

Project B12

STM investigations of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

Organic charge-transfer salts like κ -(BEDT-TTF)₂X are prototypical for quasi-two-dimensional correlated electron systems close to a Mott transition. In these materials, the tendency towards correlation-driven charge localization competes with the formation of a superconducting, long-range phase-coherent ground state. We apply scanning tunneling spectroscopy (STS) on κ -(BEDT-TTF)₂Cu[N(CN)₂]Br to study the electronic density of states (DOS) in the normal and in the superconducting state. The DOS is the key property to describe the electronic state caused by the variable many-body interactions in these materials. The experimentally obtained DOS comprises a logarithmic suppression at the Fermi edge as predicted by the Anderson-type models with weak disorder [1,2]. Our results implicate that disorder plays an important role for the two-dimensional electronic structure of charge transfer salts [2]. Hence we plan systematic studies on established κ -(ET)₂X systems with a tunable degree of disorder in close cooperation with projects B2, B6 and B11.

Furthermore, numerical fits allow to unfold the DOS in the superconducting state. Here, we find as a new property a double gap structure previously only observed for a few materials like MgB₂ [3]. Both gaps show a BCS like temperature behavior and vanish above the critical temperature T_c . A possible explanation for the two-gap structure might be the presence of two overlapping bands at the Fermi level. If interband scattering prevails over intraband scattering two energy gaps of different size will open in the superconducting phase [4].

Additionally, the two-dimensional structure of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br becomes visible in electronic structure as well as in the STM images. We can identify the layered crystal structure showing alternating stripes of the conducting BEDT-TTF and of the insulating Cu[N(CN)₂]Br anion layers [3]. In order to address the question of the symmetry of the superconducting order parameter we plan to exploit the capability of the STM to find areas of different surface orientation on surfaces cleaved perpendicular to the conducting planes.

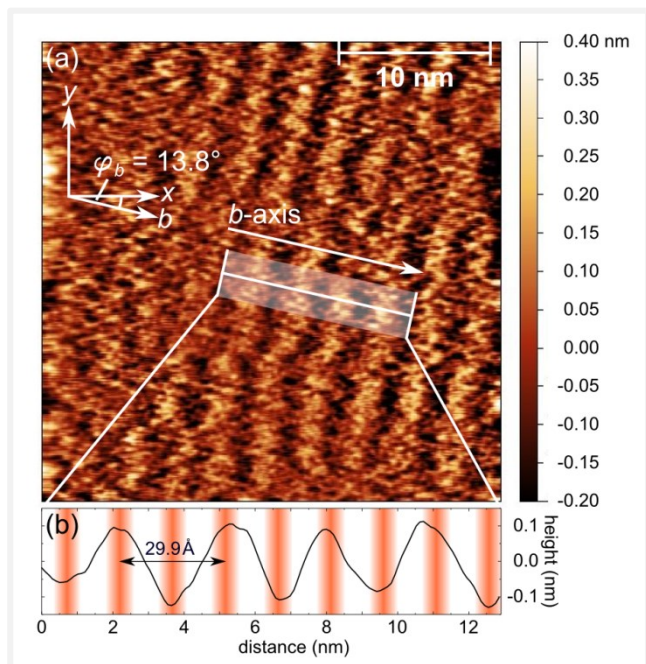


Fig.1. (a) (30x30)nm² STM image of the crystal surface revealing a stripe pattern. (b) The height profile reveals an average stripe width of 29.9Å. The red stripes indicate the position of the insulating layers.

- [1] H. Shinaoka et al., PRL **102**, 016404 (2009).
- [2] S. Diehl et al., arXiv: 1410.5245.
- [3] S. Diehl et al., arXiv: 1411.3181.
- [4] H. Suhl et al., PRL **3**, 552 (1959).

