Organic semiconductors have gained a great interest in the last years, due to their potential applications in electronic devices such as organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs). Among these organic molecules, pentacene (PEN, \text{C}_{22}\text{H}_{14}), perfluoropentancene (PFP, \text{C}_{22}\text{F}_{14})\text{, and above all, mixtures between both attract a special attention, because on the one hand they form donor/acceptor systems, and on the other hand they are expected to be structurally compatible due to their similar molecular geometry. Thus, they have been widely studied as a semiconductor p-type, n-type or p-n-junction, respectively, on various substrates such as halides for PFP [1] and PEN [2], SiO\text{2}/Si for PFP [3] or polymer gate dielectrics for PEN [4], and with optimal imaging conditions which minimize the radiation damage that destroys the organic materials [3].

Molecular orientation and ordering of different organic semiconductors depends on substrate interaction and substrate roughness. In this study we use Conventional TEM (CTEM) Bright Field (BF) and Dark Field (DF) as well as Electron Diffraction (ED) to show the difference between PEN:PFP (1:1) grown on crystalline substrates such as KCl (100) or NaCl (100) and amorphous substrates such as SiO\text{2}. In case of PEN:PFP grown on KCl well ordered films consisting of domains of elongated PEN fibers are formed directly over the substrate. Above these PEN films, bigger individual fibers consisting of PEN:PFP are distributed. The fibers of PEN films are oriented parallel to the KCl <100> directions. ED Patterns of these samples reveal a PEN [001] zone axis orientation and a fourfold ordering (figure 1). In contrast to PEN:PFP grown on SiO\text{2}, where no global ordering of the PEN molecules appears. In this case ED Pattern (figure 2) shows mainly a polycrystalline arrangement of the PEN molecules within the sample. In this way, substrates can also determine the orientation and arrangement of crystalline molecular films in organic semiconductors, playing an important role in electronic and optical properties of such materials. TEM characterization is an useful tool to understand local and extended crystal orientation by means of a combination of imaging and diffraction techniques.


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Fig. 1: ED Pattern of PEN:PFP grown on KCl and simulated pattern of PEN in [001] zone axis orientation. The reflections match PEN in the [001] zone axis orientation with fourfold ordering.

Fig. 2: ED Pattern of PEN:PFP grown on SiO₂. The Diffraction Pattern reveals the polycrystalline structure of the PEN molecules.