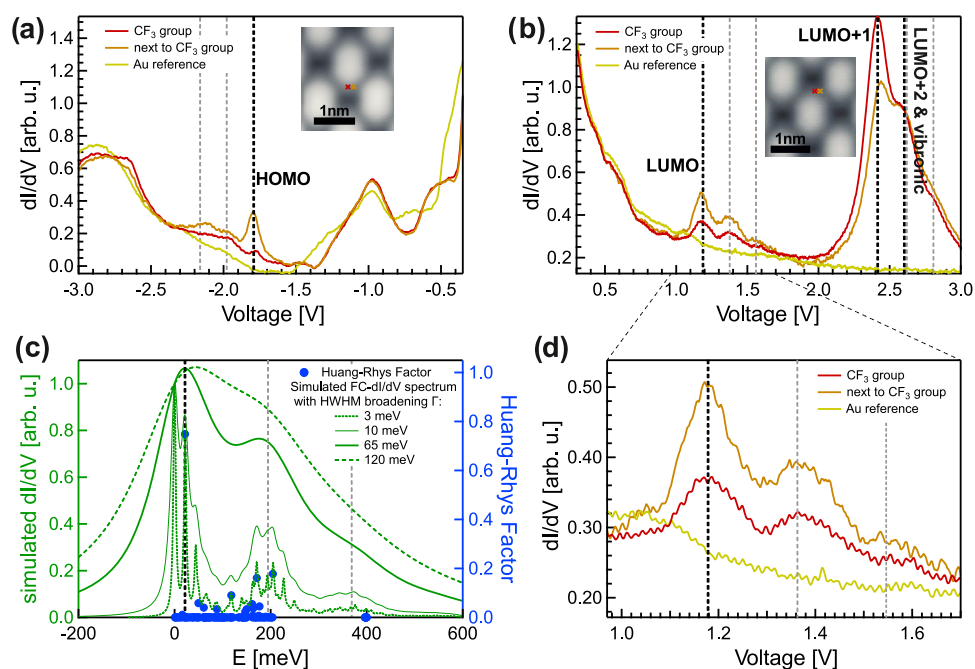


Figure 3. (a, b, d) Tunneling spectra recorded at negative (a) and positive (b) bias voltages at different positions on an individual TAPP- CF_3 molecule. (d) Zoom-in view of the region around the LUMO resonance around 1.0–1.7 V. The background spectrum of the bare Au(111) surface is displayed in yellow. The insets show STM images with color markers to indicate where the individual spectra were taken. The intensity of the molecular resonances varies strongly across the molecule. The feedback parameters for the STM images were $V_{\text{bias}} = 0.3$ V and $I_t = 300$ pA. The spectra were recorded in constant-current mode with a tunneling current of $I_t = 1$ nA. (c) Huang–Rhys factors (blue dots) and simulated Franck–Condon dI/dV spectra (green lines) of TAPP- CF_3 obtained from gas-phase DFT simulations (for details, see the [Methods](#) section and ref 59). Different broadenings were used to simulate different lineshapes. A half-width at half-maximum (HWHM) broadening of 65 meV produces lineshapes that agree well with the experimental lineshapes of HOMO, LUMO, and LUMO + 1.

decouple the slabs perpendicular to the surface, a dipole correction was employed.⁵⁷ To find the optimal adsorption position, the molecule as well as the two topmost Au layers were allowed to fully relax until the forces fell below 0.02 eV/Å.

For the analysis of the vibronic nature of side bands in the dI/dV spectra, we calculated the relaxed structures of the neutral and negatively charged free molecule (gas phase), using the B3PW91 functional and the 6-31g(d,p) basis set as implemented in the Gaussian 09 package.⁵⁸

RESULTS AND DISCUSSION

We first focus on the TAPP- $\text{CF}_3/\text{Au}(111)$ system and elucidate the adsorption structure by means of STM and DFT since it strongly influences the interfacial electronic structure. We then analyze the electronic properties of a (sub)monolayer coverage of TAPP- CF_3 molecules on the Au(111) surface in detail using STS and 2PPE, and complement these findings with DFT calculations. Subsequently, a comparison to other TAPP derivatives (TAPP-H and TAPP- C_3F_7 , see [Figure 1](#)) will be drawn by 2PPE measurements.

Adsorption Structure of TAPP- CF_3 on the Au(111).

STM images reveal that TAPP- CF_3 molecules form densely packed extended islands with mono-domain structures up to 100 nm diameter ([Figure 2a](#)). We observe no preferential orientation of the islands with respect to the underlying Au(111) substrate, suggesting a weakly physisorbed state. This scenario is further supported by the herringbone reconstruction remaining intact below the molecular layer. A close-up view on the molecular arrangements reveals a flat adsorption

geometry of the individual molecules ([Figure 2b](#)) and allows for a structural model of the molecular layer ([Figure 2c](#)).

