Plasmon Strengthening by Coupling with Molecular Excitons at Metal-Vacuum-Metal Nanocavities

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Coupling between the localized plasmons at optical nanoresonators and the excitons of quantum emitters can be strong enough to drive the formation of hybrid light matter states named plexcitons, thus providing a handle for controlling single photon states. Scanning Tunnelling Luminescence should be an important technique to characterize exciton-plasmon interaction, since it allows for an atomic control of the cavity size and shape, and for a precise knowledge of the molecular geometry in the cavity. Our incomplete understanding on the fundamental processes leading to electron-tunnelling luminescence limits our progress towards fully exploiting the enormous potential of this experimental technique.

For example, the effect of molecular adsorption on the plasmonic modes of the cavity has been previously characterized in several publications [1,2], but the results are difficult to reconcile. Light intensity was enhanced or suppressed, and the peaks were described to redshift or blueshift, depending on the molecule. These studies, however, did not consider the role of the electronic structure on plasmonic inelastic rates that we found and described recently in our group, not the normalization process that we have developed [3].

In this contribution, we will show that normalized spectra recorded with Pd-tetraphenylporphyrin (TPP) in the cavity are virtually indistinguishable of those of the bare cavity, which we attribute to the fact that the lowest energy optical transitions of Pd-TTP are in-plane polarized and, thus, cannot be coupled to cavity plasmons. On the contrary, when we use Fe-Cl-TTP, with out-of-plane optical transitions in the energy range of the cavity plasmons, the light intensity is significantly enhanced in molecule filled cavities. These results open a pathway to realize the promise brought by STML to the investigation of plasmon-exciton coupling at the nanoscale.

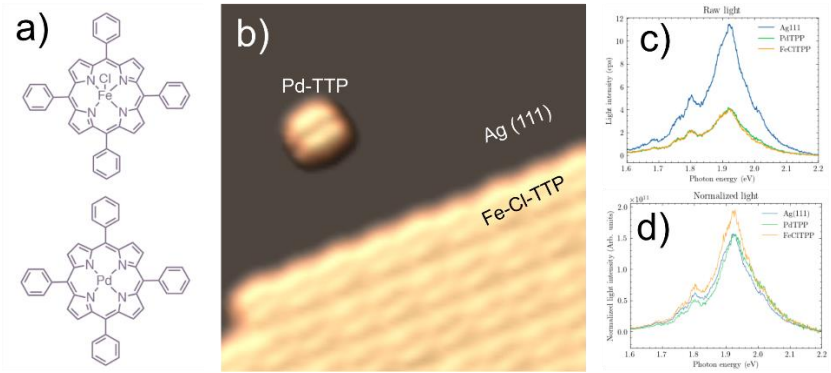

Fig. 1. a) Molecular structure investigated here. b) STM image showing both molecules on Ag(11). C) As measured electroluminescence spectra. D) Normalized electroluminescence spectra.

[1] F. Geng et al., Optics Express **20**, 26725 (2012)
[2] G Hoffmann et al., Phys. Rev. B **65**, 212107 (2002)
[3] A. Martín-Jiménez et al., Nature Communications **11**, 1021 (2020)