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# Orbital Redistribution in Molecular Nanostructures Mediated by Metal-Organic Bonds

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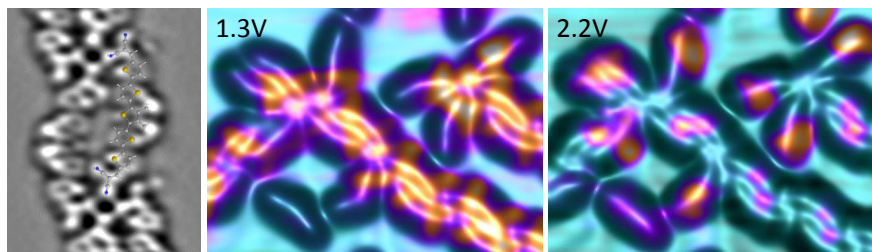
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### Abstract

Dicyanovinyl-quinquethiophene (DCV5T-Me<sub>2</sub>) is a prototype conjugated oligomer for highly efficient organic solar cells. This class of oligothiophenes are built up by an electron-rich donor (D) backbone and terminal electron-deficient acceptor (A) moieties. Here, we investigated its structural and electronic properties when it is adsorbed on a Au(111) surface using low temperature scanning tunneling microscopy/spectroscopy (STM/STS) and atomic force microscopy (AFM). We find that DCV5T-Me<sub>2</sub> self-assembles in extended chains, stabilized by intercalated Au atoms. The effect of metal-ligand hybridization with Au adatoms causes an energetic downshift of the DCV5T-Me<sub>2</sub> lowest unoccupied molecular orbital (LUMO) with respect to the uncoordinated molecules on the surface. The asymmetric coordination of a gold atom to only one molecular endgroup leads to an asymmetric localization of the LUMO and LUMO+1 states at opposite sides. Using model density functional theory (DFT) calculations, we explain such orbital reshaping as a consequence of linear combinations of the original LUMO and LUMO+1 orbitals, mixed by the attachment of a bridging Au adatom. Our study shows that the alignment of molecular orbitals and their distribution within individual molecules can be modified by contacting them to metal atoms in specific sites.

**KEYWORDS:** scanning tunneling microscopy, atomic force microscopy, metal-organic coordination, molecular orbital alignment, molecular orbital distribution

The physical and chemical properties of organic thin films are in great part determined by details of their interaction at the interface with a metal support.<sup>1,2</sup> Charge redistribution and orbital realignment can reduce drastically the optical or electronic functionality of the

film. Furthermore, hybridization of the metal with reactive molecular groups may enhance vertical charge transfer,<sup>3-6</sup> and induce conformational distortions,<sup>7,8</sup> leading to chemically new molecular species.<sup>9</sup> Even for weak interactions, the metal surface can induce dipolar perturbations to the molecular states.<sup>10-12</sup> The understanding of how molecular levels realign in the proximity of a metal is still under debate.<sup>1,2</sup>

Some organic ligands are very active in bonding to metal adatoms and forming metal-organic nanostructures<sup>13-20</sup> or even meditating the complete reconstruction of the metal surface underneath.<sup>21-25</sup> Due to this strong reactivity, metal adatoms are often captured from the surface and incorporated into the film.<sup>26-29</sup> These adatoms modify the alignment of localized and degenerated orbitals locally and lift their degeneracies by step-wise metal-ligand hybridization.<sup>30,31</sup> Recent works on insulating surfaces tracked precisely the effect of metal atoms on the molecular orbital structure,<sup>32-34</sup> which in many cases induces a renormalization of molecular states that can be described as a simple combination of free-molecule orbitals. Whether this simple picture still applies on a metal-organic interface is still unknown.

