



Charge transfer in the novel donor–acceptor complexes tetra- and hexamethoxyppyrene with tetracyanoquinodimethane studied by HAXPES

K. Medjanik^{a,*}, A. Gloskovskii^b, D. Kutnyakhov^a, C. Felser^b, D. Chercka^c, M. Baumgarten^c, K. Müllen^c, G. Schönhense^a

^a Institut für Physik, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

^b Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

^c Max Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

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ABSTRACT

The effect of charge transfer (CT) in complexes of the donors *tetra-* and *hexamethoxyppyrene* (TMP and HMP) with the classical acceptor *tetracyanoquinodimethane* (TCNQ) was studied using hard X-ray photoemission (HAXPES). Microcrystals of the complex were grown via vapour diffusion from donor–acceptor mixtures. The bulk sensitivity of HAXPES at a photon energy of 6 keV completely eliminates the problem of surface contamination for such delicate organic materials grown from solution. The donor molecules were produced using a novel synthesis route functionalizing polycyclic aromatic hydrocarbons at their periphery. For comparison, spectra were also taken from thin-film samples of the same compounds produced via co-deposition in UHV. Upon complex formation, the oxygen 1s core-level spectra (being a fingerprint of the *methoxy*-group of the donors) change from the single-line spectrum of pure HMP (TMP) to a spectrum with two distinct lines shifted by 1.4 (0.9) eV and 2.6 (2.3) eV with respect to the position of the oxygen 1s line of the pure donors. The nitrogen 1s spectra (being a fingerprint of the *cyano*-group in the acceptor) show two peaks as well with a corresponding shift of 0.9 eV and 2.0 eV in comparison with the leading line of pure TCNQ in opposite direction to the oxygen 1s spectra. These values are substantially larger than shifts in near edge X-ray absorption fine structure (NEXAFS) and ultraviolet photoelectron spectroscopy (UPS) spectra of the same complexes. The changes in the spectra are discussed in terms of the CT in the complexes. Residues of pure donor and acceptor materials in the microcrystal fractions of the complexes are evident from the presence of non-shifted lines. Peak-area analysis reveals that charge is transferred to a fraction of 60% of the molecules in the complexes.

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1. Introduction

Novel donor and acceptor molecules based on π -conjugated ring structures opened a lot of possibilities for the design of novel charge transfer (CT) systems for future applications in development of organic electronics. Modeling new CT systems is one of the main approaches for a designed control of the electronic structure of a special class of materials [1,2]. The information depth of hard X-ray photoelectron spectroscopy (HAXPES) is 10–15 nm at the conditions of the present study. This allows studying such delicate organic systems that do not offer the possibility to clean the surface by standard techniques like ion bombardment. HAXPES is thus suitable for the study of solution-grown crystals and films that were transported through ambient air. Surface contaminations from the solvent, from impurities in the solution or from ambient

air do not show up significantly in HAXPES spectra. Nevertheless, the state-of-the-art energy resolution of HAXPES provides the full chemical specificity of X-ray photoelectron spectroscopy/electron spectroscopy for chemical analysis (XPS/ESCA), combined with true bulk sensitivity.

The past decade has witnessed tremendous advances in the development of organic conductive molecular and polymeric materials and this field continues to be of great scientific and commercial interest. This field of science flourished on discovering new π -conjugated materials and by tailoring their electrical conductivity from semiconducting to metallic to the superconducting regime, when doped. Characteristic for such compounds is a highly correlated electronic ground state that can exhibit superconductivity, spin density waves, or charge density waves [2]. The first families of organic conductive and superconductive molecules are based on CT salts, where *BEDT-TTF* [*bis(ethylenedithio)tetrathiafulvalene*], *M(dmit)₂* (*dmit* = 1,3-dithio-2-thione-4,5-dithiolate), *DCNQI* (*N,N'*-dicyano-*p*-quinonedimine) *peryrene*, *tetrachalcogenafulvalenes* and their structurally related analogs are just a few of the most

* Corresponding author. Tel.: +49 61313925412; fax: +49 61313923807.

