1 Introduction

Organic molecules in solid phase form molecular crystals which differ considerably in their optical, electronic and mechanical properties from conventional inorganic solids such as covalent (atomic) or ionic crystals. This is mainly due to weak intermolecular interaction forces of the van der Waals type with bonding energies considerably lower than that of covalent or ionic bonds. The energy range of typical van der Waals intermolecular bonds ($E_{\mathrm{vdW}} = 10^{-3} - 10^{-2}\mathrm{eV}$) is by several orders of magnitude smaller than the intramolecular covalent bond energies ($E_{\mathrm{cov}} = 2 - 4\mathrm{eV}$) of aromatic molecules. In contrary to covalent and ionic crystals, where the electronic structure of valence electrons is largely determined by the crystal formation, weak intermolecular interaction forces produce only moderate changes in the electronic structure of molecules on formation of the solid phase, and, as a result, *neutral* molecules retain their identity.

The additional structural level given by the individual molecules is one main reason for interest in molecular crystals: The resources of organic chemistry provides nearly unlimited variety of molecules, which can be used to design crystals with highly specialized features. Several million organic compounds are known today, and many are commercially available.

The technological potential of organic materials concerning electronics and optoelectronics was not explored for a long time. In the 1970s, it was discovered that certain types of polymeric material can conduct electricity almost as efficiently as copper [1]. In 1987, Tang and van Slyke [2] demonstrated highly efficient organic light-emitting diodes (OLED). Nowadays, the power efficiency of OLEDs exceeds that of incandescence lamps and approaches that of discharge lamps. Thus, OLED technology is very promising for lighting purposes. However, the main vision for OLED technology is in the field of large area and flat display applications.[1] Nowadays, such displays are already commercial on small scales. Further applications are in sight, e.g. electrical sensors or batteries made entirely from plastics.

In particular, molecules with a conjugated π-electron system usually exhibit semiconducting behavior. The discovery of controlled n- and p-type doping of organic molecular systems, very similar to classical silicon technology, paved the way for organic electronics and optoelectronics [3]. All-organic thin layer devices such as transistors and diodes used for integrated circuits have already been realized. This points to one of the disadvantages of organic materials: their low carrier mobilities, which are about $1\mathrm{cm}^2/\mathrm{Vs}$ at room temperature for the best-ordered thin films (pentacene

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[1] The main advantages of OLED displays are low power consumption, low production costs, video capability, and they are self-emitters and thus viewing angle independent. In contrast, the established liquid crystal displays (LCD) only change the polarization state of the illuminating light, an effect which is viewing angle dependent.

and oligothiophene [4]), compared with mobilities somewhere between $100\text{cm}^2/\text{Vs}$ and $10^4\text{cm}^2/\text{Vs}$ for conventional semiconductors. This suggests that, in the end, organic electronics will not apply to high-speed devices as used in, i.e. telecommunication.

The group of organic materials for (opto)-electronic device applications is usually divided into polymers and "small molecules". In this context, small is meant relative to the size of a polymer. Typical representatives for small molecules contain 10 (naphtalene), 20 (perylene) or 60 (C_{60}) carbon atoms. In this thesis, we only deal with crystals of small molecules. In particular, we aim at *quasi-one-dimensional crystals*. By naming quasi one-dimensional (quasi-1D), we mean that in the crystal structure the intermolecular interactions along one lattice constant are significantly stronger than along the other two. Then, the crystal can be considered as a two-dimensional array of 1D stacks. As a model system for quasi-1D crystals, we use MePTCDI crystals.

The strong temperature dependence of the electronic bandwidths and mobilities of Organic Molecular Crystals (OMC) can be explained by a strong electron-phonon interaction. A crossover from bandlike charge transport with mobilities up to several thousand cm^2/Vs at low temperature to an incoherent hopping motion at high temperatures was observed [5]. Because of the soft lattice of VAN DER WAALS bonded molecular semiconductors, this is expected to be much more pronounced compared to covalently bonded materials, such as Si or Ge. Therefore, a detailed investigation of the exciton-phonon interaction is required. In particular, in quasi-1D materials electron-phonon coupling might play a dominant role: Theory predicts that self-trapping of free excitons always occurs for any finite exciton-phonon coupling strength (see Sec. 2.5).

In the following thesis, we will investigate excitonic and phononic properties of MePTCDI. By use of various time-resolved experimental techniques, we investigate the relaxation of excitons and phonons in time domain. The subjects of interest are threefold: First, we observe the relaxation of free excitons in the lowest exciton band to totally relaxed exciton states. Second, the homogeneity of excitonic transitions is topic of our experiments. By measuring the macroscopic polarization decay of excitonic transitions the homogeneous linewidth of these transitions can be determined. Third, the investigation of both molecular and crystal phononic properties is achieved in the time domain. Oscillations of coherent phonon wave packets and their damping are studied.

