

# Formation of Occupied and Unoccupied Bands at Molecule/Metal Interfaces

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Efficient charge transport in organic semiconductors and at their interfaces with electrodes is crucial for the performance of organic molecule-based electronic devices. Band formation fosters effective transport properties and is found in organic single crystals of large  $\pi$ -stacking aromatic molecules. At molecule/metal interfaces band formation and dispersion is a rarely observed phenomenon. Using angle-resolved two-photon photoemission supported by density functional theory calculations we demonstrate for two different molecule/metal systems, namely tetrathiafulvalene (TTF)/Au(111) and tetrafluoro-tetracyanoquinodimethane (F<sub>4</sub>TCNQ)/Au(111), band formation in the energy region of occupied as well as unoccupied electronic states. In both cases strong adsorbate/substrate interactions result in formation of interface states due to hybridization between localized molecular states and delocalized metal bands. These interface states exhibit significant dispersions. Our study reveals that hybridization in combination with a well-ordered adsorption structure of the  $\pi$ -conjugated organic molecules is a striking concept to receive band formation at molecule/metal interfaces.

Band formation at molecule/metal interfaces has attracted much interest since efficient charge transport at those interfaces would play a crucial role in any kind of organic molecule-based (opto)electronic device [1–6]. While metallic states are extended leading to delocalized charge carriers with high mobilities, molecular electronic states are localized due to weak intermolecular interactions within a thin molecular film. Contrary, in organic single crystals of large  $\pi$ -stacking aromatic molecules band formation and dispersion has been found [7–10]. However, it has been suggested that the interaction between delocalized metal and localized molecular wave functions can give rise to new delocalized molecule/metal hybrid states at the interface [11]. Thereby an unoccupied molecular state (i.e., the lowest unoccupied molecular orbital, LUMO) interacts with the Shockley surface state (SS) of single-crystal noble metal surface resulting in an energetic upshift of the interfacial hybrid state even above the Fermi level of the substrate compared to energetic position of the undisturbed SS [12–23]. Here the degree of dispersion of the hybrid or interface states are strongly dominated by the property of the SS, i.e., possessing a similar effective electron mass. Additionally, a metal-molecule hybrid state with lateral delocalization originating from the hybridization of the LUMO wave function with the delocalized metal sp-states has been proposed in the case of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA) adsorbed on Ag(110) [24, 25]. While hybridization between molecular and metal states arise in many organic/metal systems, band formation at these interfaces is a rarely observed phenomena. So far a profound understanding of the fundamental requirements and mechanisms of band formation at molecule/metal interfaces are still missing.

In this article, we demonstrate interfacial band formation and dispersion for two molecule/metal systems, namely tetrathiafulvalene (TTF) and tetrafluoro-tetracyanoquinodimethane ( $F_4$ TCNQ) adsorbed on Au(111), respectively, using angle-resolved two-photon photoemission spectroscopy (AR-2PPE) as depicted in Fig. 1 and density functional theory (DFT) calculations. TTF is a prototype electron-donating molecule and in combination with tetracyanoquinodimethane (TCNQ) one of the original initiators of organic electronics due to the exceptional high electronic conductivity in formed charge-transfer crystals [26, 27]. At the TTF/Au(111) interface a molecule to metal charge transfer type interaction takes place [28, 29]. In contrast,  $F_4$ TCNQ is a strong electron acceptor. Thus adsorption on the Au(111) surface leads to a metal to molecule electron transfer [30–32]. Here, we find for