Here, we report experimental results that illustrate the crucial role played by gold-adatoms in the assembling and electronic configuration of a functionalized oligothiophene on a metal surface. We investigate in particular a derivative with an internal acceptor-donor-acceptor architecture, A-D-A oligothiophene DCV5T-Me<sub>2</sub>, adsorbed on a Au(111) surface. DCV5T-Me<sub>2</sub> molecules are composed of a central electron-rich quinquethiophenes (5T) backbone with two terminal electron-deficient dicyanovinyl (DCV) groups linked symmetrically, and two methyl (Me<sub>2</sub>) substitutions in the central thiophene ring (inset of Fig. 1a). The interest in this molecule stems from its potential use as highly efficient photoabsorber in organic photovoltaics: power conversion efficiencies of over 7% have been achieved in vacuum-processed bulk heterojunction solar cells.<sup>35-44</sup> The combination of donor and acceptor units in these A-D-A oligothiophenes leads to reduced optical band gaps and excellent photovoltaic properties.<sup>44,45</sup> Their practical use in photovoltaic blends requires efficient charge dynamics, which is favored by the delocalized character of oligothiophene frontier orbitals and by crys-

tal packing. However, the anisotropy of the packing structure,<sup>45</sup> molecular distortions, and the reactivity of the DCV end groups may facilitate the creation of charge traps that inhibit the charge transport.

We find that DCV5T-Me<sub>2</sub> molecules are prone to bond to metal atoms *via* the cyano end-groups, and modify, in this way, their free-molecule electronic configuration. The adsorption on a gold substrate at room temperature is dominated by the coordination to gold atoms, which stabilize peculiar bi-molecular chain structures. The spectroscopic fingerprint of the metal-ligand bond is an energetic downshift of the lowest unoccupied molecular orbital with respect to the uncoordinated molecule. Interestingly, in molecules bonding to Au adatoms in only one side, scanning tunneling spectroscopy measurements reveal a redistribution of the unoccupied molecular orbitals. The new spatial distribution of the down-shifted LUMO is localized at the coordinated side, while the modified LUMO+1 is localized at the uncoordinated side. Supported by density functional calculations, we rationalize such spatial redistribution of frontier orbitals as a result of the bonding and anti-bonding combination of the original LUMO and LUMO+1 orbitals. The attachment of one Au atom is found to induce the mixing of the original molecular orbitals into a new set of renormalized orbitals that adapt themselves to the symmetry of the new configuration. Our results thus suggest that the inclusion of metal atoms into the structure of molecular films at specific sites can steer the character of frontier orbitals and, hence, modify the film functionality.

## Results and discussion

The deposition of sub-monolayer amounts of DCV5T-Me<sub>2</sub> on Au(111) at room temperature leads to the formation of extended molecular chain structures, and occasional DCV5T-Me<sub>2</sub> monomers dispersed in bare Au(111) regions between them (Fig. 1a). The chains are bi-molecular linear structures linked by a characteristic motive, differing from the packing structure of bulk.<sup>43</sup> High resolution STM image (Fig. 1b) shows that the linking motive is a

bonding node of four molecules pointing their cyano terminations towards each other. Such a bonding configuration is highly unfavorable for the bare electronegative nitrogen terminations, unless a cementing metal atom coordinates to them. Thus, we consider that Au adatoms<sup>46</sup> are trapped and incorporated into the DCV5T-Me<sub>2</sub> chain structures *via* coordination bonds with the cyano moieties of DCV5T-Me<sub>2</sub>.<sup>29</sup>

