The scientific and technological interest in colloidal quantum dots (CQDs) for more than two decades has been focused on the tunability of electronic and optical properties by variation of size and shape. This advantage has made them attractive for various opto-electronic applications, including photovoltaic cells, light sources, photodetectors or switches, as well as fluorescence tags in biological platforms. However, numerous questions remained, concerning tunability of optical transitions by electronic coupling to confined phonons or to vibrational motions of capping ligands that successively can control intra-band and inter-band relaxation processes. Furthermore, ligands' vibrational motion may influence the inter-CQDs distance, with a direct impact on charge mobility in CQDs-based opto-electronic devices (e.g., photovoltaic, LED).

This work discusses a thorough investigation of two scientific matters: (a) excitonic-vibrational coupling in CQDs, by recording the micro-photoluminescence ($\mu$-PL) spectrum of highly photo-stable individual colloidal quantum dots (CQDs), resolving induced-coupling changes normally blurred in ensemble measurements; (b) control of charge transfer between double-CQDs structure, to be explored theoretically by semi-classical model and experimentally by scanning tunneling spectroscopy (STS).

The role of surface capping ligands in colloidal growth was studied extensively through the years, recognizing their importance in passivation, isolation and surface reconstruction of individual dots, as well as controlling the rate of growth over a certain crystallographic facet, hence molding the shape of the nanostructures. Furthermore, surface capping are acting as bridge moiety to the surrounding medium and can be exchanged upon demand, to allow bounding or solvation, as well as control of inter-particle interactions. However, the influence of the capping ligands on the intrinsic electronic properties of CQDs was studied only to a lesser extends: A few studies showed that capping ligands change the carriers' potential barrier at the dot's surface, rendering a slight normalization of the electronic energy levels. Others indicated dielectric influence on internal polarity, influencing linear and nonlinear properties of the CQDs. But only a few singular studies in recent years suggested a more direct interaction between intrinsic electronic states and vibrational motion of capping ligands.\(^2,3\)

**Excitonic-vibrational coupling:** The current project shows for the first time a direct evidence for the absorption of ligand vibrational modes due to excitonic-vibrational coupling in a single CQD (see Fig. 1). The demanded spectral resolution required the use of CQDs exhibiting spectral stability, eliminating the commonly known fluorescence intermittency (called blinking) and spectral jumps. These spectral unsteadiness phenomena in CQDs have been under discussion nearly fifteen years; in the past they were correlated with the
occurrence of photo-charging and consequence nonradiative Auger relaxation, but more recent evidences also suggest involvement of charge trapping at surface sites, and may even involve the electronic-vibrational coupling. This work utilized model hetero-structure CQDs with the following composition: CdTe/CdTe$_x$Se$_{1-x}$ core/alloyed-shell, and CdSe/CdS/ZnS core/shell/shell, each of which has a different benefit, offering reduction of trapping sites at a core/shell interface, showing a minor change of band gap energy with a change in temperature and improved chemical and photochemical stability. Furthermore, our theoretical considerations showed that a "soft" alloyed core-to-shell boundary reduces overlap integral between band-edge and nearly infinite conduction band wave-functions, hence reducing the Auger nonradiative relaxation rates, consequently rendering spectral stability. The experimental results unequivocally revealed existence of ligands' vibrational resonance transitions displaced away from the zero-phonon exciton line, excited via exciton-vibrational interactions, examining samples with the discussed spectral stability.

Charge transfer between double-CQDs structure: A theoretical and experimental work is currently under development, considering a model system (see Fig. 2) comprised of double-CQDs structure positioned between a scanning tunneling microscope tip and a substrate. The model enables the examination of carrier transport process dependence on the inter-CQDs spacing and on the stiffness (viz., vibrational motion) of the bridging organic ligands.

Obviously, excitonic energy loss or/and blockage of carrier transport by the vibrational degrees of freedom of surface ligands can be deleterious for opto-electronic applications, thus, requiring special consideration (e.g., exchange or removal) upon a design of a technological device.

References