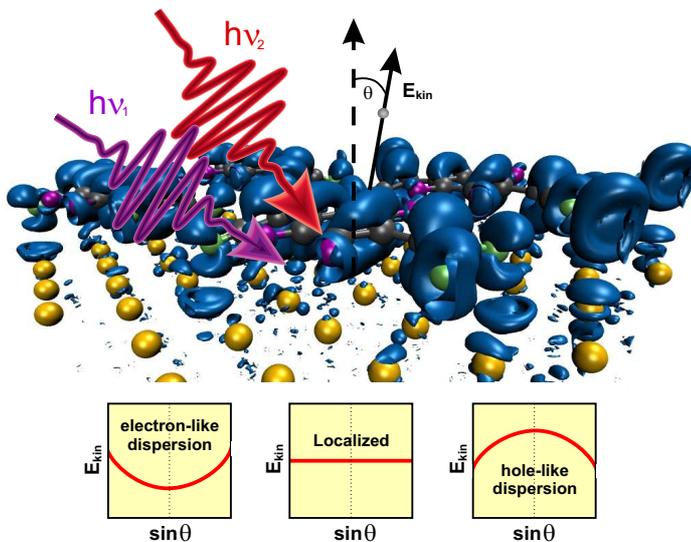


FIG. 1. **Scheme of the angle-resolved 2-Photon Photoemission (2PPE).** Angle-resolved 2PPE is utilized to gain information about the dispersion (viz. electron localization/delocalization) of electronic states at organic molecule/metal interfaces.

both systems strong dispersing occupied electronic states. Their energetic positions and effective masses differ significantly from the values known for the SS of the bare Au(111) surface as well as the modified SS due to adsorption of organic molecules. Moreover, we observe unoccupied electronic states possessing large lateral delocalizations. Our results suggest that strong adsorbate/substrate interactions promoting hybridization between localized molecular states and delocalized metal states in combination with highly ordered adsorption structure of the  $\pi$ -conjugated organic molecules is a general guide to achieve band formation at molecule/metal interfaces.

## Results

**Band formation at the TTF/Au(111) interface.** Figure 2a shows an energy level diagram of 1 monolayer (ML) TTF adsorbed on Au(111), which is based on detailed photon energy dependent 2PPE measurements and DFT calculations (see Supplementary Information, SI). Deposition of 1 ML TTF leads to a work function decrease of 1.35 eV compared to the bare Au(111) surface. Since it is known that TTF undergoes a charge transfer at the