To understand the formation of this self-assembled structure, we performed dispersion-corrected DFT calculations. In a first step, we calculated the interaction energy between two parallel aligned TAPP- CF_3 molecules in the gas phase at different relative positions and distances (see the [Supporting Information](#)). The energetically beneficial relative positions obtained with this approach qualitatively agree very well with the experimental unit cell ([Figure 2d](#)). In a second step, we determined the adsorption site of TAPP- CF_3 by running several full geometry optimizations, with the initial position of the TAPP- CF_3 molecule on the four different high-symmetry points of the Au(111) surface (top, bridge, hexagonal close-packed (hcp), and face-centered cubic (fcc) hollow). The energetically most favorable adsorption site is found when the center of the molecule is above a bridge position. The other adsorption sites are between 10 (top) and 50 (both hollow sites) meV energetically less favorable. From this, it can be concluded that the monolayer structure is mostly determined by intermolecular interactions (as opposed to molecule–substrate interactions), in line with previous conclusion (see above) that the molecule is mostly physisorbed. The adsorption energy (at the bridge site) has an overall value of -2.585 eV, which can be split into a vdW contribution of -2.852 eV and an electronic contribution ($+0.262$ eV). The latter has a positive value, indicating that the adsorption is mainly governed by vdW forces.

Electronic Structure of TAPP- CF_3 on Au(111). To resolve the electronic states of the TAPP- CF_3 molecules, we recorded differential conductance spectra (dI/dV) on the

molecular layer. The spectra of the occupied (negative bias voltage) states are shown in Figure 3a (red and orange spectra) and compared to a background spectrum on the bare Au(111) (yellow). First, we note that the broad peak at -1.0 eV is also present in the spectrum on the bare surface and can be associated with the sp band of Au. Second, the surface state of the Au(111) substrate is shifted toward the Fermi level. Third, we observe an additional resonance at -1.8 eV, followed by a broader satellite structure. These features are only present on the molecular layer and may be associated with tunneling through occupied molecular-derived states. Spectra in the regime of the unoccupied states reveal two resonances at 1.2 and 1.4 V, and two resonances around 2.35 and 2.55 V that only appear on the molecules. Notably, the spectra shown in Figure 3a,b are recorded on and in close vicinity of the CF_3 group and exhibit variations in the relative intensity of the peaks.

A better perception of the variations can be gained from differential conductance maps at the respective energies. These are shown in Figure 4. The maps at 1.2 and 1.4 eV show the

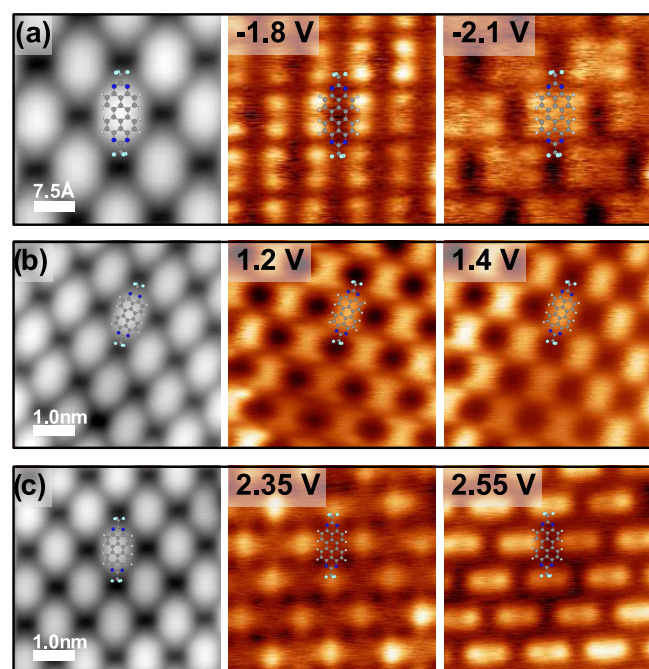


Figure 4. STM images (gray) and differential conductance maps (color) recorded in the same area as the corresponding STM images. The conductance maps were recorded in constant-height mode at the energies of the resonance peak positions, as indicated in the maps. (a) Conductance map at the energy of the molecular HOMO. (b) Conductance maps at the energy of the LUMO. (c) Conductance maps at the energies of the molecular LUMO + 1 and LUMO + 2. The setpoints for the STM images and before taking the maps were for (a, c) $V_{\text{bias}} = 0.3$ V, $I_t = 300$ pA and for (b) $V_{\text{bias}} = 0.5$ V, $I_t = 300$ pA.

