Anisotropic electron conductance channel on porous dibromobenzothiadiazole network on Cu(110) driven by reaction byproducts

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Preserving the molecular electronic character while achieving efficient charge-transport in organic networks is a fundamental but challenging prerequisite for the performance of optoelectronic and energy-conversion systems. Here, we demonstrate a mechanism enabling charge-transport in one-dimensional conductance channels bridging discrete molecular states at 2.1eV through the pores of a metal-organic network based on the redox-reacted 4,7-dibromobenzo[c]-1,2,5-thiadiazole (2Br-BTD) molecules on Cu(110) and on their residual inorganic byproducts. These conductance-paths along the [1-10] crystallographic direction rely on two adjacent and periodic contributions, namely a resonant molecular state and the confined surface-state at the pore center. Br atoms, detached from the assembled, redox-reacted molecules, drive the confinement of the Cu surface state within the pores and critically control the channel continuity through their displacement within the network. Thus, this work opens new perspectives on a charge-transport mechanism where single atoms control the order-disorder transition in an organic network.

Molecular- based structures have gained rising interest as active components in opto-electronics, energy conversion and catalytic systems. Despite their functional properties, studies have revealed that charge transport processes occur through discrete, albeit periodic building-blocks with limited orbital overlap resulting in a poor electron conductance, which reduces the efficiency of devices [woodroofe2012]. Indeed, higher electron-conductance has been observed through the backbone of structurally aligned polymers, or extended π-conjugated molecules covalently assembled by on-surface chemical reactions, which enable the delocalization of electrons[Schweicher Adv. Mat. 2020, Basagni ACSnano2016, Noriega2013]. Despite this, two additional factors, as structural disorder and the energy difference of the contact electrodes further contribute to the charge localization limiting their mobility [adv.mat2020, Noriega Nat.mat12.1038.2013;]. Here, we report on the mechanism enabling charge-transport in one-dimensional conductance channels bridging discrete molecular states at 2.1eV through the pores of a metal-organic network on Cu(110). The intermolecular charge transport occurs isoenergetically through spatially adjacent states, providing effective paths for charge-transport while preserving the molecular functional character. The effect of structural order-disorder transition created by the displacement of single atoms within the network, which disable the charge transport mechanism, will be visualized in space-resolved energy maps.

At this aim, we characterize by means of scanning tunneling spectroscopy measurements and density functional theory calculations the assembly of the redox-reacted 4,7-dibromobenzo[c]-1,2,5-thiadiazole (2Br-BTD) molecules together with its reaction byproducts on Cu(110). BTD molecules are a prototypical compound widely used in optoelectronics and photovoltaics, as the electronic structure of the thiadiazole unit is prone to adsorb visible light [Acc. Chem. Res. 2018, 51, 5, 1196-1205. J. Mater. Chem. C, 2016, 4, 6200-6214][Acc. Chem. Res. 2015, 48, 1560-1569]. [angew chem.55, 3566, 2016, JACS 1999, 121, 10068; JACS 140, 8526, 2018; Inorg.chem.54, 10738, 2015]. The adsorption and assembly of these molecules on the Cu surface leads to a spontaneous redox reaction at the two Br terminations which transmetalate with Cu adatoms detaching from the molecules according to the Ullmann C-C cross-coupling reaction scheme[Bieri2016, dong2015, sarasola2018]. By analyzing the density of states and the local surface potential across the metal-organic structure, we determine that the detached Br atoms are still part of the assembled metal-organic network and play a fundamental role in the formation of the conductance channels. . Even if not directly involved in the conductance path, the presence of Br atoms, adsorption position and bonding configuration within the metal-organic network is fundamental for the delocalization of the electron acceptor states of the sulfur termination and thus, in optoelectronics, for the transport of photo-generated charges. Structural relaxation and displacement of single Br atoms causes structural disorder, which reflects into an electronic disorder disrupting the continuity of the 1D conductance channel through disalignments of the energy levels.

