# Excited state dynamics of molecular solids embedded in optical microcavities

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The excited-state dynamics of molecular aggregates are governed by their potential energy landscape that can hardly be controlled artificially. However, it is possible to alter the excited state dynamics by a strong coupling between light and molecules: polariton formation, because it can decouple the electronic and vibrational degrees of freedom [1]. Here, we demonstrate two examples of this polaron decoupling effect on the photochemical dynamics in organic thin film embedded in optical microcavities.

In the first topic, the polariton formation effect on singlet fission (SF) of amorphous rubrene is discussed [2]. The vibronic feature of polariton states in this system is characterized through the analysis of steady state absorption spectra by using the Holstein-Tavis-Cummings model. On the basis of this analysis, we show with time-resolved spectroscopy that the SF rate following a resonant excitation of the lowest energy polariton state is indeed modulated when the cavity photon energy is changed. A numerical simulation by using the Fermi's golden rule formula with the vibronic polariton feature successfully accounts for the observed modulation of the SF rate, indicating that the polaron decoupling plays a decisive role in the nonadiabatic dynamics.

In the second example, a strong reduction of the thermal fluctuation in the electronic excitation energy induced by the strong light-matter coupling in tetraphenyldibenzoperiflanthene film is demonstrated. The ultrafast fluctuation due to the coupling with the low-frequency bath modes in the electronic excited state is revealed by two-dimensional electronic spectroscopy, and it is shown that the magnitude of the fluctuation is strongly reduced in an optical microcavity via the strong light-matter coupling.

References:

[1] F. Herrera and F. C. Spano, *ACS Photonics* **5**, 65 (2018).

[2] S. Takahashi, K. Watanabe, and Y. Matsumoto, *J. Chem. Phys.* **151**, 074703 (2019).