E-mail address: medyanyk@uni-mainz.de (K. Medjanik).

commonly studied. Fullerenes constitute another class which also exhibit superconductivity when doped with alkali metals. Research activities are being carried out around the world to produce pure fullerenes (C₆₀, C₇₀, C₇₆, C₇₈, C₈₂, C₈₄, C₉₀, and higher fullerenes) and to prepare their derivatives as well as polymers [3]. Another class of materials of high current interest are the *nanographenes* [4–7] which can be functionalized at their periphery to design large disc-type donors and acceptors.

The primary source of knowledge of the CT effect was *tetrathiafulvalene* (TTF)–*tetracyanoquinodimethane* (TCNQ) and related compounds, which were intensively studied in the middle of the last century. Today novel CT salts based on one of the components of the above mentioned well-known system, give us the possibility to improve our understanding of the CT mechanism and find out new methods to estimate the degree of CT.

We briefly recall some results of previous XPS studies of CT salts from the literature. A study of TTF–TCNQ and related compounds revealed a splitting of about 1.5 eV in the S 2p (N 1s) peak positions between neutral TTF⁰ (TCNQ⁰) and ionic TTF⁺ (TCNQ⁻) [1,8]. This splitting could be used to estimate the amount of charge transfer. The evaluation of the N 1s spectra for the determination of the CT state of TCNQ turned out not so simple because of a satellite due to shake-up of π -electrons. Evaluation of the molecular mixed valence of TCNQ was possible for the complexes (BEDT–TTF)–TCNQ and *ditetramethyltetraselenafulvalene* (TMTSF)–TCNQ, where an N 1s binding-energy difference of 1.6 eV between neutral TCNQ⁰ and ionic TCNQ⁻ occurs [9,10]. This change is accompanied by a red shift of about 30 cm⁻¹ in the frequency of the CN stretching mode (a_g mode) when going from the neutral TCNQ to the anion.

In the present study, we investigate two new CT complexes consisting of the classical acceptor 7,7,8,8-tetracyano-pquinodimethane (TCNQ, C₁₂N₄H₄) and two newly synthesized donors, i.e. the parent molecule *pyrene* being substituted at its periphery with four or six *methoxy* groups, see Fig. 1a. These functional groups transfer charge into the π -orbitals of the aromatic ring system thereby making 4,5,9,10-tetramethoxyppyrene (TMP, C₂₀H₁₈O₄) and 2,4,5,7,9,10-hexamethoxyppyrene (HMP, C₂₂H₂₂O₆) good electron donors. Indeed, for a ultrahigh vacuum (UHV)-deposited thin film of TMP–TCNQ characteristic changes of the electronic structure occur in ultraviolet photoelectron spectroscopy (UPS) and scanning tunnelling spectroscopy, along with a red-shift of the CN stretching mode measured by infrared (IR) spectroscopy, that give evidence of charge transfer in the co-deposited film [11].

Co-crystals of the complex could be grown from solution and are stable under ambient air conditions. X-ray diffraction revealed a mixed stack geometry [12] which is sketched in Fig. 1b. For TMP–TCNQ the structure did not contain intercalated solvent molecules, whereas for HMP–TCNQ one *dimethyl sulfoxide* (DMSO) molecule was intercalated per donor–acceptor pair. The symmetric distance (0.332 nm) of TCNQ to a TMP on top and a TMP below reveals that no dimerization occurs. The TCNQ molecules alternatively change from alignment to the upper and lower ring of the *pyrene* aromatic system. The *methoxy* groups at positions 2 and 7 are nearly in plane with the *pyrene* core ($\pm 6^\circ$), while the four *methoxy* groups at positions 4,5,9 and 10 are strongly twisted out of the plane by 65–85°. The shortest C–C distance is 0.3133 nm but many short contacts are found in average with 0.32–0.35 nm. Co-crystals of TMP–TCNQ were obtained without intercalated solvent molecules. Here the C–C distances are slightly larger with 0.332 nm as shortest contact of a TMP to both the on-top and bottom TCNQ neighbours. Thus a significant difference between TMP–TCNQ and HMP–TCNQ is evident. In TMP–TCNQ alternating stacks show TMP donor next to donor and TCNQ acceptor next to acceptor, such that layers of donors and layers of acceptors are formed as visible in Fig. 1b.