A prototypical image of the Cu(110) surface after the molecular deposition is shown in figure 1. A mild post annealing at 400K favors the molecular ordering into two-dimensional structures, where self-assembled dimers pile up into parallel rail-lines along the [1-10] crystallographic direction. The stacking interdimeric lateral distance is determined by the bulky benzene groups and by the two intermediate Cu adatoms resulting from the molecular dehalogenation reaction [Dong2015]. At the center of the rail (see the white dashed line of the figure 1a), two Cu-coordinated thiadiazole groups face each other, and while remaining separate of almost 1nm from the center of sideway neighboring dimers Thus, the pristine 2Br-BDT molecules self-assemble in metal-organic networks with the sulfur atoms at the center of a porous structure. Despite this porosity, mono-dimensional, highly-directional and several nanometers long conductance-channels, can be clearly observed at the center of the rail-lines, thus perpendicular to the molecular axis, in the spectroscopic energy map at 2.1eV (figure 1b).

In order to explain the mechanisms that enable the formation of conductance paths at the rail centers, we focus first on the characterization of its pristine constituents, i.e. the isolated dimers. Interestingly, at 2.1eV, energy of the conductance channel, the self-assembled 2Br-BTD single dimer is characterized by a resonant electron state observable surrounding the -S-Cu-Cu-S- bonds at the dimer center (figure 2b). However, when self-assembled, the lateral extension of this state is too small to bridge the distance between neighboring dimer centers (see figure 2d) and the resonant states remain localized in the central region of each dimer Thus, the formation of the conductance channel observed in figure 1 cannot be explained on a pure molecular basis. This observation suggests that a second contribution to the conductance should rise in the interdimeric pore region enclosing the Cu surface. Thus, these intermolecular conductance paths are enabled by a set of localized periodic contributions.

The clean Cu(110) surface is characterized by a well-known unoccupied Schockley surface-state having a band minimum at reciprocal Y point of the surface Brillouin zone at 2eV [Goldmann1985, Bartynski1986, Zeybek 2006, Jacob1986, Kevan1983]. Despite the weak visibility of a state at high momenta in scanning probe technique, a clear increase can be observed in the dI/dV signal in the pores as compared to the clean Cu(110) (figure 1 and Supp.Info), suggesting a quantum confinement effect. According to the particle in a box model, for a pore size of about 1.8 nm (Supp.Info) which perfectly matches the periodicity of the rail-lines along the [001] direction, an energy upshift of about 100meV is expected. This feature indicates that backscattering events occur each 5- Cu lattice constants this direction, that corresponds to the Y direction of the reciprocal space.

As a necessary condition for the electron backscattering and the consequential quantum confinement is a variation of the surface potential, $\Delta\Phi$, [Burgi 2002, Davis1991(?), Hasegawa1993(?), Hormandinger1994, Gross2004, Pennec2007], we have locally probed its spatial dependence for the different molecular functional groups and compared the signals of the isolated and assembled dimers [vitali2010] (see figure 3). A sharp maximum at the center, two maxima at the hetero-organic groups of each of the two BDT molecules and a shallow minima at the Cu surface characterize the potential of the isolated dimer with respect to the clean Cu(110) surface (blue line). These variations reflect the charge distribution and local dipoles as well as the capability of the surface to screen them. The potential profile observed along the dimers of the self-assembled structure resembles the one of the isolated moiety (green line) with a comparable sharp maximum at the sulfur center. However, the three maxima measured at each molecular unit of the self-assembled case differ remarkably from the two maxima observed on the isolated dimers.

The origin of this additional peak can be understood considering the structural relaxation that occurs during the self-assembly of 2Br-2Cu-BDT dimers into rail-lines. According to DFT calculations, (figure 2c-d and Supp.Info.) the inter-pair interaction promotes a structural relaxation of the Cu-oxidized 2Br-BDT molecules by which the Br atoms move towards diagonal positions between the Cu adatoms, decreasing their interaction. Specifically, two Br atoms move to the outer side (outer Br) of the molecular structure, whilst the other two stay inside (inner Br) the pore. Despite the Br atoms form a rhombus structure with the Cu adatoms bridging the BDT molecules at the benzene side, the substrate symmetry imposes some differences. The outer Br atoms interact more weakly with the Cu adatoms favoring their diffusion towards the benzo-group of the molecules in the neighboring rail-line. As a result, a zigzagging line of Br atoms is formed in the inter-rail channel as sketched in the molecular structure superimposed to the topographic image in figure 3.

