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**In situ Raman Characterization of Donor-Acceptor materials for  
Solar Cells application**

**Final Report**

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This is the final report on the short visit of Beatriz Meana-Esteban at the Instituto per lo Studio delle Macromolecole (ISMAL), Consiglio Nazionale delle Ricerche (ISMAL-CNR) hosted by Dr. Silvia Luzzati during the period 8-22.02.2009

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**Purpose of the visit:** to characterize by in situ UV-visible (UV-vis) and Raman spectroscopic different polyconjugated materials with Donor-Acceptor (D-A) properties. These materials contain a perylenediimide moiety as an acceptor unit and an oligothiophene moiety linked in the bay position of the perylene as a donor. D-A moieties in the polyconjugated backbone allow for tuning the bandgap, as well as for photoinduced electron transfer reactions which are of high interest in organic photovoltaics (solar cells).

In situ UV-vis and Raman spectroscopy are complementary techniques. Therefore, a detailed study by UV-vis spectroscopy of the materials of interest is very important since it makes possible to anticipate what part of the material will be resonantly activated with a specific excitation wavelength.

**Work carried out during the visit:** We have studied the electrochemical and spectroscopic properties during n-doping (electrochemical reduction) of new materials MEK2 and PEK2. Perylenediimide has been used in this work as the model compound. The chemical structures of the materials are shown in Figure 1.

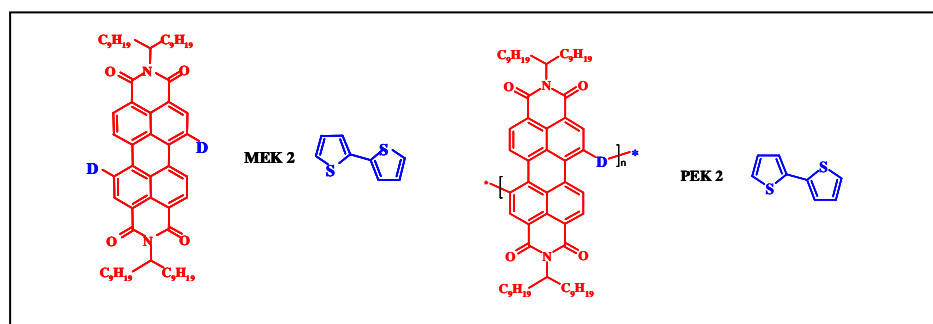


Figure 1. Chemical structures of MEK2 and PEK2

In the in situ UV-vis and Raman experiments films from the perylenediimide, MEK2 and PEK2 were dropcasted from a chlorobenzene solution on an ITO glass. The measurements were done in a flat cell with the ITO glass acting as the working electrode (WE), Pt wire as a

counter electrode (CE) and a Ag wire as a pseudoreference electrode. All the measurements were done in 0.1 M electrolyte solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in acetonitrile (ACN).

The absorption spectra of the different materials have been recorded with a spectrophotometer at various states of n-doping of the films, i.e. at different potentials applied to the film. The spectral changes of MEK2 and PEK2 are almost identical. The only difference is that in the case of MEK2 the charged species are highly soluble in the electrolyte solution (ACN-TBAPF<sub>6</sub>). Thus, the reversibility of the process is affected by the dissolution of the solid film in the electrolyte solution upon n-doping. The neutral PEK2 has three bands at 350, 475 and approx. 610 nm. These absorption bands vanish upon n-doping of the film indicating changing of the material from its neutral form to its doped form. Furthermore, new absorption bands start to grow with increasing doping level (increasing applied potential). From the UV-vis results, it can be concluded that PEK2 undergo two different transitions upon n-doping. This latter statement is based on the fact that at two different doping levels, absorption bands with different spectral pattern can be observed in the UV-vis spectra of PEK2. A possible explanation might be that in the first stage (at low doping level) the radical anion (R<sup>•-</sup>) might be formed and then, upon further n-doping of the film (higher doping levels) the dianion (R<sup>2-</sup>) is then created. Thus, both species show remarkably differences in their absorption spectra. These experimental results are in good agreement with the Cyclic Voltammetry (CV) experiments done previously.

In order to get more information about the n-doping of the materials, in situ Raman experiments have been done. A complete in situ Raman characterization requires registration of the Raman spectra not only as a function of the potential but also during different excitation wavelengths to be able to enhance the spectral regions where the different electronic transitions occur. In this work, different excitation lines have been used but the best Raman spectra have been obtained with  $\lambda_{\text{exc}} = 1064$  nm. With this excitation line, it is possible to observe best the changes taking place in the PEK2 during n-doping. The Raman spectra of the neutral PEK2 show different bands localized at 1589, 1550, a doublet at 1472 and at 1356 cm<sup>-1</sup>. During n-doping of the film, changes can be observed in the Raman spectra. At potentials corresponding to the first transition in the PEK2 (low doping levels), three new bands can be observed at 1576, 1331 and 1234 cm<sup>-1</sup>. These bands can be correlated to the formation of the radical anion in the material as previously discussed. This experimental result is in good agreement with the UV-vis since at the potential of the formation of the radical anion, an absorption band can be seen at wavelengths higher than 1000 nm. Thus, due

to the resonant effect, the species giving rise to optical absorption with energies that match those of the excitation line used will be enhanced. In this particular case, the Raman active bands of the radical anion will be enhanced and therefore, they can be clearly seen. Furthermore, at higher potentials (higher doping levels), where the second transition from the radical anion to the dianion takes place, the Raman spectra looks different, and the three bands observed previously are not longer visible. This latter phenomenon is due to the fact that in the UV-vis spectra recorded at this potential, the absorption band found at values higher than 1000 nm has disappeared. Therefore, the Raman bands that are characteristic for this new specie are weak and no visible, since resonance enhancement conditions are not fulfilled. As it has been already discussed, the vibrational behaviour of MEK2 is similar to the one in PEK2.

**Conclusions:** In situ UV-vis and Raman spectroscopy support the preliminary experimental results obtained by Cyclic Voltammetry (CV) and in situ FTIR-Attenuated Total Reflection (FTIR-ATR) spectroscopy during the electrochemical n-doping of MEK2 and PEK2 in ACN-TBAPF<sub>6</sub> solutions. These results have been done previously at LIOS.

**Projected Publication:** The results briefly summarized in this report together with the experimental results done at LIOS will result in a manuscript which is at the moment under preparation. Furthermore, an abstract to the conference European Materials Research Society (EMRS) held in Strasbourg in June 8-12,2009 has already been sent. The abstract is a joined contribution of LIOS and ISMAC.

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