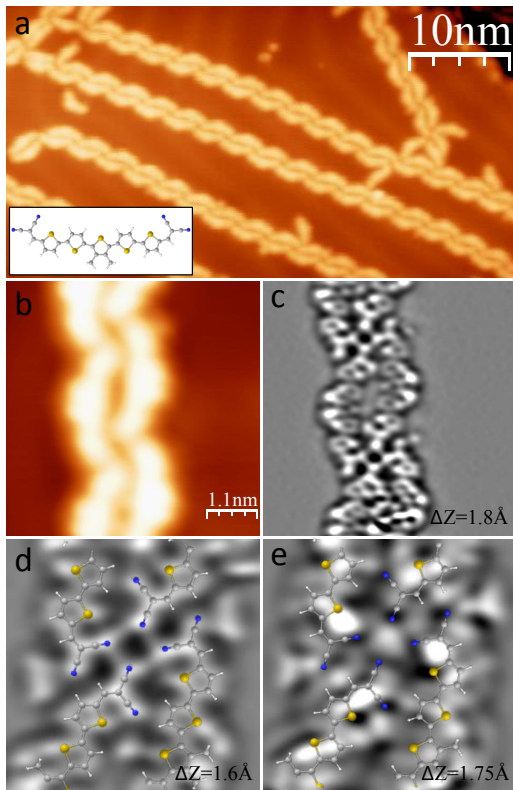


Figure 1: (a) STM image of DCV5T-Me<sub>2</sub> bi-molecular chains on Au(111) ( $I = 18$  pA,  $U = 1.0$  V). Inset: chemical structure of the DCV5T-Me<sub>2</sub> molecule (white: hydrogen, grey: carbon, blue: nitrogen and yellow: sulfur). (b) High-resolution STM image ( $I = 15$  pA,  $U = 0.1$  V) of a chain recorded with a Xe-functionalized tip. (c) Corresponding Laplace filtered nc-AFM image, plotting the amplitude of the frequency shift while scanning at constant tip-sample height. The tip was approached by  $1.8 \text{ \AA}$  towards the sample from an initial position set by the control parameters of  $I = 15$  pA and  $U = 0.1$  V over the molecule. (d) and (e) Laplace filtered nc-AFM images of the joint of four adjacent molecules around one Au atom. The tip was approached by  $1.6 \text{ \AA}$  (d) and  $1.75 \text{ \AA}$  (e) towards the sample ( $I = 21$  pA,  $U = 0.11$  V) over the molecule, respectively. The size of images in d and e is  $2.45 \text{ nm} \times 2.45 \text{ nm}$ .

To prove the incorporation of Au atoms and the bonding geometry of the coordinated

structure, we measured the molecular nanostructures with non-contact atomic force microscopy (nc-AFM, see Methods section). We acquired constant height maps of the shift in resonant frequency ( $\Delta f$ ) of a qPlus sensor. The images obtained in the regime of repulsive forces between STM tip and sample reveal the molecular structure of the adsorbed molecule.<sup>47</sup> For these measurements, we functionalized our STM tip with a co-adsorbed Xe atom.<sup>48</sup> In this way, it is possible to obtain stable images at close tip-molecule distances, and achieve intramolecular resolution.<sup>47</sup> Figure 1c shows a (Laplace-filtered) nc-AFM image acquired at the same area as the STM image of figure 1b. The molecular structure can be unambiguously identified from the  $\Delta f$  map. The thiophene backbone appears with the five thiophene rings alternating their orientation, and exposing outwards the two central methyl groups. The nc-AFM image also confirms the four-fold motives formed by four DCV groups around one common point. In spite of the large conformational flexibility of DCV5T-Me<sub>2</sub>, most of the molecules appear with this shape. DFT calculations on the free molecule (see Methods section) reveal that, although there are several DCV5T-Me<sub>2</sub> conformers with similar stability in gas phase, the shape observed in nc-AFM images (and sketched in the inset in Fig. 1a) corresponds to a global minimum of the free, uncoordinated molecule. This minimum energy configuration has a planar structure, thus enhancing its relative stability when forced to lay in a planar adsorption geometry on a metal surface. Focusing on the linking four-fold motifs, a rounded protrusion appears between the four cyano groups when imaged at closer tip-sample distances (Fig. 1e). This protrusion is unambiguously assigned to the Au atom bridging the four negatively charged cyano groups. Moreover, the four cyano groups are located around the Au adatom following a four-fold bonding arrangement, supporting that the Au adatom uniformly bonds to the four surrounding molecules (Fig. 1d).