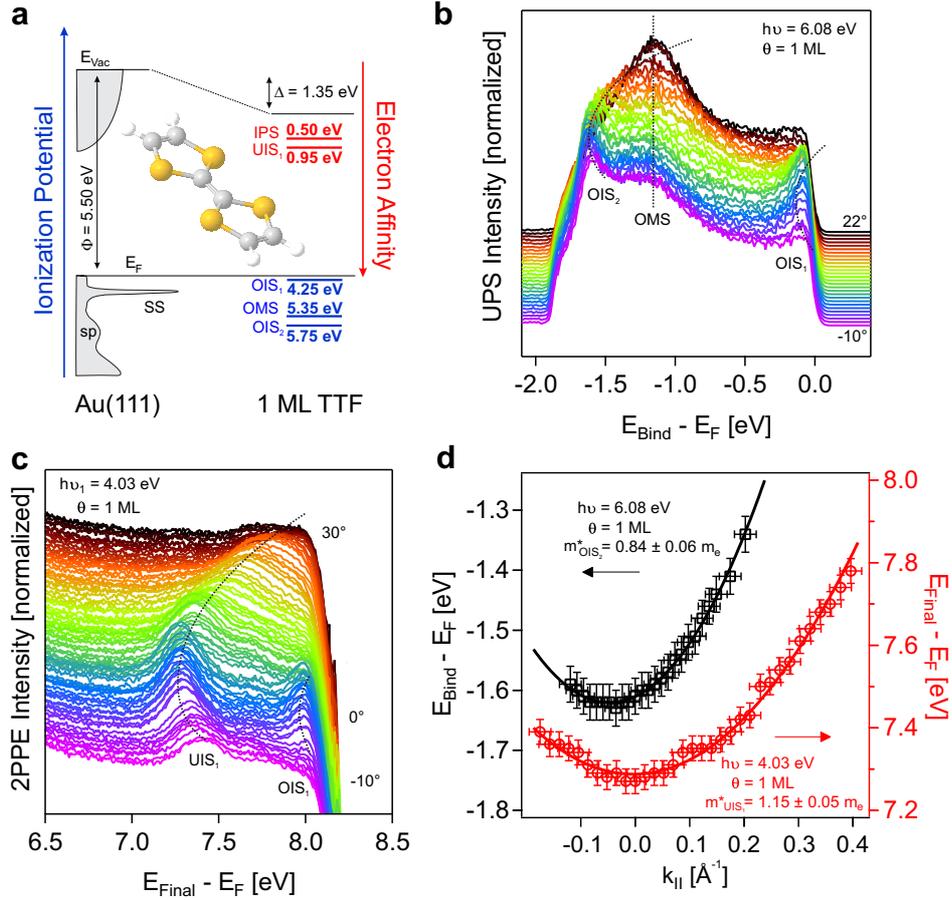


FIG. 2. **Electronic structure and angle-resolved photoemission data of 1 monolayer TTF adsorbed on Au(111).** (a) Energy level diagram of the experimentally observed electronic states. The blue levels are the ionization potentials (left axis) and the red ones are the electron affinity levels (right axis) [33–35],  $E_F$  denotes the Au(111) Fermi level, IPS an image potential state, UIS an unoccupied interface state, OIS an occupied interface state, and OMS occupied molecular state. (b) Angle-resolved UPS data obtained with  $h\nu = 6.08$  eV. (c) Angle-resolved 2PPE data recorded with  $h\nu = 4.03$  eV. (d) Dispersion of the OIS<sub>2</sub> and UIS around the  $\Gamma$ -point ( $k_{\parallel} = 0$ ). The OIS<sub>2</sub> is shown with its binding energy with respect to the Fermi level (right axis), UIS is displayed with the final state energy above the Fermi level (left axis). Parabolic fits yield the effective masses of both states around the  $\Gamma$ -point.

Au(111) surface [30, 31], i.e., the molecules donate electrons to the substrate, we assign the state located near the Fermi level ( $E_F$ ) of Au(111) to an occupied interface state (OIS<sub>1</sub>) involving the highest occupied molecular orbital (HOMO) in agreement with DFT calculations [28, 29, 36]. Figure 2b displays angle-resolved ultraviolet photoemission spectroscopy

(UPS) data in which the electron-like dispersion of the occupied interface states OIS<sub>1</sub> and OIS<sub>2</sub> is clearly visible. In contrast the occupied molecular state (OMS) is localized. Figure 2c shows the respective 2PPE data demonstrating the dispersion of an unoccupied interface state (UIS). In Figure 2d the dispersion of the OIS<sub>2</sub> and the UIS around the  $\Gamma$ -point is presented. An analysis of the data (see SI), results effective masses of  $m^* = 0.84 \pm 0.06m_e$  for the OIS<sub>2</sub> and  $m^* = 1.15 \pm 0.05m_e$  for the UIS, i.e., both electronic states possess a free-electron like behavior. The variation in energy within the measured angular range is about 270 meV for the OIS<sub>2</sub> and 350 meV for the UIS. Unfortunately, a corresponding analysis for the OIS<sub>1</sub> is not possible, since the photoemission peak crosses the Fermi edge with increasing detection angle.

**Band formation at the F<sub>4</sub>TCNQ/Au(111) interface.** In analogy to the TTF/Au(111) Fig. 3a summarizes the experimentally determined and calculated molecule-derived electronic energy levels for 1 ML F<sub>4</sub>TCNQ adsorbed on Au(111). The associated extensive 2PPE and DFT analysis is presented in the SI. The state labeled as OIS involves the LUMO. Due to a charge transfer from the metal to the F<sub>4</sub>TCNQ the LUMO becomes occupied and shifts below  $E_F$  [30–32]. Figure 3b and c show angle-resolved 2PPE data recorded at two different photon energies in order to resolve the angular dependency of the respective electronic states. The OIS as well as both unoccupied states the UIS and UMB reveal a dispersion. At first glance surprising, a hole-like dispersion with an effective mass of  $m^* = -1.4 \pm 0.1m_e$  is measured in the case of the OIS (see Fig. 3d). The variation in energy within the measured angular range is about 200 meV. An electron-like dispersion of  $m^* = 5.6 \pm 1.8m_e$  and  $m^* = 1.2 \pm 0.1m_e$  for the UIS and UMB, respectively, are measured. The energy as a function of  $k_{\parallel}$  varies about 50 meV in the case of UIS and 300 meV for the UMB.

