Time-resolved spectromicroscopy of individual phthalocyanine molecules

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Scanning tunneling microscopy-induced luminescence (STML) is a powerful tool for studying photophysical phenomena of individual molecular emitters on surfaces such as exciton delocalization [1,2] or energy transfer [3,4] with unprecedented sub-nm resolution. A typical model system consists of a chromophore such as phthalocyanine adsorbed on a few layers of NaCl decoupling layer on metal which are sufficient to prevent the nonradiative quenching of the molecular excited state [5]. The exciton decay is observed as a fluorescence signal detected in the far field from the molecule located in the STM junction. The extreme enhancement of the electromagnetic field in the STM nanocavity allows to detect signals from single molecules.

The understanding of exciton dynamics is crucial for improving organic light-emitting devices or for the potential utilization of excitons in quantum computing but is still a matter of controversy.

First attempts to measure the lifetimes of exciton in the nanocavity suggested lifetimes of hundreds of picoseconds [6,7] but later studies pointed towards a transient charge state lifetime involved in the electroluminescence excitation process [8,9] and estimated the lifetime to be several orders of magnitude lower, due to the Purcell effect of the plasmonic nanocavity.

Here we use the STM with picosecond optical excitation and detection capabilities to perform direct time-correlated single photon counting (TCSPC) using photoluminescence of single zinc- and magnesium-phthalocyanines (ZnPc, MgPc). With this technique, we could determine the upper limit of the lifetimes of the molecule in the tunable nanocavity and investigate the regime change between the micro-photoluminescence (µPL) and tip-enhanced photoluminescence (TEPL).

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