To determine the effect of the cementing Au adatoms on the molecular functionality, we studied their electronic configuration by means of STS. As a reference, we measured first spectra on the individual DCV5T-Me<sub>2</sub> monomer, lying on bare gold regions between molecular chains. DCV5T-Me<sub>2</sub> monomers appear in STM images with the same conforma-

tion as in the molecular chains (Fig. 2a). Differential conductance spectra acquired on the center and on the DCV endgroups of a DCV5T-Me<sub>2</sub> monomer show a clear peak at 2.0 V (labelled P1 in Fig. 2b) with its largest intensity at the center of the molecule, which we assign to the LUMO-derived resonance. The extended character of the LUMO along the whole molecule, is in agreement with the free-molecule orbital shape obtained from our DFT calculations (Fig. 4b), and confirms that DCV5T-Me<sub>2</sub> monomers maintain to large degree their free-molecule character upon adsorption on the Au(111) surface.

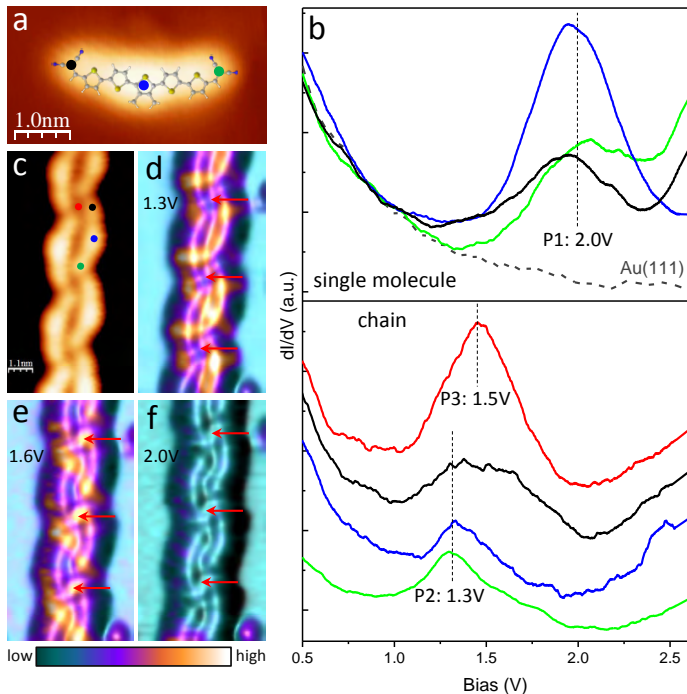


Figure 2: Electronic structure of a single molecule and of a molecule coordinated within a chain. (a) STM image ( $I = 67$  pA,  $U = 0.89$  V) of a single molecule on Au(111), with a DFT optimized configuration superposed. (b)  $dI/dV$  spectra acquired with closed feedback at different locations on the single molecule (upper panel, set point:  $I = 50$  pA,  $U = 0.5$  V) and on the molecule within a chain (bottom panel, set point:  $I = 34$  pA,  $U = 0.2$  V), at sites indicated in Fig. 2a and 2c, respectively. The energetic positions of the resonances in the  $dI/dV$  spectra are highlighted by the black dash vertical lines. Spectra on the coordinated molecule are offset for clarity. (c) STM image ( $I = 22$  pA,  $U = 0.80$  V) of a chain. (d) - (f) Corresponding  $dI/dV$  maps at the energies of the resonances of the coordinated molecules in chains (d), of the Au adatoms (e), and of the single molecule (f), that is, at 1.3 V, 1.6 V and 2.0 V ( $I = 79$  pA), respectively. In (d) - (f) the  $dI/dV$  signals (bright) are overlapped on top of a top-illuminated STM topography. The red arrows indicate the positions of the Au atoms incorporated in the chain.



