Proposed Plan

Dr. Maria Carmen Ruiz Delgado was invited by LPPI for a short stay (10 days) during 2014, but her stay was very successful. Very rich and interesting discussions were developed not only with Gjergji Sini (performing molecular modelling calculations), but also with other members of our group (Fabrice Goubard and Thanh-Tuan Bui). The collaborations with the laboratory of Dr. Maria Carmen Ruiz Delgado are now extended to the experimental applications in the domain of photovoltaic devices, with a strong accent on the Raman and SEM (scanning electron microscopy) measurements, in which the university of Malaga in Spain is very well equipped.

Vibrational infrared (IR) absorption and Raman scattering spectroscopies are universally employed for the characterization of molecular and electronic structures, offering high sensitivity and delivering experimental data directly related with atoms and their molecular bonds. Furthermore, Raman spectroscopy can also provide very relevant information on eventual conformational changes of the p-conjugated polymer backbone upon solution in different solvents; after thermal annealing of polymer thin films; during *in situ* studies on working molecular electronic devices; p-conjugational changes induced by the aggregation of a polymer, or between the crystalline and amorphous phases of a polycrystalline p-conjugated polymer; and so on. All of these characterizations with the additional advantage of not requiring for any special treatment or preparation of the sample. Since the performance of the organic electronic devices is strongly dependent not only on the single-molecular structure and conformation of individual chains but also on the interchain aggregation, the information provided by vibrational spectroscopy at both single-molecular and supramolecular level is of particular relevance.

Conjugated organic oligomers and polymers attract considerable interest for applications in organic electronics. Efficient π-conjugation and a high degree of coplanarity are key parameters for achieving HOMO–LUMO gaps or band gaps in the semiconductor region, high conductivity, high mobility, and an electrooptical response. Oligo- and polythiophenes are among the most promising and best-studied organic electronic materials, but the search for other organic semiconductors is ongoing.

Finding the computational level that can correctly describe the extent of conjugation in long π-conjugated systems is currently an important unresolved problem. The problem arises from a lack of experimental data that can be directly compared with the calculated results and from the unfeasibility of carrying out the high level benchmark calculations that are required for such large sized systems.

In this proposal, we project on two aspects:

1- Continue our present collaborations on the recently started project, focusing on the property changes at the organic-organic interfaces in dye sensitized solar cells. The deep insight gained from the excellent-quality SEM images performed at Malaga University will help our group for a much better understanding of our results.
2- Perform Raman calculations of 1D and 2D conjugated polymers using periodic boundary conditions in the CRYSTAL14 software. We propose to test the commonly used DFT functionals as well as the HF and MP2 methods. Our

results will be compared with DFT calculations on isolated long oligomers at the same level of computation. Further comparison with experimental results on different conjugated polymers (i.e, polyfuran, encapsulated polythiophene, polyselenophene, and polyethylenedioxyselenophene) will provide guidance on the most successful theoretical method.