**Theoretical modeling of the TTF/Au(111) interface.** To get additional insight into the electronic structure at the interface, we performed DFT calculations. All geometries were optimized using the PBE functional [37] augmented by the  $vdW^{surf}$  scheme [38] to account for the missing long-range van-der-Waals forces (for details see Method section). The unit cell for TTF/Au(111) determined in Ref. [36], contains two molecules in an herringbone arrangement as shown in Fig. 4a. Following the procedure proposed in Ref. [24], to separate

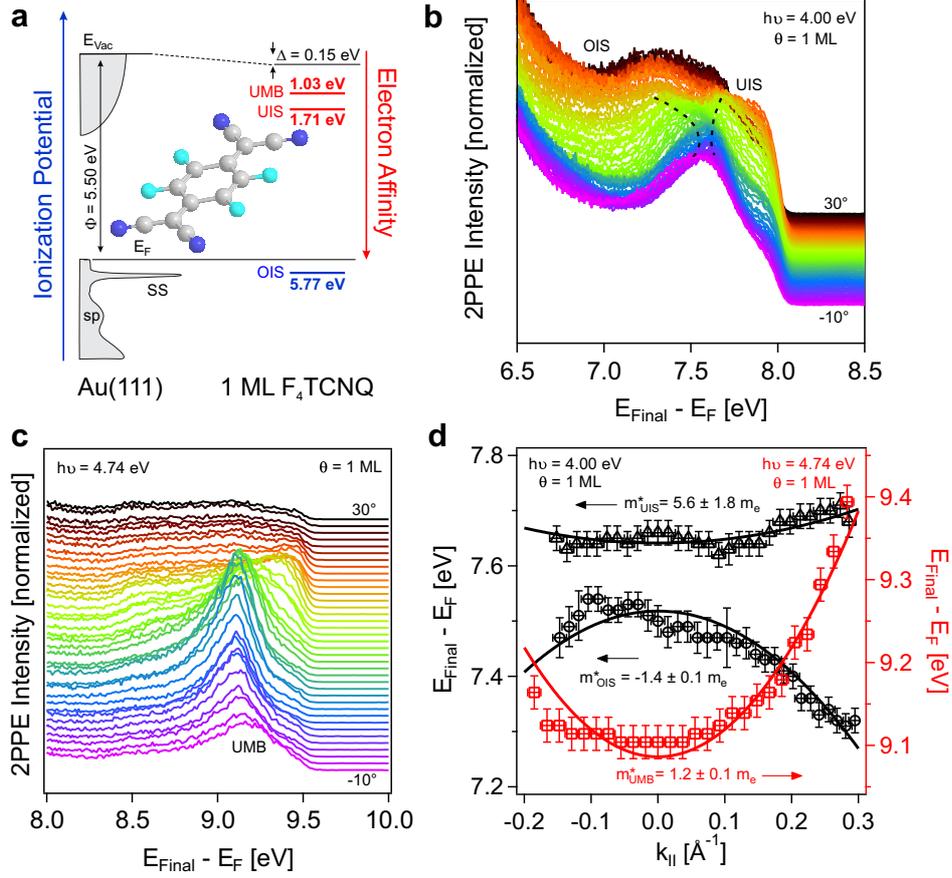


FIG. 3. **Electronic structure and angle-resolved photoemission data of 1 monolayer  $F_4TCNQ$  on  $Au(111)$ .** (a) Energy level diagram of the experimentally observed electronic states. UMB denotes an unoccupied molecular band, UIS an unoccupied interface state, and OIS an occupied interface state. (b) and (c) Angle-resolved 2PPE data obtained with  $h\nu = 4.00$  eV and  $h\nu = 4.74$  eV, respectively. (d) Dispersion of the OIS, UIS, and UMB around the  $\Gamma$ -point ( $k_{||} = 0$ ). Parabolic fits yield the effective masses of the states around the  $\Gamma$ -point.

between the influence of intermolecular and substrate-molecule interactions as well as the impact of charge transfer, we first perform calculations on a hypothetical, free-standing TTF monolayer in the same geometry as it adopts on the  $Au(111)$  surface. The results are shown in Fig. 4b. We find that already in the absence of substrate-mediated interactions, the two HOMOs of the system (consisting of the bonding and antibonding linear combination of the HOMOs of the two non-equivalent molecules and hence labelled as HOMO and HOMO\* in the plot) exhibit a noticeable dispersion of ca. 50 meV. Importantly, the HOMO exhibits an electron-like dispersion, while the HOMO\* shows a hole-like dispersion. Consequently,

the split between the bonding and antibonding linear combination is largest at the  $\Gamma$  point and decreases on its path toward the  $K$  point up to  $k=0.5$ .

