

**Report on the Short Visit of Antonio Cravino at
LIOS, Physical Chemistry, Johannes Kepler University Linz, Austria,
Prof. H. Neugebauer and Prof. N. S. Sariciftci.**

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Purpose of the visit: to investigate the photoinduced features in the IR spectrum of a low band gap conjugated polymer. In this polymer, each isothianaphthene ring is functionalized with an electron withdrawing moiety. Thus, as observed earlier by cyclic voltammetry experiments upon electrochemical doping, the polymer can stabilize both positive and negative radical-anion (the so-called polarons).¹ As photoinduced features (the so-called IR active vibrations, IRAVs) carry not only vibrational but also electronic information (IRAVs correspond to the Raman bands seen in the neutral state), this type of measurement was planned to probe photoinduced charge carrier generation in the pristine materials, as well, to study the degree of delocalization of the resulting positive and negative polarons, i.e. the hole and electron in photovoltaic devices using conjugated polymers as active material.

Work carried out during the visit: first, the specific photoinduced IR spectroscopy set-up has been mounted. This includes a series of mirrors and a defocusing lens, aligned to carry the laser beam used for photoexcitation to the front of the sample-holder, the latter being a cryostat cooled by a liquid nitrogen bath evacuated by a turbo-pump. Alternate dark/light spectra cycles are obtained by using a shutter, with on and off determined by an electromagnet driven by the spectrophotometer.

The polymer samples were obtained by drop-casting (chloroform) onto KBr pellets. Photoinduced IR spectra were recorded using a 45° geometry, exciting the sample at 514 nm (about 20 mW cm⁻²), collecting a sequence of 300 repetitions of recording 10 coadded single beam spectra under illumination and 10 coadded single beam spectra in the dark.

The photoinduced IR absorption spectrum shows a bleaching of the electronic ground-state absorption at about 9750 cm⁻¹ (according to the reported band gap of ca. 1.2 eV).¹ Two polaronic transition bands (maxima at about 6000 and 2300 cm⁻¹ - 0.75 and 0.28

eV - respectively) accompanied by IRAV features are observed. Thus, it can be safely concluded that charged state photogeneration occurs in PEHIITN. Concerning the IRAV pattern, for the modes that can be assigned to conjugated C–C single and double bonds stretching, in the range between ca. 1400 and 1000 cm^{-1} the spectrum displays four intense IRAV bands. These features, although seen at lower wavenumbers due to the low band gap of the polymer, compare well to those observed in the photoinduced IR spectra of well known systems such as polythiophenes and polydithienodithiophenes. Interesting is the behavior observed in the range between 1750 and 1700 cm^{-1} . In this range, two intense bands are seen in both the IR spectra of the neutral monomer and polymer. These bands can be assigned to symmetric (breathing) and antisymmetric stretching modes of the electron-withdrawing ring. In the photoinduced case, the symmetric stretching is further enhanced, whilst the antisymmetric one is bleached or deactivated.

This unusual behaviour indicates that only the symmetric vibration is coupled to the collective stretching-shrinking coordinate along the main backbone, a fact probably related to the structure/symmetry of the repeating unit/polymer.

To elucidate this unusual photoinduced IR behavior, further work is necessary. Besides calculations, which might provide some insight, from an experimental point of view, in-situ spectroelectrochemical experiments as well as Raman spectroscopy measurements on the neutral state of the polymer seems to be necessary.

In addition to the experimental work, A. C. has presented a seminar on recent results within the frame of the LIOS "Novel results" weekly group-meeting, and had valuable discussions with the colleagues at the host institution.

Future collaboration. As described in the above sections, future work is planned to confirm and better elucidate the obtained results. In addition, within the frame of the existing theories (e.g. the effective conjugation coordinate model) comparing the photoinduced IR spectrum to the Raman ones seems a necessary step, and we wish to collaborate with colleagues specialists in the field of Raman spectroscopy. Activity in this direction is already ongoing.

Moreover, due to the limited time of the visit, not all the envisioned experiments have been carried out. Novel conjugated materials, designed as potential donor for organic solar cells, synthesized by colleagues at SCL, Angers, might be the subject of time-resolved photoexcited spectroscopic investigation.

Projected publications. The results briefly summarized in this report seem to us intriguing, and should be of some interest for the organic solar cells community, and/or, more generally, for the chemists working on both synthesis, theory and application of conjugated systems.

Providing the the results will be reproduced, we are foreseeing submission of a manuscript to a physical-chemistry oriented journal.

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¹ H. Meng and F. Wudl, *Macromolecules*, 2001, 34, 1810.