largest intensity all over the TAPP- CF_3 's backbone, in agreement with the intensity of these peaks decaying quickly away from the molecule. Interestingly, both maps are very similar. In contrast, the maps at 2.35 and 2.55 eV exhibit the largest intensity at the CF_3 terminations. Again, both maps are similar. The distinct spatial intensities can be ascribed to tunneling through different molecular orbitals. Tentatively, we assigned these to the lowest unoccupied molecular orbital

(LUMO at 1.2 eV) and LUMO + 1 (at 2.35 eV). This assignment will be corroborated by DFT calculations below. The appearance of satellite peaks with the same spatial extent as the main peak is typically ascribed to vibronic states, which arise from the simultaneous excitation of electronic states and vibrational modes in the tunneling process.^{60–66} Further indication of this process is given by the similar spacing of the satellite peaks in LUMO and LUMO + 1.

To sustain the interpretation of the vibronic nature of the side bands, we calculated the expected dI/dV lineshape within the Franck–Condon picture. For this, we considered a free molecule in the gas phase and calculated the relaxed structures of the neutral and negatively charged molecules. From these, we derived the vibrational modes and their corresponding Huang–Rhys factor,⁵⁹ which mimics the electron–vibration coupling strength. Figure 3c shows the Huang–Rhys factors for all modes. There are several modes with a large Huang–Rhys factor, most notably at 22, 50, 118, 162, 172, 177, and 205 meV. To simulate the dI/dV spectrum, we considered individual and coupled modes with a significant Huang–Rhys factor, i.e., higher harmonics of individual and coupling of different modes and their harmonics (“progression of progressions”). Then, the intensities were convoluted with a Lorentzian lineshape.^{59,67} A set of spectra with different Lorentzian widths is shown in Figure 3c (green). The best agreement with the experimental lineshape of the LUMO and LUMO + 1 (consisting of a broad peak and a shoulder) is obtained when applying a Lorentzian width of 65 mV (half-width at half-maximum). We note that the simulations reveal an additional shoulder at ~ 400 meV above the main resonance, which can also be found as a faint signal in the experimental spectra (see close-up view on the LUMO in Figure 3d). The strong similarity of the spectral lineshape of calculated vibronic states and experimental dI/dV spectra, together with the similar spatial extent of the main peak and satellite, strongly suggest a vibronic origin of the satellite peak structure. However, we note that fine details in the relative intensity of main resonance and satellite peak vary across the molecule (compare red and orange spectra in Figure 3b,c). This behavior is not captured in the Franck–Condon picture. We suggest that vibration-assisted tunneling can account for these intensity variations.^{68,69}

We briefly note that the resonance at -1.8 eV is also followed by a satellite structure, albeit with even less resolution. We suggest that also in this case vibronic peaks contribute to the spectral intensity as the energy spacing matches the one at positive bias voltages.

Complementary insight into the electronic structure of TAPP- CF_3 molecules on Au(111) can be gained by 2PPE measurements. A detailed analysis of the observed peaks and their photon energy dependency has been published in ref 43. Here, we compile these results together with the data from the tunneling spectra in Figure 5. We find a very good agreement between the two experimental techniques. In summary, deposition of 1 ML TAPP- CF_3 leads to a work function (Φ) decrease of 0.4 eV compared to the bare Au(111) surface ($\Phi = 5.50$ eV). Again, we find that the LUMO of TAPP- CF_3 is energetically far above E_F (1.20 eV) and the HOMO far below E_F (-1.73 eV). Thus, no Fermi-level pinning occurs, and accordingly no charge transfer takes place. Both the LUMO (electron affinity level) and HOMO (ionization potential) are transport states; hence, the transport gap is 2.93 eV. Notably, the vibronic contributions related to the LUMO are also

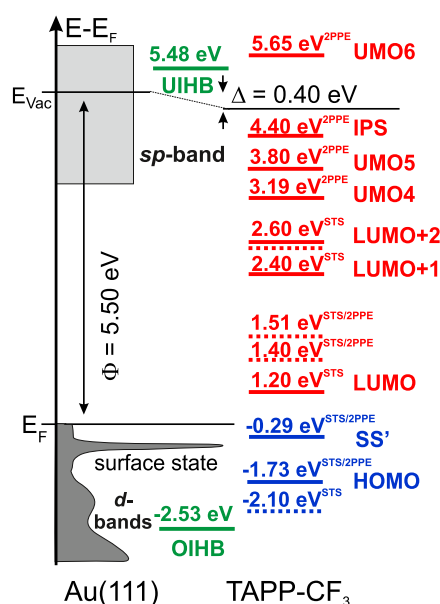


Figure 5. Energy-level diagram of TAPP- CF_3 adsorbed on Au(111) based on STS and 2PPE measurements in the sub- to monolayer regime. Dashed lines indicate vibronic transition. E_F denotes the Au(111) Fermi level, and Φ denotes the work function. UMO refers to an unoccupied molecular orbital, OIHB denotes an occupied interfacial hybrid band, and UIHB denotes an unoccupied interfacial hybrid band. SS' refers to the shifted surface state, and IPS denotes an image potential state.