The incorporation of Au atoms modifies the resonance structure of the DCV5T-Me<sub>2</sub> molecules. Lower panel of figure 2b shows STS spectra recorded on different positions within the chain structures shown in figure 2c. We find that the new LUMO state is a resonance centered at 1.3 V (P2). This state is observed with larger weight on the sites closer to the Au atoms, as pictured in dI/dV maps (Fig. 2d). On top of the Au atom, the state appears centered at 1.5 V (P3) suggesting that this corresponds to an atom-derived localized state.<sup>18</sup> In fact, the dI/dV map recorded at 1.6 V (Fig. 2e) allows to resolve the position of individual Au adatoms incorporated in the self-assembled chains, otherwise not visible in the STM topographic images (Fig. 2c). The downshift of the LUMO state from 2.0 V to 1.3 V, and its localization at the terminal groups, are ascribed to the effect of hybridization with Au adatoms, presumably mixing N lone-pair 2p electrons of cyano groups with Au 6s electron of gold adatoms.<sup>18,29-31,49</sup>

Intercalated metal atoms, therefore, modify the electronic structure of molecular layers, even on weakly interacting substrates. The redistribution and localization of electronic states induced by coordination to Au atoms may affect exciton mobility, whereas, orbital energy shifts modify energy level alignment at the interfaces. However, in real molecular devices, molecules pack in films with geometries different than chain structures reported here, such as molecules asymmetrically bonded to the metal.

To explore the effects of asymmetric bonding to metal atoms, we extend our analysis to molecules at the ends of the molecular chains, as shown in figure 3. Terminal DCV5T-Me<sub>2</sub> molecules in the chain bond to only one Au adatom at one side, while they expose an uncoordinated DCV endgroup at the other (Fig. 3a). The effect of such asymmetric coordination pattern is reflected in the electronic configuration. In figure 3b, we compare STS spectra taken over both molecular ends. At the coordinated side of the molecule, the first unoccupied resonance appears at 1.4 V similar to the symmetrically coordinated case, whereas the uncoordinated side shows only a higher-lying resonance at 2.2 V (P4). This asymmetric resonance redistribution is reflected in the spatially resolved spectroscopic maps

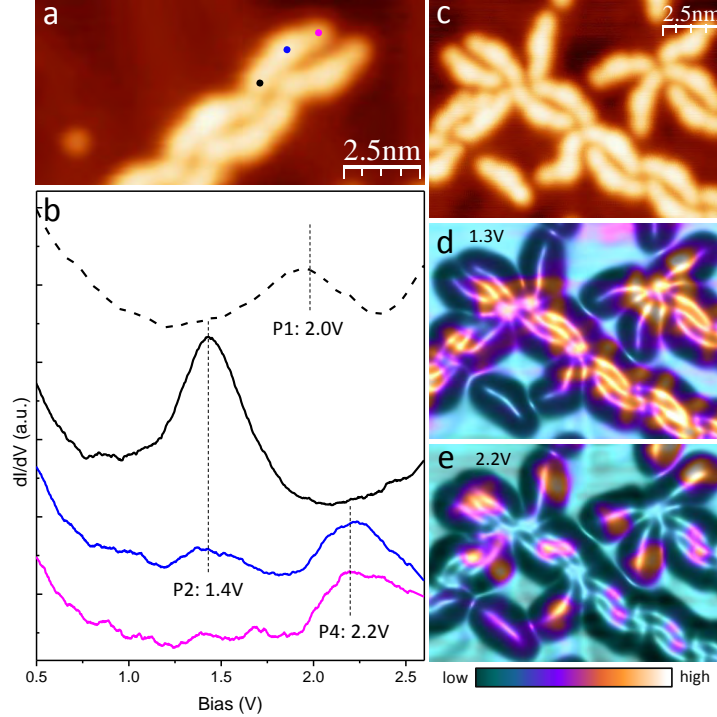


Figure 3: Electronic structure of a one-side-coordinated molecule. (a) STM image ( $I = 24$  pA,  $U = 0.71$  V) of a chain termination showing two molecules without coordination bonds at the end. (b)  $dI/dV$  spectra acquired with closed feedback (set point:  $I = 34$  pA,  $U = 0.2$  V) at different locations on the end molecule as indicated in a. The black dash spectrum taken at one side of the single (uncoordinated) molecule of Fig. 2a is shown here as a reference. The energetic positions of the resonances in the  $dI/dV$  spectra are highlighted by the black dash vertical lines, and all the spectra are offset for clarity. (c) STM image ( $I = 50$  pA,  $U = 0.80$  V) of chains with only one-side-coordinated molecules at the ends. (d) and (e) Corresponding  $dI/dV$  maps at the energies of the resonances of the coordinated sides and free sides of the terminal molecules, that is, at 1.3 V and 2.2 V ( $I = 50$  pA), respectively. In (d) and (e) the  $dI/dV$  signals (bright) are overlapped on top of a STM topography.

