

Project B12

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

We investigate small crystals of the organic charge-transfer salt κ -(BEDT-TTF)₂Cu[N(CN)₂]Br which are provided by project B6 (Michael Lang). This organic system has an interesting phase diagram [1] with a neighboring superconducting and Mott insulating phase. Because of this the superconducting properties of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br strongly deviate from BCS theory but resemble the properties of high-T_c cuprates. This has been attributed to their two dimensional structure leading to electronic correlation effects [2]. All our investigations were done under UHV-conditions ($5 \cdot 10^{-11}$ mbar) using a low temperature scanning tunneling microscope. The surface of the crystals was prepared by in-situ cleaving.

For a better understanding of the electronic properties we measured temperature dependent differential conductivity spectra using scanning tunneling spectroscopy. With this method the shape of the superconducting gap can be determined. This specifies the order parameter of the second order phase transition from the metallic to the superconducting state giving information about the possible interactions that lead to superconductivity in this material. Because of the spin singlet state of the wave function the angular momentum quantum number has to be even. This means that the symmetry of the order parameter and therewith the shape of the superconducting gap should be s-, d- or g-wave.

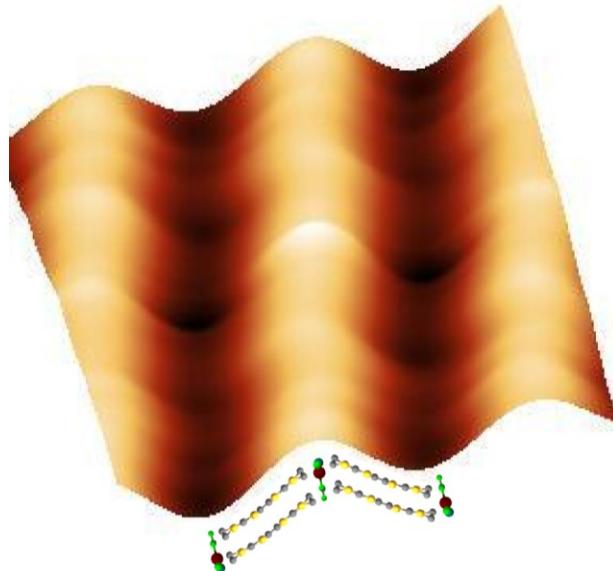


Figure 1: STM image of the layered crystal structure of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

With scanning tunneling microscopy we can investigate the two-dimensional structure of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br. In our STM images we can identify this layered crystal structure showing alternating stripes of the conducting BEDT-TTF and the insulating Cu[N(CN)₂]Br anion layers.

- [1] J. Müller, M. Lang, F. Steglich, J. A. Schlueter, A.M. Kini and T. Sasaki, Phys. Rev. B **65**, 144521 (2002)
- [2] R. H. McKenzie, Science **278**, 820 (1997)

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 [3].

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 [4]. 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-tetrafluorotetracyanoquino-dimethane (DTBBDT-F₄TCNQ) has been deposited on different substrates. 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.

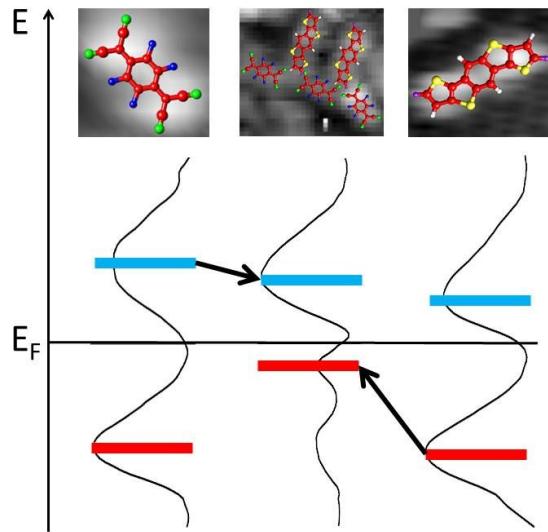


Figure 2 Illustration of the charge transfer from the donor DTBBDT (right) to the acceptor F₄TCNQ (left) in the mixed compound (center) as deduced from HOMO (red) and LUMO (blue) positions measured by STS.

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

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