observed in 2PPE. The higher-lying affinity level, LUMO + 1 (2.35 eV), is not seen in 2PPE. This might be due to a weak wave function overlap (transition dipole moment). Two further unoccupied intermediate states are found in 2PPE at 3.19 and 3.80 eV, an energy region in which STS measurements are not feasible. In addition, an unoccupied final state at 5.65 eV is observed. Notably, an occupied interfacial hybrid band (OIHB) and an unoccupied interfacial hybrid band (UIHB) have been identified as discussed in detail in ref 43 (see below).

To corroborate our interpretation of the molecular-derived resonances, we employed DFT calculations to the surface-adsorbed molecule. First of all, our calculations show that upon adsorption of TAPP- CF_3 , the work function of the interface is reduced by 0.24 eV compared to the pristine Au(111) surface. This is in excellent agreement with the experiment, for which a work function reduction of 0.40 eV was found. The reduction in work function can be explained by an induced interface dipole. Computationally, the interface dipole can be separated into a molecular contribution (which is obtained by calculating the potential jump for the hypothetical, freestanding monolayer in the geometry it adopts on the surface) and a contribution from the interaction between metal and molecule (often termed “bond dipole”). Here, the molecular contribution amounts to +0.26 eV, arising from the fact that the CF_3 groups bend out of the molecular plane during adsorption (see the Supporting Information). The bond dipole consequently amounts to -0.50 eV. We note in passing that the computational method we employ here (PBE + TS^{surf}) has a tendency to induce molecular bending upon adsorption,⁷⁰ thus overestimating the molecular dipole, while underestimating the adsorption distance.^{71–73} As a consequence, the effect of Pauli pushback is overestimated. The latter describes the effect that

the electron density spilling out from the surface is pushed back by the π conjugated electron system of the molecular adsorbate layer. As a result, it requires less energy to remove electrons from the substrate and the work function of the system is lowered.^{74,75} The slight underestimation of the work function reduction by theory (compared to the experiment) is thus fully consistent with expectations.

Remarkably, both the theoretical and experimental interface dipole values are relatively small. They are smaller than the work function reductions usually found for systems that interact only via Pauli pushback, which for inert organic molecules on gold often amounts to up to 1 eV.^{76,77} An almost zero net interface dipole has been observed for the low-coverage phase of hexaazatriphenylene-hexanitrile (HATCN) on Ag(111).⁷⁸ However, in contrast to HATCN/Ag(111), for TAPP- CF_3 /Au(111), we find that the molecule is $\approx 0.2 e$ positively charged (when applying the Mulliken charge partitioning scheme, see the Supporting Information), while the LUMO remains empty (see Figure 6a). We therefore

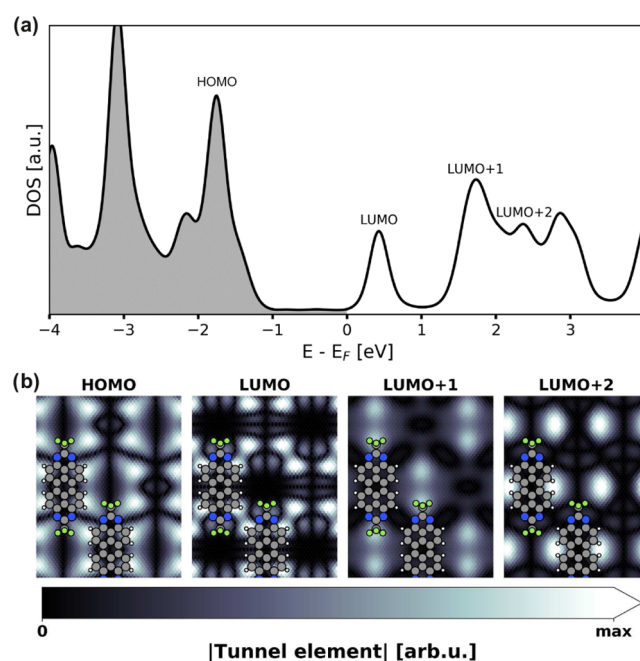


Figure 6. (a) Calculated density of states (DOS) projected on the adsorbed molecule. (b) Computed tunnel element maps for the orbitals HOMO – LUMO + 2. The elements were obtained as the overlap integral between the respective eigenstate of a freestanding molecule and a Au 6s state (representing the tip). The Au state was centered 8 Å above the substrate (corresponding to approximately 3 Å above the F atoms and <5 Å above the carbon backbone) and moved in the x - y -plane to probe different tip positions. All maps are normalized to their maximum intensity.

explain the relatively small interface dipole by the fact that the bulky CF_3 group slightly lifts the molecule from the surface, resulting in a relatively large adsorption height and, correspondingly, in a small dipole as the pushback is reduced. This hypothesis is also consistent with the observation that the TAPP-H derivative shows a larger (more negative) and the C_3F_7 derivative shows a smaller (less negative) interface dipole experimentally (see below).