The projected density of states (PDOS) (see Figure * of SI) and Bader charge analysis confirm the different configuration of the inner and outer Br atoms: whilst the bonding direction of the inner Br atoms has a planar component that suggests a bonding with the two Cu adatoms and the charge accumulation amounts about 0.4e$^-$, the linkage direction of the outer Br atoms has a predominant pz character and accumulate a little bit more charge, i.e., almost 0.5e$^-$, a quantity comparable the one predicted for the adsorption of Br atoms on Cu(110) [Migani 2006]. These differences suggest that the variation of the potential profile in the assembled species with respect to the isolated one should be associated to the outer Br atoms. Indeed, the distance between the outer Br atoms in consecutive parallel zigzag chains is about 5 lattice constants and matches the distance necessary for the quantum confinement (Supp.Info) [Goldmann1985, Zeybek 2006, Jacob1986]. Besides, the effectivity of the scattering process of the surface electrons is related to the stronger interaction of the outer Br atoms with the Cu surface, as it is the case of the linkage of the Br atoms through the pz orbitals in our system [hormandinger1994].

The direct comparison of the local surface potential along the intra rail-line and along the Cu-benzo structure (see Figure S* c, d panels) further corroborates this statement. Indeed, the periodicity and profile of the potential along the zigzag line correspond to the additional peak seen in figure 3d, while the potential measured at the Cu-Cu and inner Br atom shows a lower variation.

Despite the potential profile measured along the zigzag line (Supp.info) show a periodic distribution of maxima corresponding to the outer Br atoms, the conductance channels shown at the dI/dV map of figure 1 show also certain discontinuities. The potential measured along a line passing through the S centers (red line in figure 3) witnesses this disconnection. Actually, offsets of about 150 meV can be observed in the periodic sequence of maxima, corresponding to -S-Cu-Cu-S- at center of the dimer, and minima at the Cu enclosed in the pore regions, respectively . The regions with the lowest potential offset localize electrons [burgi, chen?] and indeed correlate with the region where the conductance channels are continuous (see also Supp.Info). Vice versa, the potential region showing the highest offset correlate with the discontinuity of the channel.

But Br atoms contribute importantly not only to the formation of the conductance channel confining the surface electrons , but also in the rupture of their continuity.

The first evidence emerges from the observation of the experimental density of states localized at the bridging position between the benzo-groups of a rail lines. Energy maps shown in figure 4 correlate the discontinuity of the conductance channel with the attenuation of the density of states at these bridging positions. DFT calculations predict that the density of states at the Cu-Cu coordination atoms changes considerably if a inner Br atom is displaced towards the pore center (see SI figure*). The displacement of the Br atom causes the reorientation of its bonding orbitals from pxy towards the pz, recalling the configuration of the zigzag line. Indeed, the partial occupation of the pore can be observed also in high-resolution topographic images (see also Supp.Info).

Upon occupation, the pore is reduced in its dimension, thus becoming too small for the quantum confinement mechanism of the wavelength of the Cu(110) surface state which it turns to be ineffective (see SI). Consequently, the iso-energetic continuity of the conductance channel is interrupted , which, in its turn, is reflected in the increase of the local potential map shown in figure 4f.

The movement of the Br atom is validated also by the measurements of the potential profile along the Cu-Benzene line shown in Supp.Info.

