

Trends in ultrafast localization dynamics of metalloporphyrin cavity polaritons

Aaron S. Rury
Department of Chemistry
Wayne State University
Detroit, MI 48202

Theoretical treatments indicate the formation of cavity polaritons through the strong coupling of spatially confined photons to molecular electronic transitions could provide access to truly quantum control of molecular excited dynamics central to chemical problems such as photocatalysis. Despite this promise, few experimental studies have carefully assessed these proposals, especially on ultrafast time scales. In this presentation, we compare the ultrafast localization kinetics of two types of metalloporphyrin molecules strongly coupled to micro-scale cavity photons to those of film-embedded molecules and establish what excited state processes change upon polariton formation. These studies indicate the avenues cavity polariton formation provides to precisely control the excited state photophysics of metalloporphyrins depend on specific molecular species strongly coupled to cavity photons. In the case of zinc (II) tetraphenyl porphyrin (ZnTPP) we find the ultrafast localization of the polariton on the lowest lying singlet excited state of ZnTPP increases as we increase the collective light-matter coupling. We model these dynamics to show interpolaritonic vibronic resonances play a key role in the polariton-amended dynamics of ZnTPP. In contrast, we find the localization of cavity polaritons formed using copper (II) tetraphenyl porphyrin (CuTPP) onto the triplet states of this molecule slows down relative to triplet formation in photo-excited solution phase molecules. We discuss initial steady-state spectroscopic results consistent with a physical mechanism explaining the localization dynamics of CuTPP cavity polaritons. By comparing these results, we propose the manner in which cavity polariton formation can act as a lever to quantum mechanically control the excited state photophysics of metalloporphyrins depends on the nature of the excited state to which cavity photons strongly couple. These physical insights will be central to any future applications of strongly coupled metalloporphyrin-cavity systems in light harvesting and photo-catalysis technologies.