Inspection of the density of states (DOS) projected onto the adsorbed molecule (Figure 6a) reveals that the LUMO is located close to the Fermi energy (at +0.43 eV). This may

easily be mistaken as an indication for Fermi-level pinning, which is not the case. The LUMO peak is more than 3 times the broadening value (0.1 eV) due to the Fermi energy. Hence, the LUMO is not populated, which would be a prerequisite for Fermi-level pinning. Rather, the proximity of LUMO and Fermi energy is coincidental and partly due to inherent shortcomings of the DFT methodology, as we discuss below. Besides the LUMO at +0.43 eV, our projected DOS shows strong molecular peaks at +1.73 and +2.36 eV, originating from LUMO + 1 and LUMO + 2, respectively. The DOS is thus qualitatively in agreement with the observed experimental values (e.g., the LUMO/LUMO + 1 separation of 1.3 eV), although the energetic position of the states is consistently at too low energies. The fact that there is no perfect agreement between theory and experiment is, per se, not surprising. Technically, Kohn–Sham orbitals are not physical observables, but they can be associated with ionization energies under the right circumstances.⁷⁹ More importantly, DFT consistently underestimates the energies of empty states, but it also misses the stabilization of ions near a surface through image charge effects.⁸⁰ At metal–organic interfaces, the latter two effects often cancel each other out, although not perfectly. There are elaborate schemes to achieve better qualitative agreement (e.g., via the use of hybrid functionals and image charge correction schemes⁸¹), but these are computationally extremely expensive.

Instead, to verify the experimental assignment, we computed the expected dI/dV maps for the HOMO and the first three unoccupied states. To this end, we calculated the overlap integrals between a hypothetical Au tip, consisting of a 6s orbital, and the eigenstate densities of the molecular monolayer (after removing the substrate for computational effort). In Figure 6b, we display maps of these tunnel elements for the HOMO and for LUMO – LUMO + 2 when scanning the tip across the surface at a height of 8 Å above the substrate (3 Å above the fluorine atoms). The map of the HOMO agrees well with the map at –1.8V, thus corroborating its previous assignment in experiment (see Figure 4). The theoretical map of the LUMO exhibits a rich structure of nodal planes along the molecular backbone. Experimentally we could not resolve these details, but the overall intensities at the molecules' center in the dI/dV maps at 1.2 and 1.4 V is consistent with the interpretation as being LUMO-derived. LUMO + 1 has the largest tunnel matrix element at the CF₃ group, similar to the experimental maps at 2.35 V. As LUMO + 2 is found 200 meV above LUMO + 1, we suggest that it overlaps with the vibronic peaks of LUMO + 1. The map at 2.55 V is thus most probably a convolution of vibronic states and LUMO + 2.

Electronic Structure of Further TAPP Derivatives on Au(111). In the following, we study the influence of the side chains on the interfacial electronic structure, in particular with respect to interfacial band formation of the other two TAPP derivatives, namely, TAPP-H and TAPP-C₃F₇ (see Figure 1) adsorbed on Au(111) by means of 2PPE.

Figure 7a displays a 2PPE spectrum of 1 ML TAPP-H/Au(111) recorded with a photon energy of 4.3 eV. The spectrum is fitted by an exponential background and Gaussian-shaped peaks. Several 2PPE features are observed. We use the characteristic behavior of photon-energy-dependent measurements to assign peaks to occupied or unoccupied electronic states (Figure 7b). Additional 2PPE data are presented in the Supporting Information. Apart from occupied and unoccupied electronic TAPP-H-derived states, the Au(111) d-bands, the