In conclusion, we have shown the decisive role of the Br atoms on the formation and rupture of the conductance channels we observe. We have demonstrated on the one hand that, the zigzag lines of Br atoms **Angstroms apart in the Cu(110) surface work effectively as bouncing walls for the confinement of surface electrons which resonantly couple to the molecular resonant state of the assembled Cu-BDT dimers, forming a continuous channel at 2.1eV, and on the other hand, we have detected the motive for the disruption of such a channel in the displacement of internal Br atoms into the pores of the metal-organic assembly. Besides, we report the strict correlation between the electronic properties of the organic structure and the local surface potential, pointing this latter magnitude as an informer of the precise adsorption position of single Br atoms, byproducts of the redox-reaction of BDT molecules on the Cu(110) surface . Although these Br-based byproducts of surface-reacted halogen-functionalized molecular moieties do not contribute directly to the conductance, they are fundamental for the quantum confinement of the sp-unoccupied Schockley surface states electrons within the pores. Thus, this work opens new perspectives on charge-transport mechanisms where single atoms control the order-disorder transition in an organic network acting on the electron level alignment of the metal-organic structure.

Acknowledgments

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In porous networks with constituents of multiple chemical nature, the exact correlation between the morphological intriguing structure and charge transport is unknown, despite the potentialities in optoelectronics and energetics [Bieri Chem Commun.2009, 6919; REF].

Figures

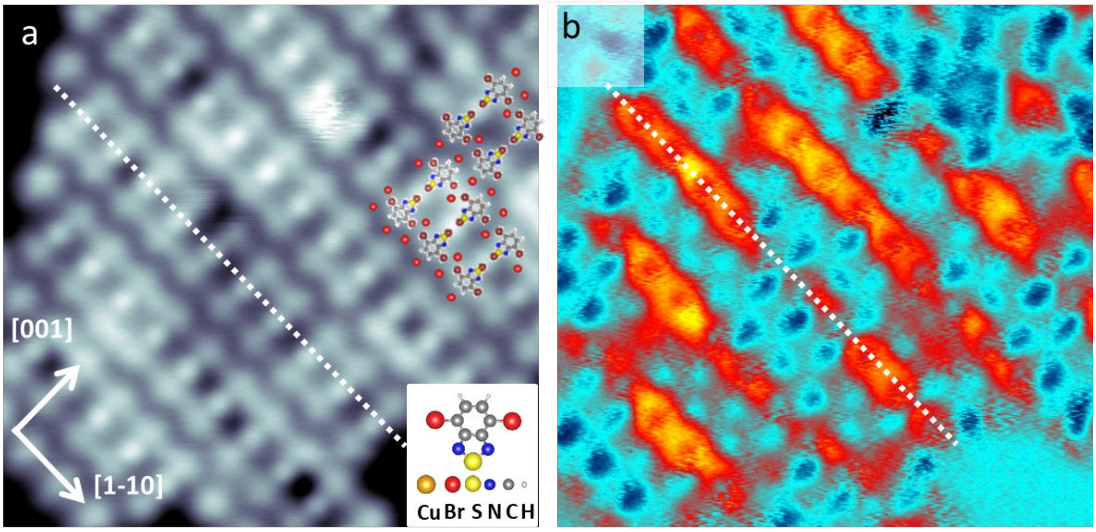

Figure 1: Structural and energy map of 2Br-BTD molecules self-assembled on Cu(110) surface. **a**. Topographic image (Image size: 11.7nmx11.4nm). Model structure is superimposed. Inset: chemical structure of the deposited dibromo-benzothiadiazole (2Br-BTD) molecule **b.** Conductance map at 2.1 eV of the metal-organic structure of panel a showing one-dimensional conductance channels along the [1-10] direction. Dotted lines highlight the topographic localization of high conductance.

