Nanoscale Chemical Imaging via Scanning Tunneling Microscopy and Advanced Raman Spectroscopy Techniques

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This talk explores a new path forward toward the goal of probing single-molecule processes via scanning tunneling microscopy (STM) and tip-enhanced Raman spectroscopy (TERS). The combination of STM imaging and optical spectroscopy will be discussed as a promising approach to raise both the spatial and spectral resolution of molecules to an unprecedented level. At the beginning of this talk, I will show you the molecular resolution imaging with multiple vibration modes detection by a plasmonic STM probe. The probe plays a key role both in achieving atomic resolution and enabling single molecule chemical sensitivity through plasmonic enhancement. Besides chemical identification of these molecular adsorbates, intramolecular vibrational distribution can be used for unraveling the intricacies of adsorbate-adsorbate/ adsorbate−substrate interactions. We have unraveled the orientation of PPDI molecules at the dynamic molecular domain boundary with ~4 nm spatial resolution by TERS mapping. TERS provides access to molecular adsorption geometries when STM provides no topographical information. Finally, Angstrom-scale spatial resolution in TERS has been achieved. At room temperature, the strong adsorbate-substrate interaction between the meso-tetrakis-(3,5-ditertiarybutylphenyl)-porphyrin (H2TBPP) and the underlying Cu(111) substrate leads to the formation of the bowl up/down conformations. Through simultaneous TERS and STM analysis on the neighboring conformational isomers, we have observed ~15 cm^{-1} spectral shift in one of the porphyrin-ring Raman modes and analyzed the origin of this shift using DFT calculations.