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Summary of the thesis

The development of single molecule-based techniques in the last decades has enabled directly selecting, tracking, and measuring an individual molecule. Single molecule spectroscopy can directly observe the properties of individual molecules usually hidden in ensemble averages. In this thesis, the structural dynamics of a single quantum emitter, served by hypericin, is characterized. Hypericin, isolated from St. John's wort, does not only have large potential in modern medicine but also exhibits fascinating structural dynamics, such as dissociation, conformation and tautomerism.

By using confocal scanning microscopy combined with radially/azimuthally polarized laser modes, three-dimensional reorientation of the transition dipole moment of a single molecule, due to the charge redistribution during tautomerism, is observed. The transient reorientation is detected in a fluorescence time trace as a sudden fluctuation. To quantify the temporal properties of the tautomerism, photon autocorrelation function is used to extract the intensity fluctuations. The results show the distinct influence of the local environment, such as PVA matrix and deuteration effect.

The local photonic environment of a molecule is modified by the microcavity/nanocavity. The theoretical principles and experimental results are presented for a coupled molecule. A significant change of the radiative emission rate and of the fluorescence spectra is discussed. It allows us to measure the absolute quantum yield by using a tunable microcavity. The results show the possibility of controlling tautomerization by changing the photonic environment.

Subsequently, molecular dissociation is discussed by single molecule surface-enhanced Raman spectra profiting from near field enhancement of nanocavity. Furthermore, the theoretical model reveals the importance of the radius of the nanoparticles and the gap distance between them in order to achieve maximum emission enhancement. A fast experimental optimization strategy towards optimal fluorescence enhancement is outlined.

Key words: Single molecule, Fluorescence, Hypericin, Fabry-Perot interferometers, Surface plasmon resonance, Raman effect, Surface enhanced