

# Bulk sensitive photoemission studies on novel designed charge-transfer salts

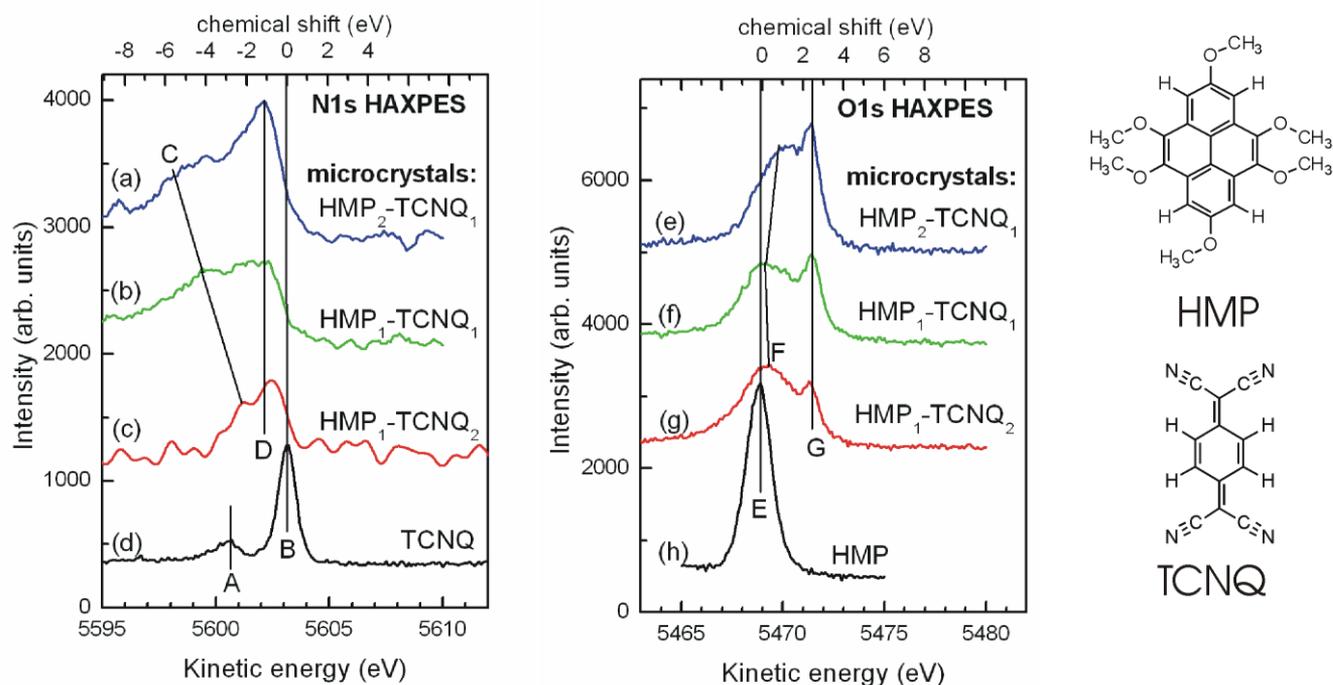
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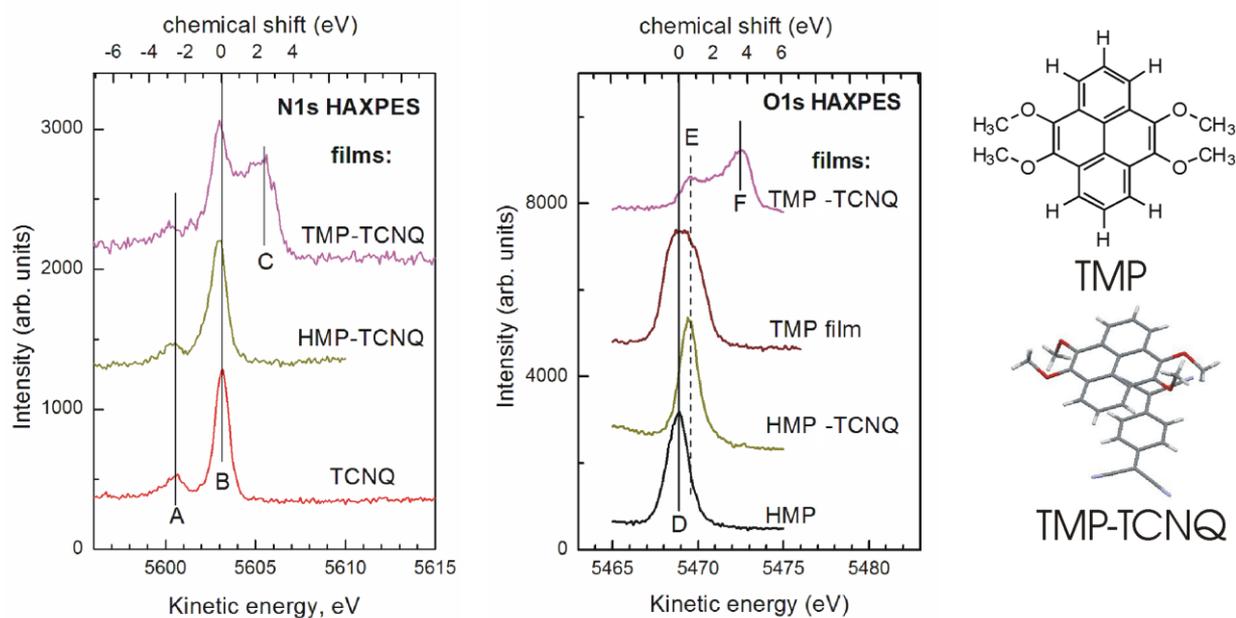
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Organic charge-transfer (CT) compounds are a class of materials that exhibit a variety of competing interactions between the charge, spin and lattice degrees of freedom, leading to a wide range of interesting physical properties. Organic molecules with  $\pi$ -conjugated ring structures offer a huge potential for the design of novel charge-transfer compounds [1]. New organic CT-materials became more and more interesting, because they can behave as both semiconductors and insulators due to their covalent bonds. Research in this field is not only fuelled by potential applications in organic electronics but also by fundamental questions regarding the nature of the new electronic states formed in the CT complex.