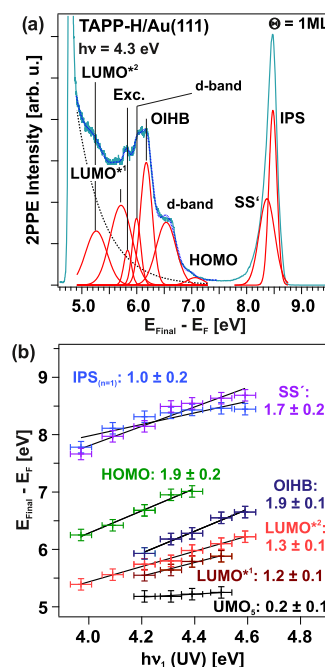


Figure 7. (a) 2PPE spectrum recorded with a photon energy of $h\nu = 4.3$ eV at 1 ML TAPP-H/Au(111). The energy axis reveals the final state (E_{Final}) of photoemitted electrons with respect to the Fermi energy E_{F} ($E_{\text{Final}} - E_{\text{F}} = E_{\text{kin}} + \Phi$); thus, the low-energy cutoff corresponds to the work function (Φ) of the adsorbate/substrate system. The spectrum is fitted by an exponential background and Gaussian-shaped peaks. (b) Photon-energy-dependent peak positions to assign the observed photoemission signals to occupied, unoccupied intermediate or final electronic states. A slope of 1 suggests that a peak originates from an unoccupied intermediate state, a slope of zero suggests that it is from an unoccupied final state (located above the vacuum level), and a slope of 2 is related to peaks originating from occupied states. LUMO* indicate vibronic contributions related to the LUMO.

shifted surface state (SS'), as well as the first ($n = 1$) image potential state (IPS) are observed. Moreover, a peak deriving from an OIHB is identified (see below). The observed energy levels are compiled in Figure 8, right column. Analogous measurements and their analysis have been applied to a monolayer of TAPP-C₃F₇ on Au(111) (data can be found in the Supporting Information). The results are also shown in Figure 8.

Comparison of the three derivatives allows us to identify the following similarities and differences: Adsorption of a monolayer of all of these molecules leads to a shift of the Au(111) surface state (SS') of around 200 meV toward the Fermi level. Similar shifts have been observed for many organic molecules on Au(111), where charge transfer to the substrate is negligible and ascribed to a modification of the image charge and work function (Φ).^{13,53,82–87} Indeed, we find a reduction of the work function for all three molecules, the largest one for TAPP-H by 0.74 eV.

While the work functions for 1 ML TAPP-CF₃/Au(111) ($\Phi = 5.10 \pm 0.05$ eV) and 1 ML TAPP-C₃F₇ ($\Phi = 5.17 \pm 0.05$ eV) are very similar, the work function possesses a smaller value for 1 ML TAPP-H/Au(111) ($\Phi = 4.76 \pm 0.05$ eV). STM results indicate an almost equal unit cell area for TAPP-CF₃ and TAPP-C₃F₇ (see Figure 2c and the Supporting Information); thus, a similar Φ value is expected, when considering a similar pushback effect. In the absence of the

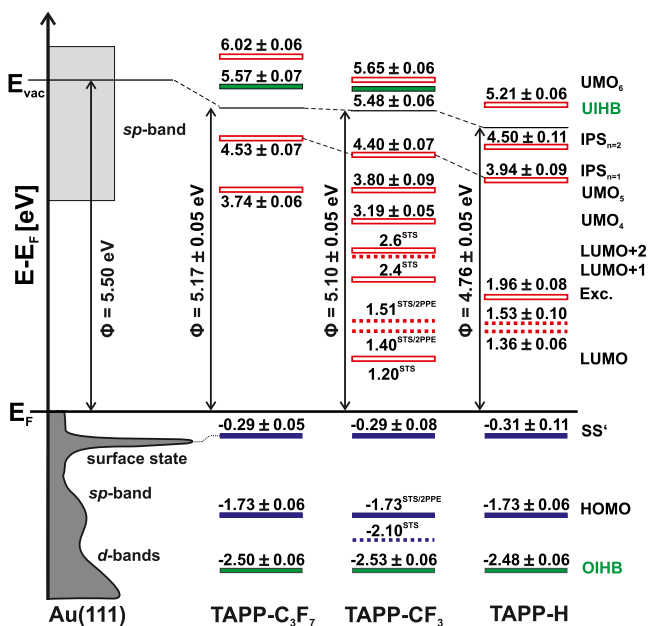


Figure 8. Energy-level diagram of 1 ML TAPP-R ($R = -\text{H}, -\text{CF}_3, -\text{C}_3\text{F}_7$) adsorbed on Au(111). E_F denotes the Au(111) Fermi level, and Φ denotes the work function. UMO refers to an unoccupied molecular orbital, OIHB denotes an occupied interfacial hybrid band, and UIHB denotes an unoccupied interfacial hybrid band. SS' refers to the shifted surface state, and IPS denotes an image potential state. Dashed lines indicate vibronic transitions. Exc. names an excitonic state.

fluorinated alkyl side chains, i.e., for TAPP-H, the packing density is most likely increased, leading to a stronger reduction of Φ . Since the image potential states (IPS) are pinned to the vacuum level, their energetic position follows the work function shift.