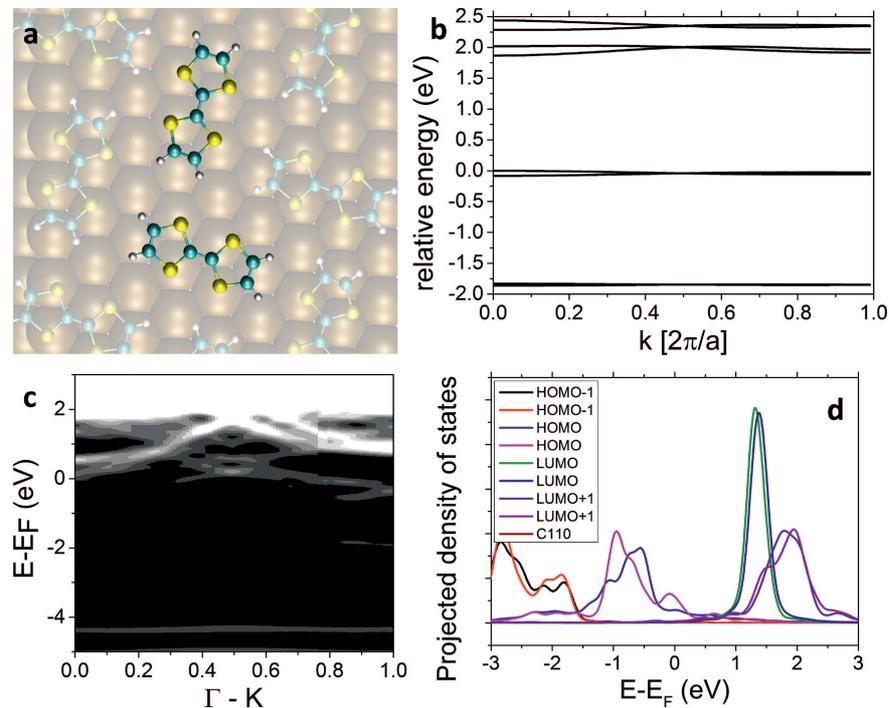


FIG. 4. **Modeling the TTF/Au(111) interface.** (a) Structure of the TTF/Au interface used for the calculation. The two molecules in the unit cell are highlighted. (b) Dispersion of the states of the hypothetical, free-standing monolayer. (c) Surface band structure along the  $\Gamma - K$ -direction, projected onto the molecule. Lighter areas carry greater weights on the molecule. (d) Density of states of the TTF/Au interfaces, projected onto the molecular orbitals. Note that since there are two molecules in the unit cell, all orbital (HOMO-1, HOMO, LUMO) appear twice.

As a next step, we calculated the electronic structure of the TTF monolayer when adsorbed on a five-layered Au(111) slab. We find that the work function decreases by  $-1.4$  eV, in excellent agreement with the experiment (see Fig. 2a). Figure 4c displays the surface band structure along the  $\Gamma K$ -direction. Between  $E_F$  and  $E_F + 1$  eV, we find a strongly dispersing unoccupied state that has hybridized with the substrate. The region at even higher energies is almost exclusively dominated by states of the organic molecules. In the energy region of occupied states the graph is characterized by a lack of clearly distinct features. To understand this puzzling behavior, we projected onto each molecular orbital separately (see Fig. 4d). It becomes evident that the split HOMO-HOMO\* pair, that dispersed over

ca. 50 meV in the isolated monolayer, has hybridized strongly with substrate states and now covers a range of more than 1 eV. Also most other  $\pi$ -orbitals, in particular those in the region between -5 eV and  $E_F$ , are strongly hybridized, covering a large range of energies and hence showing a very low density of states for any given energy interval. The dispersion is found to be even larger for the HOMO-1, which covers a range of almost 2 eV.

**Theoretical modeling of the F<sub>4</sub>TCNQ/Au(111) interface.** For the modelling of F<sub>4</sub>TCNQ on Au(111), we use the unit cell proposed by Faraggi *et al.* [32] based on STM measurements. The unit cell contains only a single F<sub>4</sub>TCNQ molecule (in contrast to TTF). The network between the F<sub>4</sub>TCNQ molecules is mediated by Au adatoms, as shown in Fig. 5a. Therefore we perform the analysis in three steps. First, a hypothetical free standing monolayer of F<sub>4</sub>TCNQ in the same geometry as it adopts on the surface has been calculated. Due to the relatively large separation between the molecules, none of the orbitals show any appreciable dispersion. The situation changes qualitatively when we also consider the Au adatoms. Most notably, the band structure shown in Fig. 5b becomes metallic. The band at the  $E_F$  displays a clear hole-dispersion at the  $\Gamma$ -point. The bandwidth amounts to approximately 300 meV.

