Polarized Raman Spectroscopy as a Probe of Polymorphism and Molecular Orientation in TIPS-Pentacene

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TIPS-pentacene is a benchmark organic semiconductor characterized by a rich polymorphic landscape, with several crystalline phases separated by very small energy differences [1]. As a consequence, controlling and identifying the molecular packing in thin films remains challenging, particularly when solution-based deposition techniques are employed. In this work, we combine Raman spectroscopy with X-ray diffraction to investigate the structural properties of TIPS-pentacene in both bulk single-crystal form and thin films deposited by BAMS (bar-assisted meniscus shearing), with a particular emphasis on the capabilities of polarized Raman spectroscopy.

Low- and high-frequency Raman measurements reveal that thin films deposited under optimized growth conditions retain the same polymorph as the bulk crystal, despite the strong tendency of TIPS-pentacene to form alternative phases in confined geometries. Polarized Raman spectroscopy in the high-frequency region, dominated by C–C ring stretching modes of the pentacene backbone, is used to probe molecular orientation. By analyzing the polarization dependence of the average Raman intensity, we demonstrate that the molecular alignment in the thin film closely matches that of the bulk crystal.

A direct comparison between Raman spectra acquired with the incident polarization aligned along the crystallographic *a* axis of the bulk crystal and along the elongation direction of wire-like domains in the film establishes a clear correspondence between film morphology and crystallographic orientation. This result complements X-ray diffraction data, which show strong out-of-plane orientation and pronounced in-plane texture, and allows the elongation direction of the film domains to be unambiguously assigned to the *a* axis of the bulk structure.

Overall, this study demonstrates the central role of Raman spectroscopy in resolving structural questions that are difficult to address by diffraction alone in polymorphic organic semiconductors. Through polarization-dependent measurements, Raman spectroscopy provides direct access to molecular orientation and allows subtle differences in packing and texture to be identified. In this case, Raman spectroscopy not only confirms the preservation of the bulk polymorph in thin films, but also establishes a direct link between molecular orientation, crystallographic axes, and film morphology. These results highlight polarized Raman spectroscopy as a powerful and versatile tool for investigating polymorphism and structural order in organic semiconductor materials, particularly in thin films where kinetic effects and confinement play a critical role.

References

[1] Diao, Ying, et al. "Understanding polymorphism in organic semiconductor thin films through nanoconfinement." *Journal of the American Chemical Society* 136.49 (2014): 17046-17057.