Real-time *in situ* studies of structure and optical properties of PTCDI-C$_8$ molecules

S. Bommel$^{1,2}$, L. Pithan$^2$, C. Weber$^2$, A. Zykov$^2$, G. Santoro$^1$, S.V. Roth$^1$, J. Megow$^2$, S. Kowarik$^2$

$^1$Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

$^2$Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 14, 12489 Berlin, Germany

Structural and optical properties of molecular materials are not only essential for the rational design of opto-electrical devices like organic photovoltaic (OPV) cells and organic field-effect transistors (OFETs), but also for the understanding of intermolecular interactions. The molecular arrangement/molecular orientation plays a decisive role for the performance of organic devices as it determines the interaction strength of a molecule and the incoming light in OPV cells as well as the charge mobility in organic-field effect transistors.

We performed a temperature-dependent study of the crystallinity and molecular arrangement of the organic semiconductor PTCDI-C$_8$ [1] using Grazing Incidence X-ray Diffraction (GIXD). The experiments were performed in situ at the Micro- and Nanofocus X-ray Scattering (MiNaXS) beamline P03 at PETRA III, DESY [2]. Our experimental results clearly benefit from the high photon flux and the low divergence at P03/PETRA III as GIXD maps could be acquired with good statistics on short timescales during molecular re-orientation. In this report, we summarize our key findings of our study: we observed a crystalline organic thin film with a high structural order. Furthermore, we found a profound impact of temperature on the unit cell parameters of PTCDI-C$_8$ indicating a molecular rearrangement combined with a change in molecular orientation.

Figure 1 shows the GIXD maps for temperatures of -40°C and 100°C. The maps contain several pieces of information:

- High structural order in PTCDI-C$_8$ thin films is indicated by Bragg reflections up to the 5$^{th}$ order
- Molecular rearrangement with temperature seen by a change of Bragg reflection positions (note the blue arrows)
From the positions of Bragg reflections the unit cell for all applied temperatures was calculated. PTCDI-C$_8$ forms a triclinic unit cell with a large c-axis of 20.8 Å for 140°C indicating an upright-standing molecule. In Figure 2a) the evolution of the c-axis and the β-angle with temperature is shown. An increase of the c-axis with a slope of $3 \cdot 10^{-3}$Å/K was found attributed to molecular rearrangements as well as thermal expansion. The decrease of the β-angle from 108° at -60°C to 102° at 140°C indicates a molecular rearrangement by a change of molecular orientation.

![Figure 2](image)

Figure 2: a) Unit cell parameters c and β as a function of the temperature and b) temperature-dependent photoluminescence spectra for PTCDI-C$_8$

We directly correlated the x-ray structure with optical properties in a simultaneously performed measurement. We acquired temperature-dependent photoluminescence (PL) measurements, in which a 532 nm laser was used for excitation of the molecules. In Figure 2b) the temperature-dependent PL spectra are shown. We observe a large impact of temperature on the intensities as well as the emission energies of the optical transitions. The energy of the optical transition $E_{10} - E_{01}$ in the PL spectra shifts from 1.80 eV for -60°C to 1.85 eV for 140°C. These changes in the optical properties with temperature are traced back to, firstly, the temperature-dependent molecular arrangement and, secondly, to the thermal occupation of electron states as revealed by preliminary MD simulations. Interestingly, the structural as well as the optical changes are reversible identifying PTCDI-C$_8$ as a candidate for switching molecular properties in future applications.

In conclusion, our experiments provide new insights in the understanding of changes of molecular orientation of PTCDI-C$_8$ on SiO$_2$. The analysis of the temperature-dependent Bragg reflection intensities will enable us to extract the molecular orientation as a function of T by molecular structure factor calculations [1].

References