At ca.  $\Delta E = -1$  eV we find an additional strongly dispersing state. In contrast to the former LUMO, however, it exhibits a clear electron-like dispersion. A visual inspection shows that this orbital is comprised of the former HOMO and the  $d_{z^2}$  orbital of the Au adatom. Interestingly, we find the total bandwidth to be also approximately 300 meV. In the energy region of unoccupied states, most states retain molecular orbital character and do not show a k-dependent dispersion exceeding 100 meV, with one notable exceptions at approx.  $\Delta E = 2.75$  eV, which shows an electron-dispersion character. Although this level show clearly molecular character, it appears not to be associated with low-lying molecules orbitals from the (metal-free) F<sub>4</sub>TCNQ molecule, and hence we designate it as a new interface state.

As a final step, we place the F<sub>4</sub>TCNQ/Au network onto the 5-layer Au(111) slab. Our calculations show that the work function is reduced by  $\Delta\Phi = 0.2$  eV, in very good agreement with the 2PPE result (see Fig. 3a). This corroborates the choice of our unit cell, including the surface adatoms (without adatoms, the work function *increases* by 0.2 eV). The surface band structure shown in Fig. 3c shows that the character of the frontier states of the F<sub>4</sub>TCNQ-Au network is mostly retained upon contact with the bulk metal. The band

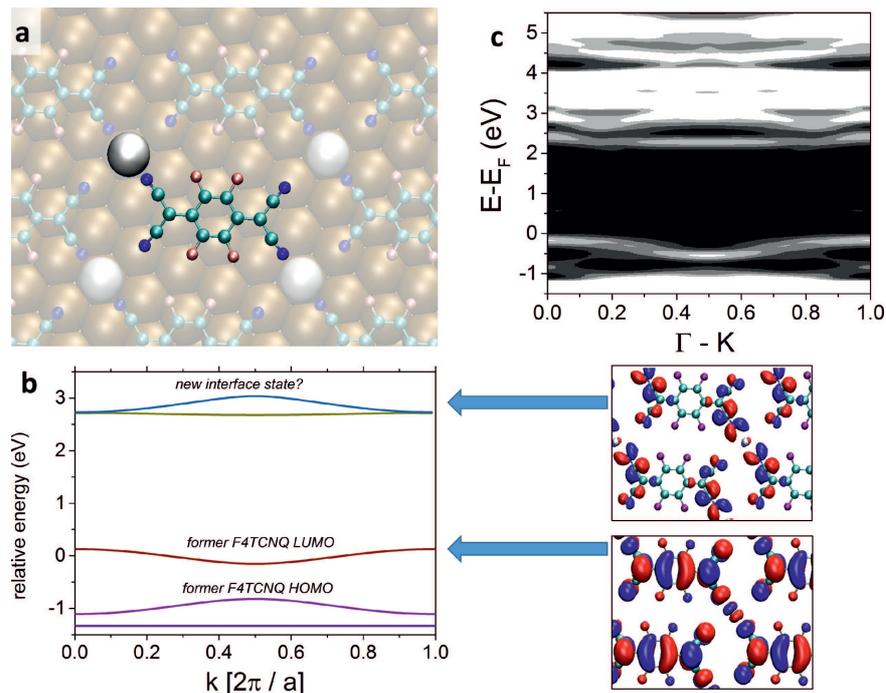


FIG. 5. **Modeling the  $F_4TCNQ/Au(111)$  interface.** (a) Structure of the  $F_4TCNQ/Au$  interface used for the calculations. The molecule and the surface adatom are highlighted. (b) Dispersion of the states of the hypothetical, free-standing monolayer. (c) Surface band structure along the  $\Gamma - K$  direction, projected onto the molecule. Lighter areas carry greater weights on the molecule.

corresponding to the former LUMO can now be found directly below  $E_F$ , indicating that it becomes fully filled upon contact. The energy region of unoccupied states (2 – 2.5 eV above  $E_F$ ) shows a non-dispersive state followed by a state with a weak electron-like dispersion.