at the corresponding resonance voltages. At 1.3 V, the  $dI/dV$  signal is localized at the joints of cyano groups, corresponding to the position of Au adatoms and coordinated DCV groups (Fig. 3d). In contrast, the spectroscopy map at 2.2 V (Fig. 3e) shows  $dI/dV$  signal only at the free sides of the terminal molecules. These  $dI/dV$  maps corroborate the fact that the molecular orbital alignment and spatial distribution within individual molecules are strongly modified by metal-ligand coordination.

The origin of the resonance splitting and redistribution cannot simply be explained by a bare orbital shift. As reported in ref. [34], coordination to Au atoms enables the mixing

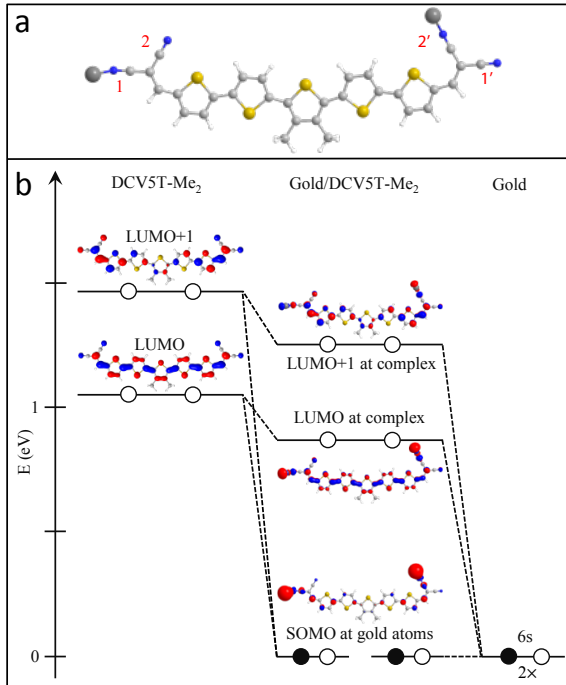


Figure 4: DFT calculations of the Au/DCV5T-Me<sub>2</sub> complex with two Au atoms. (a) The relaxed structure. The grey circles represent Au atoms. The distances between Au atoms and nitrogen atoms from the molecule are 2.2 Å, which are within the range of coordination bond length. (b) Schematic diagram of the calculated energy levels and density of states of the orbitals participating in the formation of the metal-ligand complex. Unoccupied and occupied states are represented by open and filled circles, respectively.

of molecular states with gold orbitals. To determine the degree of orbital mixing in these systems, we have carried out DFT calculations of molecular orbitals and charges for (i) an isolated molecule and for a molecule coordinated with (ii) one Au atom and (iii) two Au atoms. Due to the weak interaction of the supporting Au(111) substrate with the DCV5T-Me<sub>2</sub> molecule<sup>12</sup> and the negligible spatial overlap between adjacent molecules, these results reproduce the main trends observed in our experiments. DCV5T-Me<sub>2</sub> has four non-equivalent cyano groups, which are labeled as 1, 1', 2 and 2' in figure 4a. To simulate the experimentally determined bonding structure, we calculated a metal-organic complex with two Au atoms bonded at sites 1 and 2'. The energy optimized structure reproduces a CN-Au bond length of 2.2 Å, which is characteristic for coordination bonds.<sup>13</sup> Similarly, the complex with only one Au atom (located at site 2', Fig. 5a) possesses a coordination bond with bond length

of 2.3 Å. Hence, our simulations reproduce the chemical activity of CN endgroups to form a local bond with gold atoms.