Novel charge-transfer compounds at metal interfaces

The interplay of electronic correlation effects with low dimensionality and geometric frustration of charge-transfer (CT) compounds provides a large playground for variable many-body interactions. Novel systems of molecules with tailored donor and acceptor character provide a vast multitude of possible modifications. Understanding the electronic structure of this class of materials as well as their metal-organic interfaces is crucial for designing specific electronic properties. An important precondition for the implementation of organic charge-transfer salts in electronic devices is the fabrication of thin films with appropriate molecular orientation. Deposition of films under ultrahigh vacuum (UHV) conditions promises the formation of well-defined interfaces and extends the range of charge-transfer systems to donors and acceptors that are not solvable and therefore cannot be fabricated by wet chemistry [5].

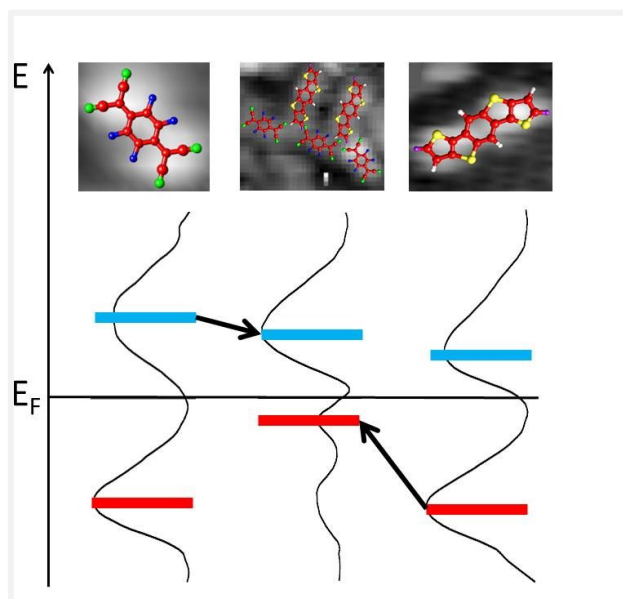


Fig.2. Illustration of the charge transfer from the donor DTBDT (right) to the acceptor F₄TCNQ (left) in the mixed compound (center) as deduced from HOMO (red) and LUMO (blue) positions measured by STS.

The present work aims at an understanding of the electronic structure of charge-transfer compounds by systematic variation of donor and acceptor strength of novel families of molecules. In project B12 we investigate donor-acceptor compounds as thin films deposited in-situ in UHV. The thin films are investigated by scanning tunneling microscopy (STM) and spectroscopy (STS) allowing the characterization of occupied and unoccupied electronic states near the Fermi level. Results from ultraviolet photoelectron spectroscopy and near-edge X-ray absorption spectroscopy performed in project B8 provide complementary information covering a larger energy range [6]. The donor and acceptor molecules are synthesized in project B10.

An acceptor molecule in direct contact with a metal surface tends to form a negatively charged species, while the donor molecule tends to transfer charge from the molecule to the metal. As a consequence, the substrate may provide an additional free parameter for tuning the electronic interaction within the CT compound.

A molecular monolayer of the novel charge-transfer salt dithienobenzodithiophene-tetrafluorotetracyanoquinodimethane (DTBDT-F₄TCNQ) has been deposited on different substrates [7]. STS reveals the energetic positions of molecular orbitals including the highest occupied (HOMO), the lowest unoccupied (LUMO) molecular orbital and also interface states of acceptor and donor in the pure and in the mixed phase. The mixed charge-transfer phase exhibits a significantly shifted HOMO close to the Fermi edge depicting a charge-transfer of less than one elementary charge between donor and acceptor. The total amount of the transferred charge depends on the underlying metal substrate. The binding energy of the CT-HOMO decreases from 0.35 eV to 0.15 eV for increasing electronegativity of the substrate, thus revealing the tunability of the hole injection barrier.

[5] K. Medjanik et al., *Physical Review B* **82**, 245419 (2010).

[6] K. Medjanik et al., *J. Am. Chem. Soc.* **134**, 4694 (2012).

[7] D. Bayer, et al. *Phys. Rev. B* **89**, 075435 (2014).