## Discussion

Merging the experimental and theoretical results we clearly find band formation in the energy region of occupied as well as unoccupied electronic states for both the TTF/Au(111) and  $F_4TCNQ/Au(111)$  interface. In both adsorbate/substate systems the molecular electronic structure is strongly modified due to the adsorption on the metal resulting in a hybridization between molecular and metal states. Thus, reflecting the electron donating character of TTF (unfilled HOMO) and the electron accepting nature (filled LUMO) of  $F_4TCNQ/Au(111)$ . Additionally, the perfect agreement between the calculated and the measured work function shift due to adsorption of a monolayer in both adsorbate/substate systems demonstrates the

well-chosen adsorption structure (unit cell) for the DFT calculations.

For TTF/Au(111) we experimentally observed an occupied interface state (OIS<sub>1</sub>) close to  $E_F$  at the  $\Gamma$ -point, which crosses  $E_F$  for higher detection angles. According to our DFT calculations this state results from a strong hybridization between the TTF HOMO and substrate states (sp-band or SS). Theory and experiment show an electron-like dispersion of the OIS<sub>1</sub>. At higher binding energies (around -1.6 eV) a further electron-like dispersing state OIS<sub>2</sub> ( $m^* = 0.84 \pm 0.06m_e$ ) with a bandwidth of 270 meV is experimentally observed. Based on the calculation we attribute OIS<sub>2</sub> to an interfacial hybrid state involving the TTF HOMO-1. In the region of unoccupied electronic states the UIS exhibits an electron-like dispersion ( $m^* = 1.15 \pm 0.05m_e$ ) with bandwidth of ca. 300 meV. DFT found also a strongly dispersing unoccupied hybrid state at the TTF/Au(111) interface, but at lower energies. It has to be pointed out, that the calculated energetic positions of unoccupied electronic states are done for the neutral molecule, while in 2PPE we determine electron affinity levels, i.e., the energetic position of a negative ion resonances [33–35, 39]. However, most likely UIS results from wave function mixing of a TTF LUMO+n and the unoccupied sp-band of the gold substrate.

For the F<sub>4</sub>TCNQ/Au(111) interface an occupied interface state (OIS) possessing a hole-like dispersion with an effective mass of  $m^* = -1.4 \pm 0.1m_e$  is found. A recent ARPES study also found this dispersing state, which has been proposed to arise from the F<sub>4</sub>TCNQ Au-adatom network [40]. Our calculations are based on the well-known adsorption structure of F<sub>4</sub>TCNQ on Au(111) [32], namely the F<sub>4</sub>TCNQ-Au network (see Fig. 5a), in which each adatom is surrounded by four (equivalent) F<sub>4</sub>TCNQ-molecules. Thereby the distances are not equidistant, *viz.* the distances from the top left and bottom right F<sub>4</sub>TCNQ to the adatom are shorter (therefore called *short diagonal* hereafter) than the distances from the top right and bottom left F<sub>4</sub>TCNQ molecules to the Au adatom (called the *long diagonal* hereafter). A visual inspection of the state crossing the Fermi-edge indicates that it is derived from the former F<sub>4</sub>TCNQ LUMO and reveals the origin of the hole-like dispersion. The LUMO is inversion symmetric (i.e., is gerade), as is the Au  $d_{xz}$ -orbital that links the F<sub>4</sub>TCNQ molecules across the short diagonal. At  $k = \Gamma$ , the linear combination between the Au-state and the F<sub>4</sub>TCNQ LUMOs is strongly antibonding respect along the short diagonal and non-bonding (i.e., the overall between the LUMOs and the Au-orbital essentially cancels) across the long-diagonal. Any phase factor this lattice-periodic function picks up (i.e., for

any  $k \neq 0$ ) leads to a decrease of the bonding character, and thus a reduction in energy (i.e., hole-like character). For this band we calculated a bandwidth of approximately 300 meV in good agreement with our experimental findings and literature [40]. However, we determined an effective mass of the hole which is by a factor of three higher than the published value of  $m^* = -0.46m_e$  [40]. In the energy region above  $E_F$  two electron-like dispersing unoccupied electronic states UIS and UMB are identified in 2PPE. The UIS can most likely correlated with the calculated interface state found around  $\Delta E = 2.75$  eV (see Fig. 5b). We suggest that it results from hybridization between a higher lying unoccupied  $F_4TCNQ$  state (LUMO+n) and the Au(111) sp-band at the interface. In contrast, for the UMB we recently demonstrated that intermolecular hybridization leads to band formation [41].

