INVITED

2-Dimensional Polymers studied by TERS

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Abstract

Monomolecular layers are usually difficult or impossible to characterize in terms of their nanoscale molecular composition. Tip-enhanced Raman Spectroscopy (TERS) not only shows excellent spatial resolution in the low nm range, but is also very useful for rendering monolayers spectroscopically visible. Examples of monomolecular layers where a nanoscale characterization would be highly desirable include self-assembled monolayers (SAMs), Langmuir-Blodgett layers, lipid membranes, and a new class of compounds, 2-dimensional polymers (2DPs). 2DP polymer sheets can be synthesized via the formation of covalent linkages, via π-π noncovalent interactions, via transmetallation, and by other means. After polymerization, 2DPs display remarkable mechanical robustness and can be transferred to surfaces and grids. Similar to graphene and its derivatives, 2D polymers with precisely controlled molecular structures and cavities show promise for a range of applications, including energy conversion and storage, gas storage and separation, sensing, and catalysis.

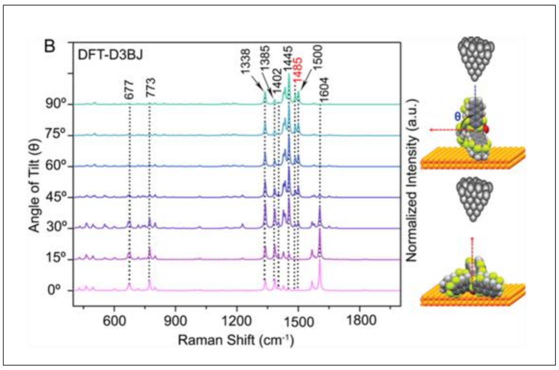

Figure: DFT simulation of TERS spectra of a partially fluorinated "carboxy fantrip" monomer that forms 2D polymers via noncovalent π-π stacking interactions. The Raman intensities at 1485 and 1604 cm^{-1} are strongly dependent on the tilt angle, which allows the homogeneity of the 2D polymer layer to be assessed.

In this contribution, TERS studies as well as theoretical calculations to aid the interpretation of the experimental results on several 2DP systems will be presented. TERS maps with pixel sizes as small as 2 nm showed ordered vs. disordered areas, and reacted vs. unreacted monomers.

References:

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