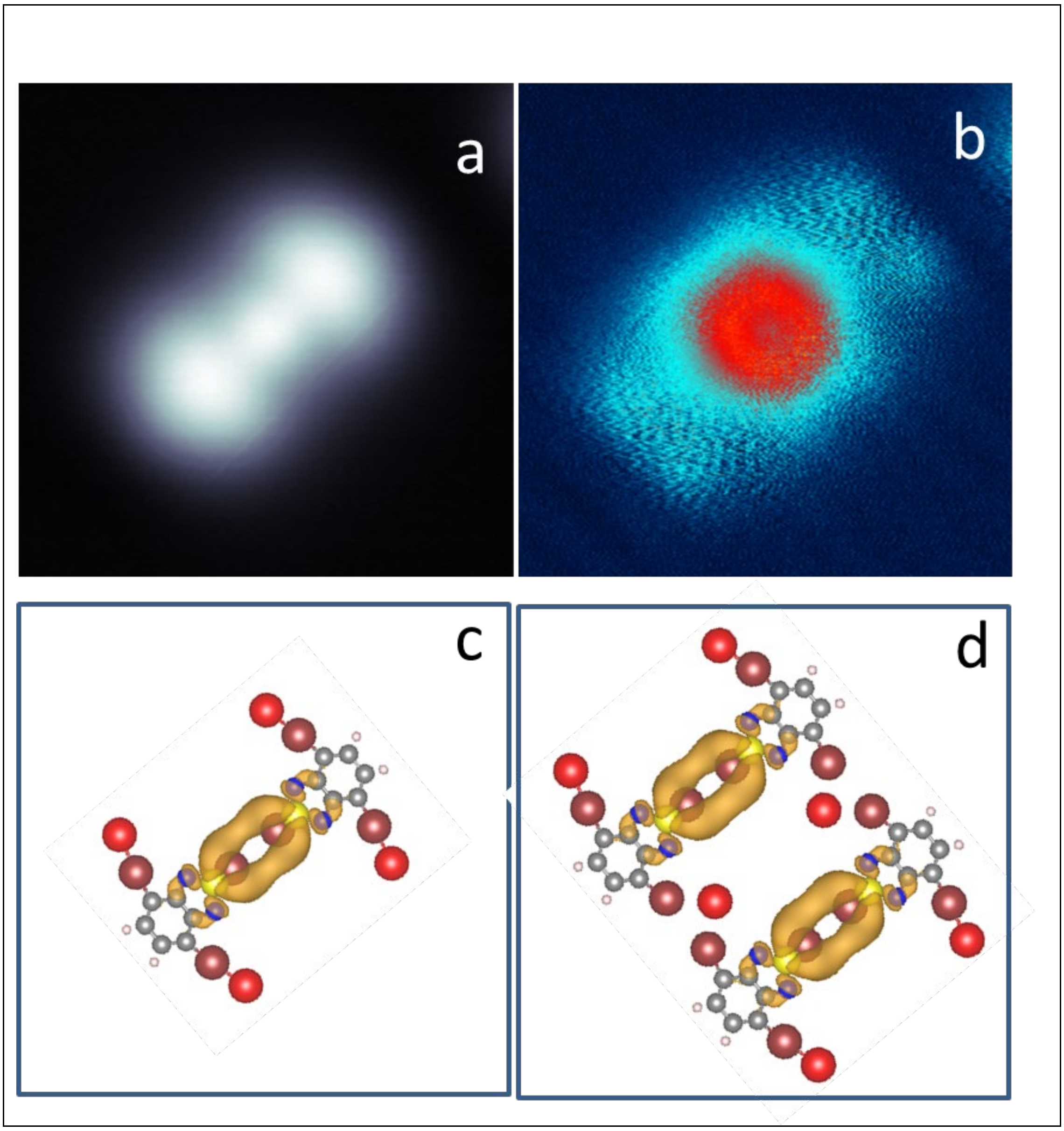

Figure 2: **Metal-organic structure forming upon assembly of 2BrDBT dimer on Cu(110) surface**. **a.** Topographic and **b**. DOS map of an isolated dimer at 2.1 eV. Image size:4.5x4.5nm**. c-d.** Simulated images of the dimer and dimer pair structure in gas-phase. The localized DOS at the center of the dimer is superposed to the structure.