For both molecule/metal interfaces we unambiguously find occupied and unoccupied band formation due to wave function mixing of localized molecular states with delocalized metal bands, which clearly differs from the results of former studies [12–21]. In the latter cases, the dispersing states resulted from a shifted SS of the noble metal surfaces due to the adsorption of the organic molecules, possessing a similar reduced mass as the SS, but upshifted in energy. This is the case for almost all systems as nicely demonstrated in Ref. [22]. In the case of PTCDA and NTCDA adsorbed on Ag(110) [24, 25], respectively, the situation is different, since hybrid states with lateral delocalization originating from the hybridization of the LUMO wave function with the delocalized metal sp-band are identified. However, comparing both here studied adsorbate/substrate systems we have to notice that they are very different with respect to their unit cell (TTF/Au(111): two molecules per unit cell;  $F_4TCNQ$ /Au(111): one molecule per unit cell) and their charge transfer interactions (TTF: electron donating;  $F_4TCNQ$ : electron accepting). They are very similar concerning the strong hybridization between occupied as well as unoccupied molecular states with metal band.

In order to draw general conclusions about prerequisites needed to achieve band formation at molecule/metal interfaces on basis of our results we want to stress the following aspects: (i) Strong electronic interactions between the adsorbate and metallic substrate resulting in hybridization of localized molecular states and delocalized metal band are required. For strong electron donor or acceptor molecules intense adsorbate/metal interactions are expected and accordingly hybridization (note that PTCDA and NTCDA on Ag(110) also

undergo charge transfer [24, 25]). Hybridization is a requirement for band formation but hybridization does not necessarily lead to band formation. (ii) Thus, a well-ordered adsorption structure of the molecules is necessary to allow a lateral delocalization of electrons in the hybrid or interface states and promote band formation. Following these requirements may open a way to design molecule/metal interfaces allowing efficient charge transport which is important in organic molecule-based electronic devices.

## Methods

**Sample preparation.** The Au(111) single crystal was prepared by Ar<sup>+</sup> sputtering and annealing at 800 K. TTF or F<sub>4</sub>TCNQ molecules were evaporated from a Knudsen cell onto the substrate held at liquid nitrogen temperature (ca. 100 K) in the case of TTF and at room temperature (ca. 300 K) for F<sub>4</sub>TCNQ deposition. The film thickness was adjusted and measured via temperature-programmed desorption which allows thermally activated self-organization and provides samples with full monolayer coverage on a Au(111) surface (see SI).

**Photoemission experiments.** 2PPE allows investigation of occupied and unoccupied electronic states [42] in a pump-probe scheme, while the variation of the detection angle provides insights into the dispersion ( $k_{\parallel}$ ), i.e., the degree of localization/delocalization of occupied and unoccupied electronic states (for further details see SI). The tunable femtosecond laser system which delivers laser pulses over a wide range of photon energies, and the 2PPE setup is described elsewhere [43].

**DFT-calculations.** All calculations were performed with the FHI-aims code [44] using "tight" default numerical settings as shipped with the code. We tested explicitly that these settings yields converged of total energies and work function shifts to 10meV or better. A  $\Gamma$ -centered k-grid was used with a sampling of  $7 \times 7 \times 1$  k-points for both TTF and Au. The interfaces were modelled using the periodic slab approach, allowing for at least 30 Å vacuum between the periodic replicas in z-direction and using a self-consistently determined dipole correction to avoid spurious electrostatic interactions (**cite doi:** ). The self-consistent field cycle was converged until the total energy changed by less than  $10^{-6}$  eV and the sum of eigenvalues changed by less than  $10^{-2}$  eV. Geometry optimizations were performed relaxing all but the bottom three metal layers until the residual force was smaller than  $10^{-3}$  eV/Å.

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## Author contributions

D.G. and P.T. conceived and designed the photoemission experiments, D.G. performed the

photoemission experiments. O.T.H. conducted the DFT calculations. All authors analyzed and discussed the data and co-wrote the manuscript.

### **Additional Information**

Supplementary information is available.

### **Competing financial interests**

The authors declare no competing financial interests