**Lattice dynamics and structure in organic semiconductors by THz spectroscopy**

**Abstract*:*** *the research proposal is based on the on the on-going activities of the Spectroscopy and Computational Chemistry Group (SC2) at the Department of Industrial Chemistry “Toso Montanari”. The group’s interests lie in the experimental and computational study of structural and spectroscopic properties of organic molecular crystals. Experimental techniques such as micro-Raman, micro-IR, UV/visible spectroscopic methods, together with X-ray and AFM measurements in collaborations with other researchers, allow for the investigation of the solids both in bulk and thin-film phases. A posteriori dispersion corrected DFT simulations are employed to understand the spectroscopic properties and elucidate processes such as phase transitions and structural transformations in these systems as well as the electron-phonon coupling.*

Organic Semiconductors (OSC) with proper functionalization, have emerged as attractive candidates as active layers in several new electronic technologies. These encompass various applications from displays (OLED) to unconventional flexible, stretchable and/or wearable devices, phototransistors, easy processable large area electronics, organic photovoltaics (OPV), energy storage (redox flow batteries, organic electrodes, pseudo-/super-capacitors, gas storage and separation), photocatalytic systems, sensing applications, and others. Moreover, OSC are based on abundant, eco-friendly, and cheap elements, nominally C, O, N, S, with negligible content of critical raw materials. This hallmark is crucial in the development of the next generation of sustainable functional materials.

However, the worldwide use of OSC in electronics-related applications, is hampered by the lack of predictive understanding of the inter-relationship between solid-state packing and performance of the device (whatever type of device). Indeed, different crystal structures are available for the same molecular compound (a well-known phenomenon named polymorphism). Different polymorphs also have different vibrational patterns, which translate in different electron-phonon coupling (EPC), which shapes the OSC transport characteristics. Indeed, low frequency vibrational modes (THz), like translations and rotations of the molecule as a whole, are responsible for the dynamic disorder which contributes to the modulation of on-site energies and electronic transfer integrals. Thus, polymorphism is critically important in defining the macroscale electronic properties in OSC.

Moreover, the bare polymorph structure prediction has limited power to advance the required knowledge. This is because, in most of the real-world applications, OSC are packed in solid-state form onto a substrate, and the substrate stabilizes the energetically favourable polymorph, regardless of its stability in bulk form. That is, the substrate selects the polymorph, and if the polymorph is metastable, crystal structure predictions will not point to it.

Thus, studies on real structures are required not only for the EPC, but also for the OSC electronic properties, which can dramatically differ from single crystal (most stable polymorph per-se) to thin solid film (most stable polymorph interacting with the substrate).

X-ray techniques are the methods of choice for the study polymorphs, but the analysis may present problems, especially when the small energy differences cause different phases to occur in the same batch, or even in the same crystallite. Our research group has since long showed how low-frequency Raman spectroscopy can be of fundamental assistance in these cases. In fact, micro-Raman spectroscopy in the lattice phonon region represents a very versatile technique currently employed to diagnose the presence of different structures grown in a variety of environments, such as films, nano-crystals or at solid interfases. The modes detected in the low energy region of the vibrational spectrum (lattice phonons) owe their properties to the weak dispersion forces of the intermolecular field and are therefore distinctive of a given structure.

The aim of this project is to extend the knowledge and expertise on how a change in the lattice dynamics reflects in a change of the electronic properties of the OSC. Micro-Raman and Micro-FTIR spectroscopy will be used together with a wide range of solid-state characterization methods such as XRD, GIXRD, AFM available through collaborations within the University of Bologna, at CNR (Bologna) and at University of Parma (UNIMORE). The project will focus on the study of different class of compounds: variably substituted benzothieno-benzothiophenes (BTBT), dinaphtho-thieno-thiophene (DNTT), tri-isopropylsilyly-ethynyl pentacene (TIPS) and tetramethyl-triethylsilylethynyl pentacene (TMTES); charge transfer (CT) materials where the combination of Donor and Acceptor molecules (D-A) leads to bandgap tuning and useful ambipolar mobility, like BTBT, especially asymmetric, as “D”, and fluoro-substituted tetracyanoquinodimethane, TCNQ-Fx (x = 2,4) as well as tetracyanonaphthoquinodimethane, F6-TCNNQ,

**Work Plan**

As already evidenced from project plan, the experimental technique most widely employed for the study of the systems of interest will be the Raman and FTIR microscopy, available at the Dpt. of Industrial Chemistry “Toso Montanari” with particular emphasis to its use in the spectral region of the lattice phonons. Especially for FTIR a setup to reach the THz range will be object of the present project to complement the Raman data. Management, maintenance and possible implementation of the available experimental set-up will be required in the course of the research activity.

Specific objectives of our proposal are be summarized here:

1. Implementation of an experimental setup for THz FTIR.
2. Structural and spectroscopic characterization of the different compounds described in the project plan in the bulk form.
3. Fabrication of films with the derivatives, selecting solvent and substrate to optimize the film characteristics. For film deposition, techniques such as spin-coating, drop-casting and bar-coating will be investigated.
4. Structural, morphological (XRD, GIXRD, AFM) and spectroscopic (RAMAN, FTIR) characterization of the films. XRD and micro-Raman/FTIR in the low frequency will be used to determine the formation of polymorphs. The Raman technique will be precious to test whether the samples are chemically and physically homogeneous on a micro-scale (*i.e.* if only one crystal form is present).
5. The films most promising from a structural and morphological point of view will be implemented in the fabrication of OFETs (Organic Filed Effect Transistors). The OFET response can provide information on all the parameters describing the efficiency of the charge transport in these systems.