We look first into the effect of the metal-organic bond on the orbital structure of the complex with two Au atoms. Figure 4b presents the calculated energy levels and spatial distribution of atomic and molecular orbitals around the chemical potential. The LUMO and LUMO+1 of the isolated molecule interact with the 6s states of the gold atoms, resulting in a set of new orbitals (central column of Fig. 4b). The states with the lowest energy are two singly occupied orbitals (SOMO) localized at the gold atoms (regarded as the zero point of the system) and mainly with Au(6s) character. Above them, other states exhibit the symmetry and characteristic nodal structures of LUMO and LUMO+1 orbitals of the isolated molecule, with a down-shifted energy alignment. The coordination bond with the gold atoms is weak, amounting to 284 meV. A Mulliken analysis of the charge distribution shows no significant charge transfer between the Au atoms and the molecule, but just some charge redistribution within the molecules.

For the case of bonding to only one single Au atom, the simulations reproduce the asymmetric spatial distribution of the molecular states. Figure 5b shows the calculated energy levels and orbital amplitude isosurfaces for the complex with only one Au atom bonding to the 2' site. Three new orbitals are generated at the metal-molecule complex from the two original orbitals at the molecule and the Au(6s) state (central column of Fig. 5b). The SOMO state near the zero point energy is localized at the Au-N node. We also find here no significant charge transfer between the Au atom and the molecules, and an overall energy down shift of the renormalized LUMO and LUMO+1 states, in consistency with the experimental case. However, now the states show a clear asymmetry in the orbital shape: the new LUMO appears localized around the molecular end contacting with Au atom, whereas the new LUMO+1 state shows larger intensity at the opposite side of the metal-ligand bond.

We note that for the free, uncoordinated molecule, the LUMO is mirror symmetric with respect to the center of the molecule, whereas the LUMO+1 is anti-symmetric (Fig. 5c