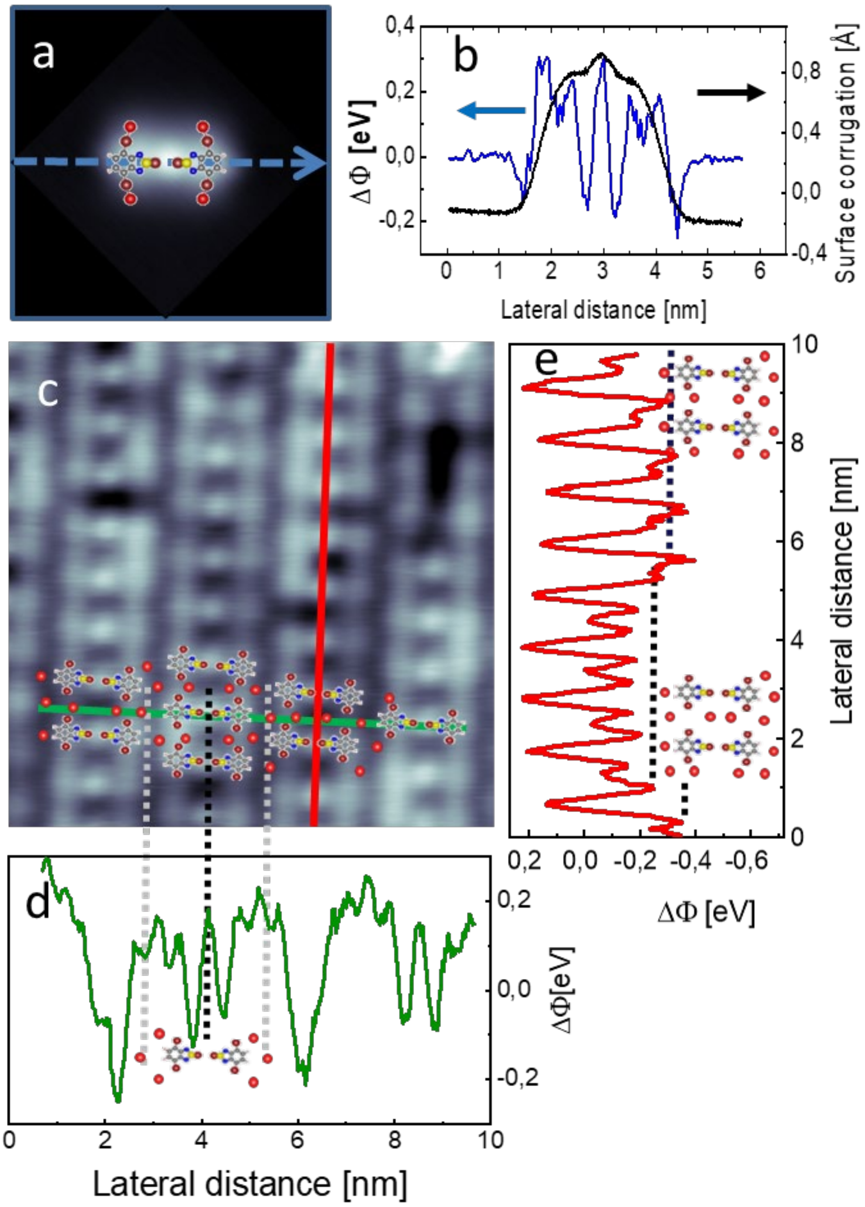

Figure 3. Local surface potential measured on isolated and self-assembled 2Br-2Cu-BDT dimer on Cu(110) : **a**. Topographic image of isolated dimer. (Image size: 5.7x5.7nm) **b**. Potential variation profile (blue) along the dimer and its topographic corrugation along the line traced in a. **c.** Topographic image with the proposed structural model superimposed. (Image size: 10x10nm) **d-e**. Local surface potential profile measured along the blue and red lines traced on c. Dot-lines are a guide to the eyes to relate the potential with the dimer centers (black) and to the Br atom positions (gray).