The HOMO of all three species is located at -1.73 eV, while the unoccupied states vary between the molecules. In the case of TAPP-H/Au(111), we observe vibronic contributions belonging to the LUMO (at 1.36 and 1.53 eV) similar to TAPP- CF_3 /Au(111). In addition, an unoccupied state at 1.96 eV is observed, which may be attributed to an excitonic state related to the LUMO + 1, observed by STS in TAPP- CF_3 /Au(111) at 2.4 eV. Some states in TAPP-H/Au(111), e.g., the UMO_4 and UMO_5 , and in TAPP- C_3F_7 /Au(111), the vibronic states associated with the LUMO are not detected. The reasons are not obvious. However, in all TAPP-R/Au(111) systems, we find interfacial occupied and unoccupied hybrid bands (OIHB and UIHB), which show pronounced dispersions as we will demonstrate by angle-resolved 2PPE in the next section.

Band Formation at the TAPP/Au(111) Interfaces.

Recently, we observed the dispersion of the UIHB and OIHB for the TAPP- CF_3 derivative on Au(111).⁴³ Since a different packing or ordering behavior is expected for the three TAPP derivatives due to the varying size of the side groups, we studied the influence of the side chains with respect to interfacial band formation of the other two TAPP derivatives, namely, TAPP-H and TAPP- C_3F_7 (see Figure 1). To be able to conclude that band formation has occurred and to measure dispersion in angle-resolved photoemission, lateral extended

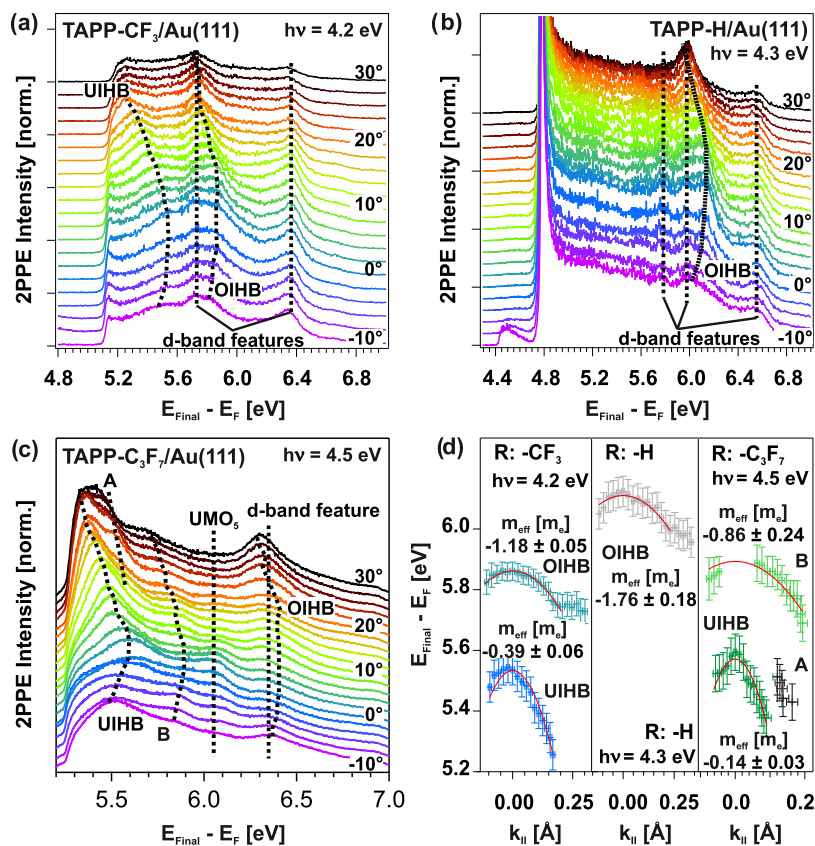


Figure 9. (a–c) Angle-resolved 2PPE measurements at the TAPP-R/Au(111) interfaces. (d) Hole-like dispersion of the OIHBs, UIHBs, and a state labeled as B (see text) around the Γ -point ($k_{\parallel} = 0$). Parabolic fits yield the effective masses (m^*) of the states around the Γ -point.

interfacial hybrid states (bands) must be formed. This is only feasible if the molecules on the surface display well-defined long-range order. To check for similar interfacial bands, we recorded angle-resolved 2PPE spectra also for the two other derivatives (Figure 9a–c). A compilation of the dispersions is shown in Figure 9d, evidencing a hole-like dispersion of both the OIHBs and UIHBs.