From the spectroscopic point of view the complexes TMP(HMP)–TCNQ bear the advantage that oxygen is only contained in the *methoxy* group of the donor. Hence, the O 1s spectra directly probe the functional group that is responsible for the amount of charge transfer. Analogously, nitrogen is only contained in the *cyano*-group of the acceptor. So, the N 1s spectra probe the acceptor sites as was exploited in earlier work [8–10,13–15].

2. Sample preparation and experimental details

The synthesis of the *methoxy*-substituted *pyrene* derivatives 4,5,9,10-tetramethoxyppyrene and 2,4,5,7,9,10-hexamethoxyppyrene is discussed by Kawano et al. [12]. TCNQ is commercially available (Alfa Aesar GmbH & Co KG). Microcrystals of TMP–TCNQ and HMP–TCNQ were grown by vapour diffusion of *hexane* into a *dichloromethane* solution (5 ml, 6.2×10^{-3} mol/l) of the components. Solutions with donor–acceptor mixtures of 1:2, 1:1 and 2:1 stoichiometry were prepared. This allows investigating possible differences in crystals growing in donor-rich or acceptor-rich solutions. The components were combined in a glass vial ($V = 7 \text{ cm}^3$; 1.5 cm diameter) and dissolved under sonication. Vapour diffusion assisted crystallizations were performed in a gas-tight chamber ($V = 120 \text{ cm}^3$), filled with 15 ml *hexane*. The vial containing the solution was placed inside the chamber which was sealed for 4 days. The crystallites have sizes in the range from several 10 μm to several 100 μm .

Optical microscopy (Fig. 1c and d) revealed mixtures of dark and transparent crystals in the vial. Crystallites of the CT complex appeared dark orange, whereas crystallites of the pure donors TMP or HMP are colorless transparent and TCNQ is transparent with light green color. The different fractions were separated using an own developed micromanipulator under the optical microscope. Fig. 1c and d show fractions of microcrystals before separation and the same fraction after separation of the colored co-crystals, respectively. Although all sufficiently large transparent crystallites had been removed, a residue of very small transparent crystals remained, partly being attached to the larger crystallites of the complex.

Thin films of TMP–TCNQ have been prepared by UHV co-deposition using a special type of double-evaporator [11,16]. The TMP–TCNQ mixed phase was deposited in very good quality by loading one crucible with a mixture of both molecules. The base pressure before evaporation was about 3×10^{-9} mbar. Clean Au films were used as substrates with high electronegativity, providing a good reference for the Fermi energy. About 20 nm of Au were evaporated onto Si(1 0 0)-wafers immediately before deposition of the organic films. The workfunction of the fresh Au films was consistently 5.3 eV. This indicates that the Au surface is textured and exhibits Au(1 1 1) facets. The substrate was kept at room temperature; the crucible temperature was 120 °C.

Atomic force microscopy (AFM) images of a TMP–TCNQ film deposited on Au are shown in Fig. 1e. 3D-islands with lateral sizes in the 1 μm range and height in the 100 nm range appeared on a smooth background. The crystallites tend to form rows with lengths of up to one micrometer. The films look dark orange giving evidence for an optical gap in the visible spectral range. Films of pure TMP and TCNQ look transparent and faint yellow, respectively. We suggest that the complex grows in a *Stranski–Krastanov* type mode [17] where an initial smooth multilayer covers the whole surface (smooth areas in the AFM images, Fig. 1e) before 3D crystallites are formed. Similar microcrystals with sizes in the sub-micrometer range have been observed for the (BEDT–TTF)–TCNQ mixed phase [18]. After separation, the microcrystal fractions were deposited on carbon tape. Thin films were evaporated in situ immediately before the experiment.

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