

## Indigoids investigated by Micro-Raman spectroscopy in bulk and thin film phases.

**Arianna Rivalta, Alice Fiocco, Andrea Giunchi, Tommaso Salzillo, Elisabetta Venuti, Raffaele G. Della Valle, Aldo Brillante**

Department of Industrial Chemistry "Toso Montanari" e INSTM-Udr Bologna, University of Bologna, Viale del Risorgimento 4, 40136 Bologna (Italy) - [arianna.rivalta2@unibo.it](mailto:arianna.rivalta2@unibo.it)

Organic semiconductor materials, such as acenes, oligothiophenes and rubrene have the potential to challenge silicon based semiconductors, with the goal of making devices that, although not efficient as those silicon-based, are cheaper and have the advantage of flexibility and large area integration [2]. The search of materials for applications in organic electronics has seen in the past years a growing interest in small molecules of natural origin, to be used in eco-friendly devices where all components are designed from biocompatible and biodegradable compounds [1]. Among these, Indigo, which is currently the most-produced dye in the world, has shown excellent ambipolar charge carrier mobilities [3].

The phenomenon of polymorphism is very common in organic crystals and it is well known that the packing has important effects on the charge mobility. In this contribution we report on the characterization of both the known  $\alpha$  and  $\beta$  polymorphs of Indigo by Raman spectroscopy [4]. Raman spectroscopy in the lattice phonon region is a most effective tool to recognize polymorphism in molecular materials while the intramolecular vibrations are normally used to probe the chemical purity. For the indigo system we found that the intramolecular vibration can also be selectively affected by the different molecular packings as a result of the strong intermolecular hydrogen-bonds which characterize these structures.

In Figure 1, the enlarged interval at the low wavenumbers (lefthand side) highlights the unique pattern of the lattice phonon modes for polymorphs  $\alpha$  and  $\beta$  as compared with the weaker bands at 173 and 184  $\text{cm}^{-1}$ , which belong to intramolecular modes and lie at the same wavenumbers in both forms. In the interval 1450 - 1650  $\text{cm}^{-1}$ , where the strongest and most characteristic bands of Indigo are detected, originating from the so-called chromophore group, the two phases display instead markedly different spectral profiles. This has been interpreted as the consequence of the different intermolecular hydrogen-bond pattern of either phase, resulting from the different packing and affecting the vibrational dynamics of functional groups involved in the H-bridges.

The application of Raman spectroscopy to Indigo thin films has been very successful and has been shown to outperform XRD techniques in the identification of structurally very similar polymorphs.

Indigo, and all the indigoids in general, with polymorph differing only by slight changes and by the occurrence of surface-induced structures, appear to be interesting and challenging systems for the Raman investigation here presented.

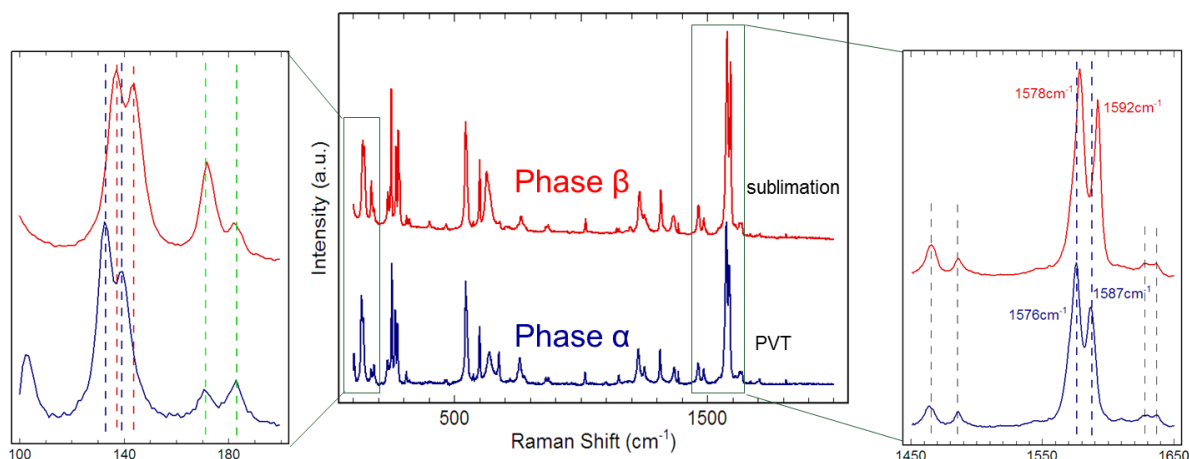


Figure 1: Raman spectra of polymorphs  $\alpha$  (blue trace) and  $\beta$  (red trace) of Indigo in the wavenumber range of the intramolecular vibrations. Centre: extended spectrum; left and right: zooming of the intervals. See text for details

### References

- [1] Głowacki, E. D. G. Voss, G Sariciftci, N.S., *Adv. Mater.* **25**, 6783 (2013).
- [2] Brillante A., Bilotti, I. Della Valle, R.G Venuti, E. Girlando, A., *CrystEngComm*, **10**, 937 (2008)
- [3] Głowacki, E. D. Voss, G. Leonat, L. Irimia-Vladu, M. Bauer, S. Sariciftci, N. S., *Isr. J. Chem.*, **52**, 540 – 551, (2012)
- [4] Von Eller, H. Structure de Colorants Indigoïdes. III-Structure Cristalline de L'indigo. *Bull.Soc.Chim.Fr.* **1955**, 1433–1438