European XFEL Science Seminar

Tuesday, May 14th 2024, 13:00 *in person XHQ / E1.173*

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in collaboration with:
Laser for Science Facility, STFC, U.K., ALVRA beamline at SwissFEL, and FXE instrument at EU XFEL

“Controlling Photoinduced Charge Transfer Pathways with Infrared Pulses”

One of the major challenges of the fascinating field of photoinduced charge separation - a fundamental process which lies at the heart of reactions in natural and artificial systems powered by the energy of light – is how to control reaction pathways, and direct reactivity “at will”.

Nuclear-electronic (vibronic) coupling is of particular interest in this regard since the Born-Oppenheimer approximation is not valid on the ultrafast timescales intrinsic to photo-processes. Perturbing vibronic coupling may thus offer a way to affect photochemical reactions.[1-2] Such perturbation can be achieved by introducing a narrow-band IR pulse after initial population of an excited state to selectively affect vibration(s) that are coupled to electron transfer processes; the overall sequence of ultrafast pulses used is {UV$_{pump}$- narrowband IR pump - broadband IR$_{probe}$}.

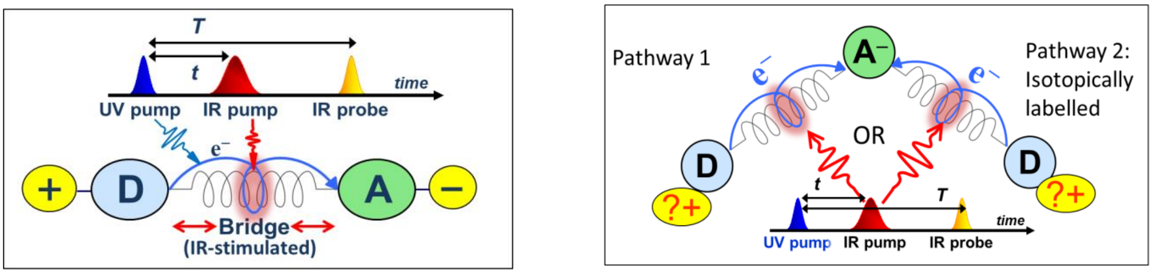
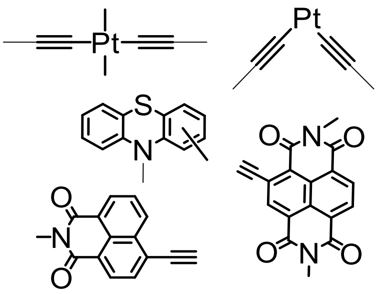


Fig 1. Modulation of electron transfer in a linear D-B-A system (Left), and in a “fork” system which has two electronically identical, but vibrationally distinct pathways.



Examples of *B*, *D*, *A* building blocks

The presentation will focus on recent work on IR-perturbation of photoinduced charge separation in transition metal Donor-Bridge-Acceptor complexes. In the first type of systems, D-B-A, (Fig. 1, left), selective excitation of bridge-localised vibrational modes in the excited state was shown to drastically change the yield of the product states, up to 100%.[3-4] In the second, fork-type, system D-B-A-B-D (Fig. 1, right), which have *competing* electron transfer pathways differing only by isotopic labelling of the bridge, ^{13}C *vs.* ^{12}C, selective IR-excitation of either bridge affects the yield of charge-separation along both ‘arms’.[5] This effect potentially offers the means to direct electron flow along a pre-selected reaction pathway. The effect of the lifetime of the branching state, the driving force for various processes involved,[6] and the strong vs. weak-coupling regimes on the IR-control efficiency will be considered. The suggested mechanisms – derived from ultrafast TRIR, TA, Fluorescence upconversion, and FSRS experimental methods, as well as quantum-chemical calculations - will be discussed in the broad context of the state-of-the-art in the field.

Recent results on time-resolved X-ray spectroscopy of charge-transfer Pt(II) complexes – and plans to use it to follow structural changes in the course of IR-control – will also be discussed.

[1] Z Lin, et al J. Am. Chem. Soc., 2009, 131, 18060; [2] Y. Yue, et al, Dalton Trans., 2015, 47, 8609.
[3] M. Delor, et al Science, 2014, 346, 1492. [4] M. Delor, et al, Nature Chem., 2015, 7, 689.
[5] M. Delor, et al, Nature Chem., 2017, 9, 1099. [6] A. Auty, et al, Chemical Science, 2023, 14, 11417.

Host : Sakura Pascarelli

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