第８回機能物質化学講演会のお知らせ

日時：2012 年 5 月 24 日（木）午後 3 時～午後 4 時 30 分

場所： J 棟 505 室

概要： 仏リール第 1 大学の Michel SLIWA 博士（CNRS 研究員）が来日するにあたり、本学相模原キャンパスで蛍の生物発光に関わるオキシルシフェリンの超高速分光研究についての講演会を開催いたします。

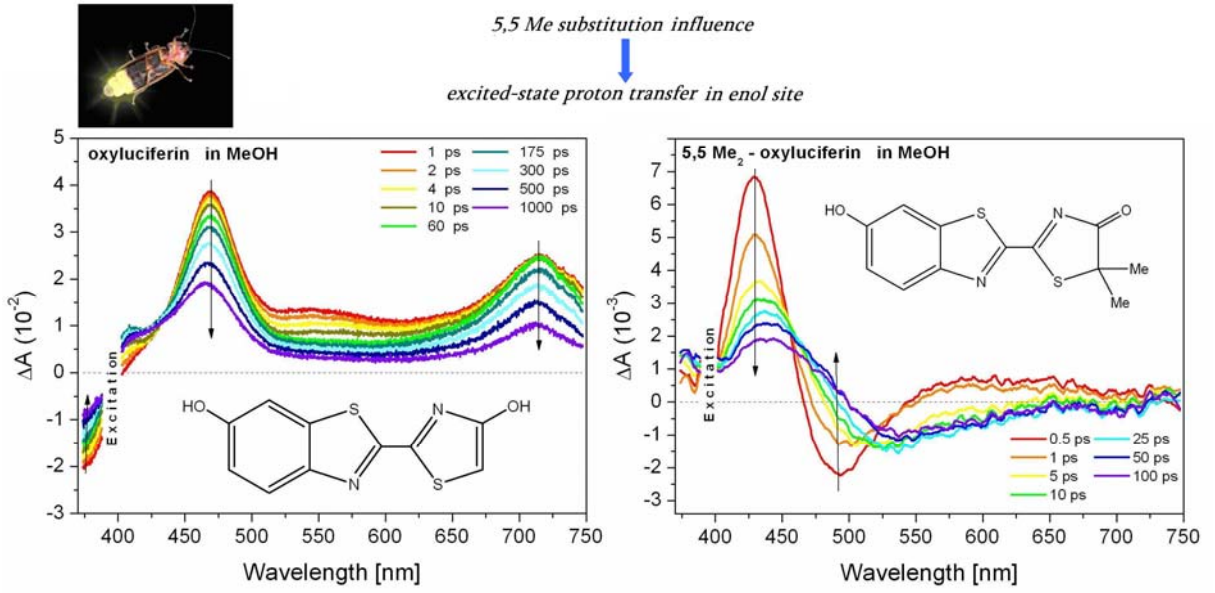
講演題目：Ultrafast spectroscopy of Oxyluciferin and its synthetic derivatives: the origin of the bioluminescence of fireflies

講演概要：

The chemical origin and mechanism of firefly bioluminescence is still under debate. The emitting light arises from the electronic de-excitation of oxyluciferin (Oxy), an organic compound resulting from the oxidation of the luciferin substrate inside an enzyme called luciferase. Interestingly, different fireflies emit light from green to red (510-670 nm) despite the same emitter. This color tuning is still not being completely understood and thorough study on oxyluciferin photochemistry is needed to clarify firefly bioluminescence mechanism.

So far the steady-state absorption and emission spectra were recorded and assigned to the six possible chemical forms of the emitter and its anions. The concentration ratio of the different species in solutions of Oxy is determined by several factors such as pH, solvent polarity, hydrogen bonding, presence of additional ions, and π-π stacking [1,2]. To explore the nature of the emitting species, a series of substituted model molecules, 4-MeOxy, 4,6-Me_2Oxy, 6-MeOxy and 5,5Me_2Oxy, were synthesized. We analyzed their stationary absorption (UV/Vis/IR) and fluorescence spectra in different solvents and pH. To assign precisely the IR spectra the synthesis of ^{13}C and ^{15}N labelled analogues of Oxy were achieved. To understand dynamics of the emitter we undertook ultrafast time resolved (fluorescence, absorption) studies of oxyluciferin and its derivatives in solvents with different polarity and proticity (H_2O, MeOH, CH_3CN). Presented results are the first femtosecond transient absorption data on oxyluciferin and its derivatives. All the measured spectra exhibit multi-band character with the intensity and lifetime depending on each derivative and solvent. The chemometric analysis of spectra allowed us to assign particular excited absorption bands to individual species in deactivation processes. The results are compared to femtosecond fluorescence data reported for luciferin by the group of Huppert [3]. They concluded on ultrafast exicted state proton transfer with the solvent from the phenolic group. Our results suggest that this process in oxyluciferin occurs from the enol site. The origin of the luminescence and the ultrafast dynamics of

oxyluciferin in firefly will be discussed. Obtained results open also the perspective for purposefully designed emitters exhibiting optimized performance of the polarity-dependent emission and being applied as fluorescence probe *in vitro* and in cells.



[1] Naumov, P.; Ozawa, Y.; Ohkubo, K.; Fukuzumi, S. *J. Am. Chem. Soc.* 2009, 131, 11590.
[2] Naumov, P.; Kochunnoony M. *J. Am. Chem. Soc.* 2010, 132, 11566.
[3] Presiado, I.; Erez, Y.; Huppert, D. *J. Phys. Chem. A* 2010, 114, 9471.

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