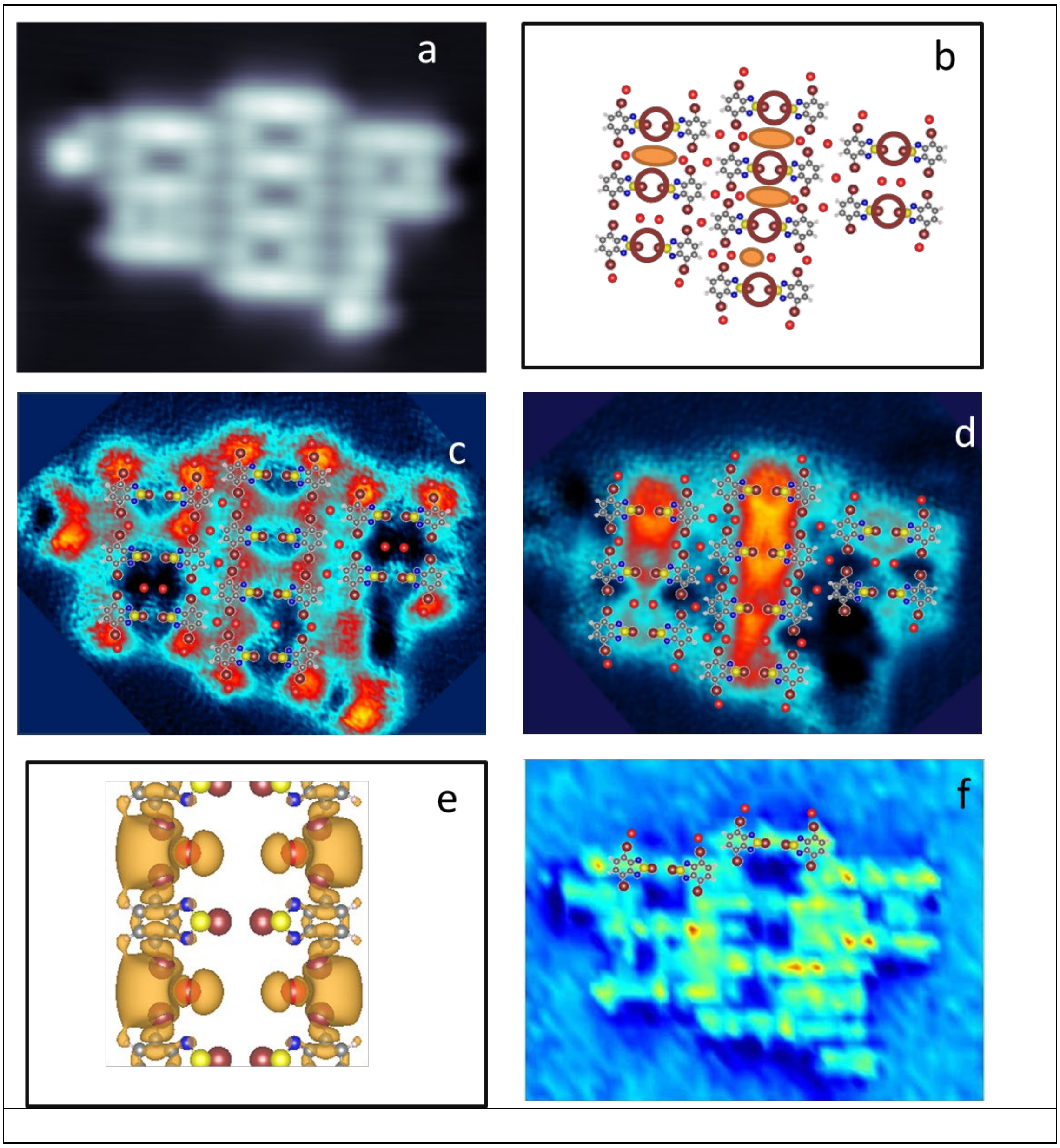

Figure 4. Self-assembled dimer structure: **a.** Topographic image (size 10x6.3nm). Sketch of the proposed mechanism originating the 1D-conductance channel. Orange circles correspond to the region of confined surface state. Red circles highlight the localized resonance at the S dimer bond. **c-d.** Constant energy maps at 1.6 and 2.1eV, respectively. Localized density of states with a characteristic triangular shape (red contrast) are seen in-between dimer pairs at the lowest energy in correspondence of the continuity of the 1D channel. **e.** DFT calculation of the density of states localized at the Cu-Br structure between dimers. **f.** Two-dimensional plot of the measured surface potential landscape showing a clear correlation between conductance and surface potential.