As already demonstrated in our previous study for the TAPP-CF₃/Au(111) interface, the effective masses (m^*) of the OIHB and UIHB are $m^* = -1.18 \pm 0.05 m_e$ and $-0.39 \pm 0.06 m_e$, respectively.⁴³ For the TAPP-H/Au(111) interface, the OIHB possesses an effective mass of $m^* = -1.76 \pm 0.18 m_e$. In the case of the TAPP-C₃F₇/Au(111) system, the UIHB exhibits an effective mass of $m^* = -0.14 \pm 0.03 m_e$. The dispersion of the OIHB is visible, but the peak positions cannot be precisely identified, since the 2PPE peak is merged into the broad contribution of the nearby d-bands. Thus, a determination of m^* is impossible. Additionally, we observe two dispersing states labeled as A and B (Figure 9c). Unfortunately, these peaks overlap with other 2PPE features, in particular under normal emission ($k_{\parallel} = 0$). This renders an assignment to occupied or unoccupied states via photon-energy-dependent measurements difficult. In the case of state B, extrapolating an energy $E_{\text{Final}} - E_{\text{F}} = 5.9$ eV from the parabolic fit at $k_{\parallel} = 0$ would result in an energetic position of an unoccupied state at 1.4 eV or for an occupied state at -3.1 eV with respect to E_{F} . This state has an effective mass of $m^* = -0.86 \pm 0.24 m_e$.

While hybridization between molecular and metal states occurs in many organic/metal systems, experimental evidence for interfacial band formation via dispersing electronic states is rarely observed. Only for strong electron acceptors (F4TCNQ/Au(111),^{39,40} PTCA/Ag(110),⁴¹ NTCDA/Ag(110)⁴²) or a donor (TTF/Au(111)⁴⁰), dispersing interface bands have been proposed. In all cases, a charge transfer between molecular states and the surface state of the metallic substrate appears (Fermi-level pinning). In contrast, for the TAPP derivatives adsorbed on Au(111), no charge transfer occurs, since the HOMO is far below E_{F} (-1.73 eV) for all three adsorbate/substrate systems and the LUMO of TAPP-CF₃/Au(111) (1.20 eV) as well as the UMO₁ (1.36 eV) of TAPP-H/Au(111) are energetically far above E_{F} . As discussed in detail for TAPP-CF₃/Au(111),⁴³ interfacial band formation is only possible if wave function mixing of localized molecular states with delocalized metal bands takes place. The OIHBs are energetically located in the Au(111) d-band region.^{88–90} Thus, we suggest that occupied TAPP states hybridize with the d-band, leading to the emergence of the OIHBs. The UIHBs lie within the energy regime of the unoccupied metal sp-band.^{88,90} Hence, we propose a hybridization between the unoccupied molecular state and this band. Note that due to the planar adsorption geometry of the TAPP-R molecules on the Au(111) surface in the monolayer regime (see the Supporting Information and refs 26 and 43), intermolecular band formation can be excluded.

CONCLUSIONS

In summary, we have investigated the electronic structure of three tetraazaperopyrene derivatives on Au(111) in great detail by complementary experimental techniques and density functional theory. We find strong similarities between the derivatives, suggesting common adsorption properties. Most notably, all of these derivatives develop interfacial hybrid

bands, which we ascribe to hybridization of higher-lying molecular states with the sp- and d-bands of the substrate. Band formation with the substrate is rather surprising as the energy-level alignment of all molecules indicates the absence of charge transfer. Indeed, we find several indications that the molecules are weakly physisorbed on a Au(111) surface, such as an intact herringbone reconstruction below the molecular layer and the persistence of the surface state. Interfacial band formation while molecular properties are preserved can be considered to be beneficial for charge injection into the organic semiconductor.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c04217>.

Temperature-programmed desorption data for TAPP-R (R: H, CF₃, C₃F₇), calculated molecular interactions of TAPP-CF₃, two-photon photoemission data for TAPP-H and TAPP-C₃F₇, and scanning tunneling microscopy images of TAPP-C₃F₇ (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank N. Krane for discussions and initial code development to calculate vibronic spectra. A.S., D.G., B.G., L.H.G., and P.T. acknowledge funding by the German Research Foundation (DFG) through collaborative research center SFB 1249 “N-Heteropolycycles as Functional Materials” (projects A02 and B06). Funding by the SFB 951 “Hybrid Inorganic/Organic Systems for Opto-Electronics” (Project no. 182087777; K.J.F.) and by the International Max Planck Research School “Functional Interfaces in Physics and Chemistry” (D.R.) is gratefully acknowledged. Funding through the project of the Austrian Science Fund (FWF): Y1157-N36 “MAP-DESIGN” is gratefully acknowledged (A.J., J.J.C., and O.T.H.). Computational results have been achieved using the Vienna Scientific Cluster (VSC).

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