We studied UHV- deposited thin films and microcrystals of tetra- and hexamethoxyppyrene as donors with the strong acceptor tetracyanoquinodimethane ( $\text{TMP}_x/\text{HMP}_x - \text{TCNQ}_y$ ), which were grown from solution via vapour diffusion in different stoichiometries  $x:y = 1:1, 1:2$  and  $2:1$  [2,3].



**Figure 1.1** Nitrogen 1s (left panel) and oxygen 1s (right panel) HAXPES spectra for solution-grown microcrystals of the CT complexes  $\text{HMP}_x\text{-TCNQ}_y$  and for pure TCNQ and HMP films. Spectra were taken at  $h\nu = 6001.9$  eV at PETRA III, Hamburg (energy resolution 440 meV).



**Figure 1.2** Same as Fig. 1.1 but for UHV-deposited thin films of the CT complexes HMP - TCNQ and TMP - TCNQ. Spectra taken at  $h\nu = 6001.9$  eV at PETRA III, Hamburg (energy resolution 440 meV).

Typical N 1s and O 1s spectra are shown in Fig. 1.1 for fractions of solution-grown 3D crystallites and in Fig. 1.2 for UHV-deposited films, respectively. In all cases the spectra of the compounds are compared with spectra of the pure donors and acceptors taken under exactly the same conditions. Sizeable chemical shifts (referenced to the pure donors and acceptors) and peak splittings are evident that also give important information on the degree of charge transfer in different compounds. Nitrogen is only contained in the cyano-group of the acceptor. The N 1s spectrum of TCNQ shows two peaks (A and B). In the spectra for the microcrystals (Fig. 1.1), the signals (C and D) show a shift up to 6 eV to higher binding energies, i.e. lower kinetic energies. This is in qualitative agreement with literature data for other TCNQ-containing compounds [4]. Likewise, oxygen is only contained in the methoxy groups of the donors and shows a splitting into two peaks (F, G) and a shift up to 2.5 eV in opposite direction, with respect to pure HMP. For the HMP - TCNQ film we observed only a small shift of signals A and B towards higher binding energies. For the TMP-TCNQ film, however, an intense new peak (C) appears, shifted by 2.2 eV to lower binding energy. In pure HMP the O 1s signal appears as a pronounced line at the highest binding energy (signal E (D in Fig. 1.2)), whereas in the compounds different signals with lower binding energies occur. The chemical shift is in opposite direction as for N 1s. The spectra of the  $\text{HMP}_x\text{-TCNQ}_y$  microcrystals (Fig. 1.1) reveal two bonding states of oxygen, one of which stays fixed (shifted by 2.2eV) but varies strongly in intensity (G) and the other one (F) is broadened and changes its energy position for the 2:1 compound (spectrum e).

## References

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