Control of optical properties of molecules near plasmonic structures is a key issue in nanophotonics, particularly for the development of ultrasensitive microscopic techniques and molecular plasmonic devices. One fundamental issue here is to understand the interplay between molecular excitons and surface plasmons in nearby metallic nanostructures. While extensive research has been carried out to such end using far-field photon-excited techniques, luminescence arising from near-field excitation by electrons or photons in a molecular junction of a scanning tunneling microscope (STM) can provide additional information on the local electromagnetic properties with ultrahigh resolution and could thus offer insights into the nature of optical transitions and the coupling and energy transfer between excitons and plasmons at the single-molecular scale.

In the first part of this talk, I shall demonstrate single molecular electroluminescence arising from the intramolecular optical transitions of a designed porphyrin molecule that is self-decoupled and of preferred dipole orientations. The generation and detection of molecule-specific fluorescence is found to depend on two crucial factors: The first is the strength of electronic decoupling to suppress fluorescence quenching and the second is the spectral matching of the nanocavity plasmon resonance to the molecular vibronic transitions for coupling the light to the far field. These findings help to substantially deepen our understanding on the coupling and decay of electronic excitations in single molecular optoelectronics and may offer new strategies for the development of electrically driven organic point-light sources and nanoscale optoelectronic integration.

On the other hand, visualizing individual molecules with chemical recognition is a longstanding target in catalysis, bio-science, and molecular nanotechnology. Molecular vibrations provide a valuable “fingerprint” for this identification. In the second part of the talk, I shall describe another application of the nanocavity plasmon to the single-molecule tip-enhanced Raman scattering (TERS) experiments. I shall demonstrate unprecedented sub-molecular Raman spectroscopic mapping with spatial resolution below 1 nm, resolving even the inner structure of a single molecule and its configuration on the surface. These findings demonstrate that Raman spectro-microscopy has gone intra-molecular and sub-nanometer, which opens up a new avenue to probe chemical identification, optical processes and photochemistry at the single-molecule scale.

References