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Crystal growth of new charge-transfer salts based on π -conjugated donor molecules

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ABSTRACT

New charge transfer crystals of π -conjugated, aromatic molecules (phenanthrene and picene) as donors were obtained by physical vapor transport. The melting behavior, optimization of crystal growth and the crystal structure are reported for charge transfer salts with (fluorinated) tetracyanoquinodimethane (TCNQ- F_x , $x=0, 2, 4$), which was used as acceptor material. The crystal structures were determined by single-crystal X-ray diffraction. Growth conditions for different vapor pressures in closed ampules were applied and the effect of these starting conditions for crystal size and quality is reported. The process of charge transfer was investigated by geometrical analysis of the crystal structure and by infrared spectroscopy on single crystals. With these three different acceptor strengths and the two sets of donor materials, it is possible to investigate the distribution of the charge transfer systematically. This helps to understand the charge transfer process in this class of materials with π -conjugated donor molecules.

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1. Introduction

Designing new organic materials and tuning their physical properties by adding or removing charges has a long history [1], but the detailed understanding of mechanisms is still a matter of current research. Organic charge-transfer (CT) salts offer a huge variability in crystal structures and physical properties ranging from metallicity over superconductivity to Mott insulators [2,3] on one side. Organic semiconductors on the other side find application in various diodes and organic electronics due to their flexibility and relatively high mobility [4]. Also, a new class of multi-ferroicity was found in organic charge transfer salts and introduced a new research field [5].

In the last years, the class of phenacenes attracted a lot of attention. For potassium doped phenanthrene ($n=3$ benzene rings) [6], picene ($n=5$) [7] and dibenzopentacene ($n=7$) [8] superconducting phases were discovered with a T_C of 5 K ($n=3$), 18 K ($n=5$) and 33 K ($n=7$), respectively. The charge transfer process in crystals based on these three compounds is of interest, as the reproducibility of these

samples is still under debate [9] and only few experimental studies have been reported. In this paper, we expand the sets of charge transfer (CT) salts based on aromatic donor molecules as reported for phenanthrene/TCNQ [10] and picene/TCNQ- F_4 [11] and present the crystal structures of new charge transfer salts phenanthrene/TCNQ- F_x ($x=2, 4$) and picene/TCNQ- F_x ($x=0, 2$). With respect to the weak donor ability of phenanthrene and picene (HOMO: 6.1 eV, 5.5 eV [12]) and the strong acceptors TCNQ, TCNQ- F_2 and TCNQ- F_4 (LUMO: 4.2 eV, 4.55 eV and 5.24 eV [13]) neutral CT are expected. With the two known structures of PHN/TCNQ and PIC/TCNQ- F_4 , we yield a set of two donors with three different acceptors. By changing the fluorine content in the acceptor, the overall charge transfer is increased. These novel materials expand the materials basis for the recently suggested HOMO–LUMO engineering [13] utilizing charge-transfer compounds.

2. Experimental details

2.1. Crystal growth

Phenanthrene (PHN) and picene (PCN) as donor molecules (D) were purchased by TCI with a purity of >97% and >99%, respectively. TCNQ, TCNQ- F_2 (2,5-configuration) and TCNQ- F_4 as

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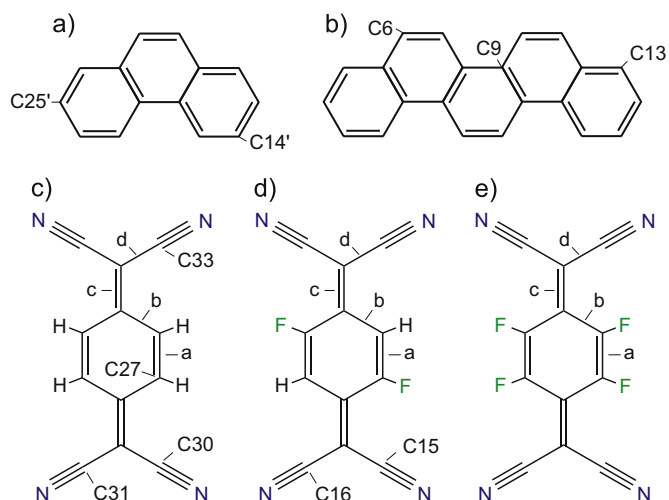


Fig. 1. (a) Phenanthrene and (b) picene used as donor molecules and (c) TCNQ, (d) 2,5-TCNQ-F₂ and (e) TCNQ-F₄ as acceptors are shown. The bond lengths (a)–(d) are marked in the acceptors to describe structural effects of charge-transfer. The colors representing different atoms in the molecules are as follows: grey (C), white (H), blue (N) and green (F). The numbers of C atoms refer to selected distances between acceptor and donor molecules, discussed within this work. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

acceptors (A) were also purchased by TCI with purities of > 99%, > 98% and > 98%, respectively. These starting molecules are shown in Fig. 1. The acceptor strength increases for higher fluorinated acceptors with an electron affinity of 2.85 eV for TCNQ; 3.02 eV for TCNQ-F₂ and 3.20 eV for TCNQ-F₄ [14].

