

Scanning tunneling microscopy-induced luminescence (STML) combined with high-resolution atomic force microscopy (AFM) is a powerful tool for studying the photophysics of individual molecular emitters on surfaces. However, the mechanism of energy conversion between tunneling electrons and photons in decoupled systems placed in a nanocavity of STM is not fully understood as it depends on many variables.

This thesis presents a range of proof-of-concept experimental approaches. The viability of CO-terminated tips for STML is demonstrated by performing subnanometer-resolved spectroscopy and mapping of photon intensity acquired over zinc phthalocyanine on NaCl/metal substrate. For the same molecule, time-resolved phase fluorometry is devised and is used to reveal the exciton and charge dynamics as a function of the applied bias voltage. Of more fundamental character, the role of the chromophore environment on its exciton emission and binding energy is studied. For the first time, we observed and explained the presence of molecular librations in molecules on the surface from a comb-like emission line resulting from the exciton-libron coupling and the chiral adsorption geometry. Finally, exciton delocalization in molecular aggregates is mapped using the tip nanocavity capable of detecting the dark states, inaccessible in far-field spectroscopies. The experimental results are compared to theoretical simulations and discussed extensively.