

Project B8

Electron spectroscopy of novel charge- transfer complexes

Modeling of new charge transfer (CT) systems based on novel donor and acceptor molecules is one of the main approaches for designing devices in organic electronics. For this purpose controlling of the electronic structure of materials is an important factor. The present work aims at understanding of the electronic structure of various organic CT salts from different families of materials. In project B8 we investigate donor-acceptor thin films co-evaporated *in-situ* in ultra-high vacuum. Such thin films can be investigated using spectroscopic methods like ultraviolet photoelectron spectroscopy (UPS) [1-3], inverse photoelectron spectroscopy (IPES), infrared spectroscopy (IR) [1] or near-edge X-ray adsorption fine structure (NEXAFS, fig. 1) [3,4] and scanning tunneling microscopy (STM) [1]. The donor and acceptor molecules are synthesized in project B10.

NEXAFS measurements give a direct access to the unoccupied states, which prove the presence of the partial CT effect. Figure 1 shows nitrogen K-edge spectra of pure F4-TCNQ (acceptor), trimethoxy triangulene (donor) and the complex. Redistribution of the electrons results in a changing in position of the peaks and intensity drop of signal A via upon formation of the complex. This is indicative of the filling of the acceptor orbital.

- [1] K. Medjanik et. al., Phys. Rev. B 82 245419 (2010).
- [2] K. Medjanik et. al., Phys. Chem. Chem. Phys. 12, 7184-7193 (2010).
- [3] A. Chernenkaya et. al., in preparation.
- [4] K. Medjanik et. al., J. Am. Chem. Soc. 134, 4694-4699 (2012).

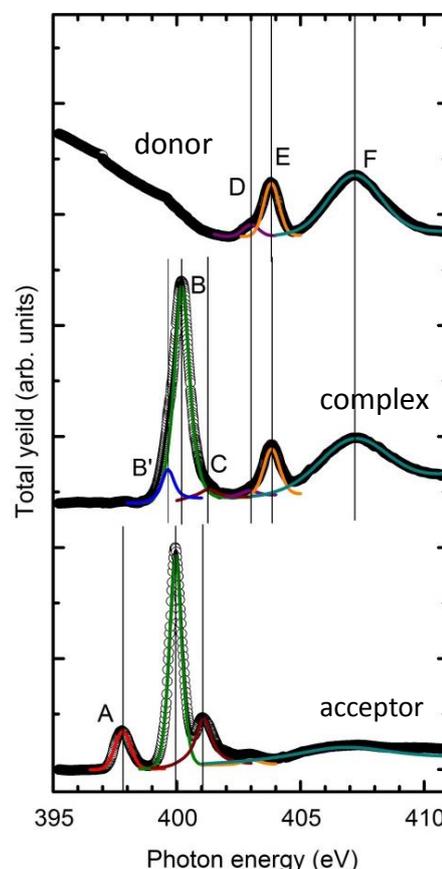


Fig. 1. Nitrogen K-edge NEXAFS spectra of the donor trimethoxy triangulene (top), CT complex (centre) and acceptor F4-TCNQ (bottom). Circles denote experimental data. Thin curves on the spectra show positions of the transitions as obtained from a multipeak fit routine. The yield scales are normalized to the maxima of peaks B.

Investigation on phase transitions and spin correlations of cation-radical salt $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$

The new asymmetrical molecule DOEO (1,4-(dioxandiil-2,3-dithio)ethylenedithiotetrathiafulvalene) and its cation-radical salt $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$ (where TCE is 1,1,2-trichloroethane) were synthesized in the Institute of Problems of Chemical Physics in Chernogolovka, Russia [1]. The molecular structure of DOEO has a base skeleton similar to BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) but the non-coplanar dioxane fragment makes adjustments to the packaging layers of cation-radicals (fig. 2) and therefore shows some notable differences to the familiar kappa-phases. The metal anion has a closed shell configuration and carries no spin.

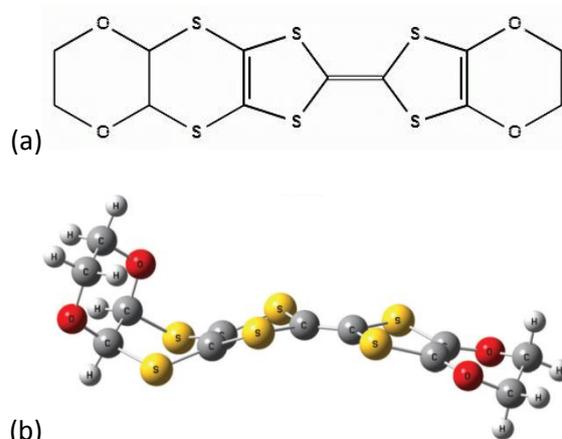


Figure 2. (a) Chemical structure of the DOEO molecule; (b) The spatial arrangement of atoms in the DOEO molecule.

We investigate $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$ crystals that are synthesized in Prof. Yagubskii group (Chernogolovka, Russia) using SQUID magnetometry and transport study at ambient and high pressures (in collaboration with the project B6) as well as using synchrotron techniques like near-edge X-ray adsorption fine structure (NEXAFS) and hard X-ray photoelectron spectroscopy (HAXPES). It was shown before that the temperature dependence of resistivity in $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$ crystals at ambient pressure is non-trivial [1]. There is a maximum at $T = 120$ K and a minimum at $T = 70$ K in resistivity. Moreover we found evidence of an antiferromagnetic phase that exists in $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$ below 40 K [2]. Therefore these crystals look very interesting and promising for further studies and understanding of the origin of phase transitions. In particular $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$ crystals are possible candidates for a superconducting state at temperature below 7 K due to the comparability to the BEDT-TTF salt. We aim to make a full characterization of phases and phase transitions in $(\text{DOEO})_4[\text{HgBr}_4]\cdot\text{TCE}$ and to build a complete pressure-temperature phase diagram.

[1] A.A. Bardin et. al., *Coord. Chem.*, 32, 88 (2006).

[2] A. Chernenkaya et. al., in preparation.