Seminar

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ORGANIC SEMICONDUCTORS: PHASE PURITY CONTROL BY LATTICE PHONON CONFOCAL RAMAN SPECTROSCOPY

After years of purely scientific interest, organic semiconductors have suddenly gained attention by applied and industrial research. The goal is to make devices not as efficient as the silicon based, but cheap and offering the advantages of flexibility and large area integration. Two problems have still to be completely overcome: i) The chemical purity of the samples, as organics are quite delicate in the preparation process and towards atmospheric contamination; ii) The physical impurities, including polymorphism. Here we address the second problem, showing that confocal Raman spectroscopy in the region of lattice phonons provides a most convenient tool for *in-situ* characterization and phase control of organic semiconductors.

We choose pentacene to illustrate the method. Pentacene has the record room temperature mobility among organics, and its polymorphism has been widely investigated. By modelling the crystal structure and lattice phonons, we have shown that two pentacene polymorphs exist, with slightly different crystal structures, but significant differences in the lattice phonons frequencies. Lattice phonon frequencies indeed depend on the curvature of the inter-molecular potential, so that they are sensitive to different molecular arrangements. Raman spectroscopy should then be able to discriminate the two phases, that we name **C** and **H**.

Using the micro-Raman technique, we have sampled many different crystals of pentacene, showing that two different types of spectra are consistently obtained, the most common one being associated to the **H** phase. On the other hand, **C** phase may be embedded in the **H** phase. The next step is to use confocal Raman mapping in the spectral region of the lattice phonons, which represents the fingerprint of the dynamics of the individual crystal lattice. By scanning the surface with steps as close as 5 µm, we obtain a series of Raman images which provide crucial information on the phase homogeneity of the crystals. By exploiting the confocality of the micro-Raman technique, we can also check the sample at different sample depths. The resulting Raman images are not obviously related to the crystal morphology: Pentacene phase purity has not to be taken for granted, even for single crystals. Being non destructive, Raman mapping can also be used to check the efficacy of methods, such as annealing, aimed at improving the crystal quality.

The extension of the method to other organic semiconductors, notably tetracene, oligothiophenes, and rubrene, is also presented.

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