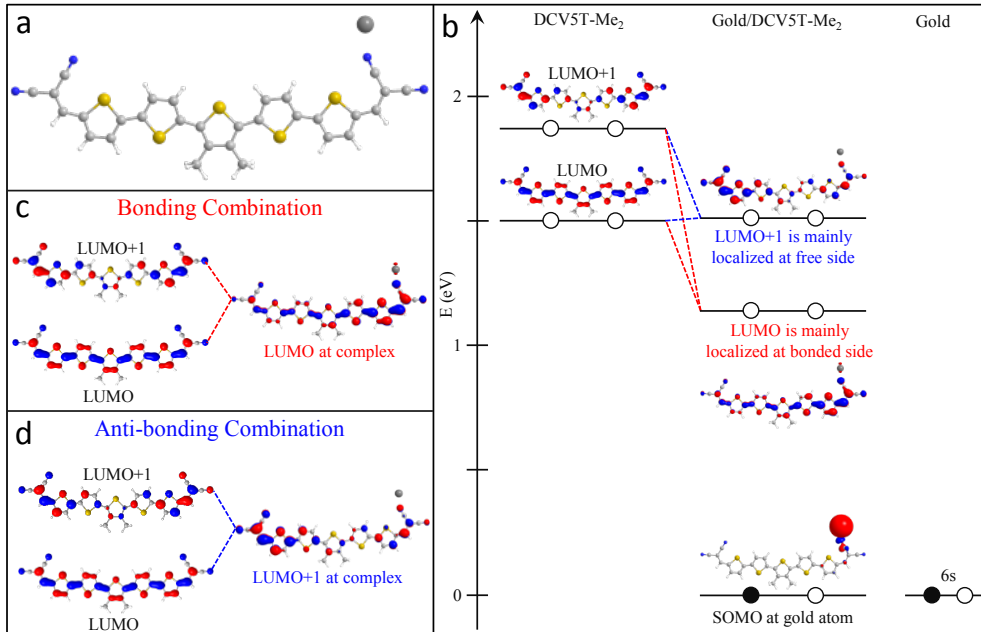


Figure 5: DFT calculations of the Au/DCV5T-Me<sub>2</sub> complex with one Au atom. (a) The relaxed structure. The grey circle represents the Au atom. The distance between Au atom and nitrogen atom from the molecule is 2.3 Å. (b) Schematic diagram of the calculated energy levels and density of states of the orbitals participating in the formation of the metal-ligand complex. Unoccupied and occupied states are represented by open and filled circles, respectively. (c) and (d) The new LUMO and LUMO+1 orbitals with asymmetric shape at the complex originate from the bonding combination and anti-bonding combination of the original LUMO and LUMO+1 orbitals of the molecule, respectively.

and 5d). Hence, the renormalized molecular states necessarily involve the mixture of free-molecule states to adapt themselves to the new geometry. This can be interpreted at the very basic level as a linear combination of free molecular orbitals. In fact, our DFT results show that the Au(6s) states mix with only the LUMO and LUMO+1 orbitals of the free molecule giving rise to a new set of states with a spatial distribution adopting the symmetry of the singly coordinated molecule. The molecular and atomic occupied states, in contrast, remain fairly unperturbed. Comparing the orbital shapes from figure 4b, the splitting of the original LUMO into two asymmetric states is then described by the respective addition and subtraction of some weight of the original LUMO+1 to (Fig. 5c) and from (Fig. 5d) the free LUMO.

## Conclusions

In summary, we have shown that A-D-A oligothiophene DCV5T-Me<sub>2</sub> self-assembles on a Au(111) surface *via* the capture and coordination to Au adatoms, mediating the formation of metal-organic chains. The coordination with the metal proceeds *via* terminal CN groups and causes a characteristic energy downshift of the LUMO-derived state with respect to uncoordinated single molecules. Interestingly, we observe that for molecules showing coordination to Au adatoms in only one of the two ends, the down-shifted LUMO appears localized at the coordinated side with the new LUMO+1 localized at the opposite side. We interpreted this new set of states using a linear combination of molecular orbitals, in which the Au atom triggers a mixing of unoccupied states to produce a new set of orbitals that are adapted to the new bonding geometry. This depicts a tuning strategy to manipulate the orbital character of molecular films by the inclusion of intercalated metal atoms in their structure.

## Methods

Our experiments were performed in a combined STM/AFM at a temperature of 5 K and under ultrahigh vacuum conditions. Nc-AFM measurements were carried out using qPlus tuning fork design,<sup>50</sup> operated in frequency modulation mode with sub-angstrom oscillation amplitudes. The Au(111) surface was cleaned by repeated cycles of Ne<sup>+</sup> sputtering and subsequent annealing to 750 K. DCV5T-Me<sub>2</sub> molecules were evaporated on the sample kept at room temperature from an organic molecular evaporator with a quartz balance for controlling the deposition coverage. All the STM topographic images were acquired in constant current mode with typical parameters of 20-120 pA and 0.5-1.4 V, whereas AFM images were acquired by mapping the frequency-shift ( $\Delta f$ ) of the qPlus sensor in constant height mode. To increase the resolution in AFM images, the STM tip was functionalized with Xe atoms co-deposited on the surface. The dI/dV spectra and maps were recorded with a

lock-in amplifier with typical modulation amplitude of 12 mV and frequency of 740 Hz. The topographic data were processed with Nanotec WSxM software<sup>51</sup> and the spectra data were processed with Mike Rubys Spectroscopy Manager.<sup>52</sup>

DFT calculations were performed using the GAUSSIAN 03W program package.<sup>53</sup> All calculations including geometry optimizations and electronic excitation energies were carried out on isolated molecular assemblies using the B3LYP exchange-correlation functional. The 6-31G and LanL2DZ basis sets were chosen for single molecule and Au/molecule systems, respectively, as a compromise between accuracy and applicability to large molecules and metal atoms.

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