Single crystals were grown by physical vapor transport (PVT) [15,16] in closed glass ampules. For this purpose, the starting materials (as powders) of D and A were ground together and transferred into a glass ampule, which was cleaned by ethanol and acetone before and baked in a box furnace for at least 24 h to remove water (as described in Ref. [11]). The glass ampule was evacuated to $p=10^{-3}$ mbar before closing. The experimental oven setup and a typical temperature gradient used in the experiments are shown in Fig. 2 with T_{source} as the temperature at the hottest position with the source material and $T_{crystal}^x$ with $x=1, 2, CT$, where x denotes the crystal growth temperature of material 1, material 2 and the CT complex, respectively. Typical crystal growth conditions are listed in Table 1.

The crystal growth zone lies in a region with a steep temperature gradient, which results in the best crystal growth as mentioned and suggested in Ref. [17]. The growth procedure lasted ca. 50 h until all starting material is sublimed and subsequently the ampule was removed from the hot oven. The section with the crystal growth zone of an ampule after the growth procedure of phenanthrene/TCNQ is also shown in Fig. 2. Here, TCNQ (orange) resublims first at $T_1=170$ °C as orange crystals, the CT complex (T_{CT}) and (transparent) phenanthrene (T_2). All charge transfer crystals grow in a 1:1 stoichiometry with the applied starting conditions. There is no other stoichiometry detected as for example 2:1 in Coronene₂/TCNQ-F₄ [18]. Besides the growth of CT salts in a closed system, the oven can be used also for crystal growth or purification of organic semiconductors (molecular crystals with one type of molecule). Here, the crystal growth is performed under a stream of argon and a flat temperature gradient in the oven is necessary.

For phenanthrene/TCNQ small needle-like crystals were obtained with a source temperature $T_{source}=200$ °C. For phenanthrene/TCNQ-F₄, this method with a pressure of $p=10^{-3}$ mbar results only in micro-crystallites (smaller than 50 μm), where a separation from the glass walls after the growth

procedure is not possible. For optimization of the crystal growth conditions, we varied the argon gas pressure inside the ampule. For this purpose, the ampule is first evacuated to $p=10^{-3}$ mbar and then refilled with argon as inert gas. The pressure amounts to the value at room temperature. In Fig. 3 typical results are shown for two different argon pressures for phenanthrene/TCNQ. The single crystals in the first case for a pressure of $p=10^{-3}$ mbar are smaller than 1 mm and have a width and thickness of 250 μm in average. For the second case with an inert gas pressure of 0.5 bar, larger crystals up to a length of 2 mm in average are detected.

The improved crystal growth conditions are reflected in more block-like crystals by higher inert gas pressure. This can be due to increased sublimation temperatures and modified growth rates for different pressures mentioned in Ref. [17]. Higher pressures might lead to a suppressed nucleation rate due to a smaller oversaturation at the ampule walls in the crystal growth regime. Therefore, the crystals grow slowly and a block-like habitus appears.

2.2. DTA

For a better understanding of the crystal growth conditions, differential thermal analysis (DTA) measurements were performed with phenanthrene, picene, TCNQ, TCNQ-F₄ and a mixture of donor and acceptor materials shown in Fig. 4. The starting materials were filled into DTA glass ampules. The ampules were evacuated to $p=10^{-3}$ mbar, refilled with 0.5 bar argon and closed as described for the growth ampules above. The measurements were obtained by a STA 409 from NETZSCH and a DTA sample holder

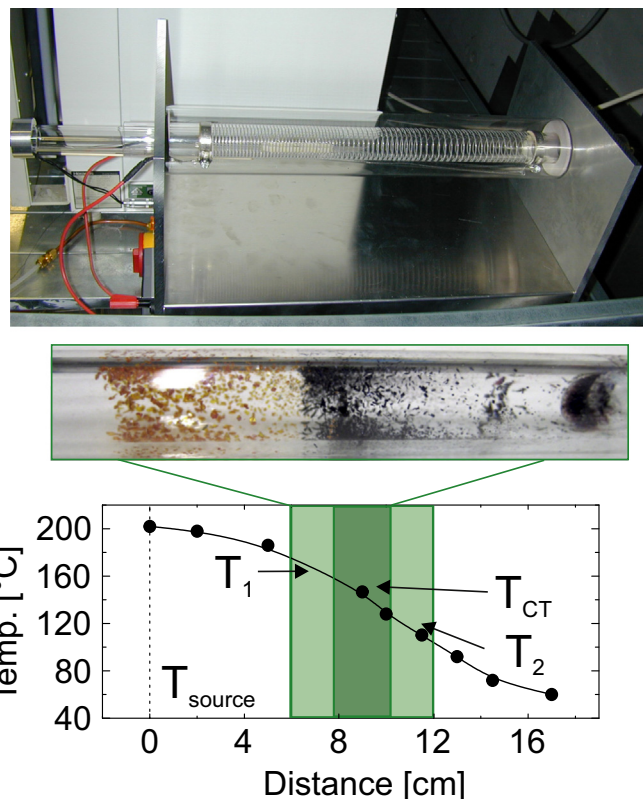


Fig. 2. The PVT oven for crystal growth is shown on the top designed after the working principle used in Ref. [19]. A typical temperature profile for phenanthrene based CT crystals is shown at the bottom with the hottest zone of around 200 °C. TCNQ resublims first at $T_1=170$ °C as orange crystals, the CT complex ($T_{CT}=140$ °C) and the phenanthrene at $T_2=110$ °C as transparent crystals. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

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