This part of the thesis is organized as follows: In the next section, we will briefly introduce our model system for a quasi-1D organic molecular crystal - MePTCDI. The specific advantages of this system will be motivated. In Chapter 2, we will give the necessary theoretical background for describing optical properties of OMCs. Additionally, the current status of modeling the optical properties of MePTCDI is presented. In Section 2.6, we address the open questions concerning this system we are going to answer. In Chapter 3, we introduce the experimental setups and techniques. As the experimental setups are rather extensive, including, e.g. the realization of a home-built optical amplifier, they are given in some detail. Therefore, it is indispensable to introduce some concepts of nonlinear optics. The necessary background for data interpretation is provided. All experimental results are given in Chapter 4. We present numerous results covering the range from the slowest relaxation processes concerning luminescence decay in the ns-time up to the fastest processes. In this context, the dephasing of excitonic transitions is the fastest relaxation process with time constants of less than 100fs. Conclusions and an outlook for further investigations are presented in Chapter 5.

1.1 The Model System of MePTCDI

A number of perylene derivatives form quasi-one dimensional crystals, for instance the prominent representatives PTCDA and MePTCDI (for an overview see [6, 7]). These molecules have a planar conjugated π-electron system which causes strong absorption in the visible. The substituent at the periphery of the molecule, for MePTCDI the group $N-CH_3$, is sensitively responsible for the energetic position of the absorption maximum. The monomeric absorption is given in Fig. 2.3.

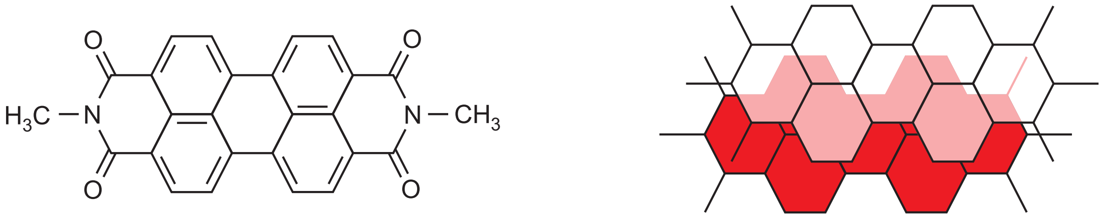

Figure 1.1: Left: Chemical structure of MePTCDI (N-N′-dimethylperylene-3,4,9,10-dicarboximide). Right: Molecular pair within the 1D stack. The offset of the molecules perpendicular to the molecular planes is 3.40Å.

A characteristic property of the quasi-1D crystal of MePTCDI is its strong intermolecular overlap in the one-dimensional stacks. In MePTCDI, the molecular planes have a distance of 3.40Å [6], which is on the order of the plane distance in graphite (3.35Å). Thus, a nearest-neighbor pair within the stack has a sandwich-like geometry with the molecules shifted with respect to each other within the molecular plane as shown in Fig.1.1. Still, a large fraction ($\approx 50\%$) of the conjugated electron systems lies directly above each other [8]. This leads to a strong mutual penetration of the molecular wave functions. We refer to this situation by the term "strong intermolecular overlap". An immediate consequence expected for this system are large electronic bandwidths. Hence, such materials should develop qualitative similarities to covalent crystals with the advantage of high charge carrier mobility, which is technologically extremely important. However, experimental mobilities in the quasi-1D crystal PTCDA are about $3 \cdot 10^{-2}\mathrm{cm}^2/\mathrm{Vs}$ (vapor-deposited layers at room temperature [9]). Presently, it is not clear whether higher mobilities can actually be achieved or if other effects (strong electron-phonon coupling) will compensate the advantage of larger intermolecular overlap.

In the framework of this thesis, we have mainly worked with polycrystalline thin (approx. 15nm) films of MePTCDI grown by physical vapor deposition (PVD) in high vacuum ($p < 10^{-3}$Pa) on a room-temperature glass substrate. Before deposition, the material has been purified by gradient sublimation. The average size of the polycrystallites within the layer will be in the range of $20-100$nm. This estimate results from atomic force microscopy (AFM) and X-ray diffraction measurements on 100nm films of MePTDI and PTCDA on various substrates [10, 11, 12]. There are no systematic studies on the preferential orientation of the micro-crystallites relative to the substrate for different substrate materials. For thin layers of MePTCDI on a polymer film, the (102) plane was found to be mainly parallel to the substrate. In other words, the molecular planes are mainly parallel to the substrate.

Thin films of MePTCDI are of technological importance for the usage in low-cost devices as OLEDs, organic solar cells, or as transport layers for organic electronics [13, 14]. However, to understand intrinsic crystal properties of MePTCDI it is favorable to compare the results with measurements on single crystals. The used crystals are of maximum size of about $300 \times 300 \times 3000\mu$m and stem from multi-stage gradient sublimation (see Fig. 1.2). They were kindly provided by the group of N. Karl (Stuttgart). The long lateral surfaces of the needle-like crystal are (011), resp. the equivalent planes $(0-11)$, $(01-1)$, $(0-1-1)$. The crystallographic investigations to obtain the orientation of the molecules within the crystals were also performed in this group.