

# Ultrafast 2D UV and visible spectroscopy of (bio)chemical systems

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We review our recent studies, using 2D transient absorption deep-UV spectroscopy, on electron transfer in hemoproteins and on the charge carrier dynamics in Titanium dioxide. We then present our recent studies using visible coherent 2D on the energy transfer in diporphyrins and on pentacene crystals.

Following the implementation of deep-UV ( $< 300$  nm) 2D transient absorption (TA) spectroscopy,<sup>1</sup> we investigated the Tryptophan (Trp) fluorescence decay in myoglobins (Mb), showing that in ferric ones, one of the Trp's does not only decay by FRET but also by electron transfer (ET) to the heme.<sup>2</sup> We extended these studies to the ferrous deoxy form showing that the ET also occurs therein.<sup>3</sup> We will show more recent results on ligated ferrous Mb's that confirm the generality of the phenomena. We then present the first 2D UV studies of a transition metal oxide (Titanium dioxide), which reveals new hitherto unknown excitonic bands, which turn out to have a 2D nature in the 3D lattice.<sup>4</sup>

We recently implemented a coherent 2D visible set-up that provides sub-10 fs pulses in the range from 420 to 900 nm. We will present results we obtained to investigate singlet fission in pentacene crystals and singly-fused diporphyrin systems in solution, showing clear signatures of interchromophoric vibronic coupling (see figure).

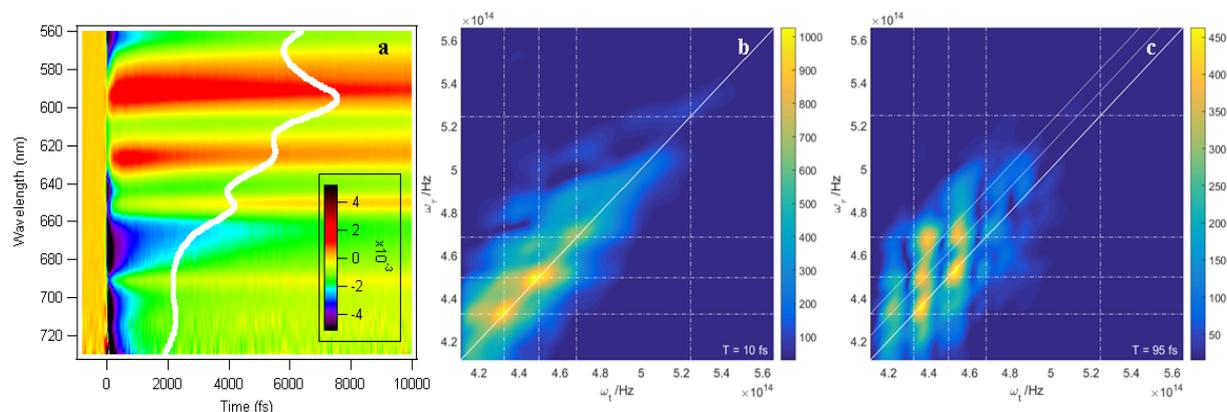


Fig.1 (a) Transient absorption measurements showing the first 10 ps evolution upon 490 nm excitation. The white trace shows the static absorption spectrum. (b) 2D spectrum at 10 fs population time showing the diagonal peaks. (c) 2D spectrum at 95 fs showing cross diagonal peaks showing the correlation between the Q bands.

<sup>1</sup> *An Ultrabroad Femtosecond 2D Transient Absorption Set-Up in the Ultraviolet*

G. Auböck, C. Consani, F. van Mourik and M. Chergui, *Optics letters* **37** (2012) 2337

<sup>2</sup> *Ultrafast tryptophan-to-haem electron transfer in myoglobins: a two-dimensional UV spectroscopy study*

C. Consani, G. Auböck, F. van Mourik and M. Chergui, *Science* **339** (2013) 1586-1589

<sup>3</sup> *Tryptophan-to-haem electron transfer in ferrous myoglobins*

R. Monni, A. Al Haddad, F. van Mourik, G. Auböck and M. Chergui, *PNAS* **112** (2015) 5602-5606

<sup>4</sup> *Two-dimensional excitons in a three-dimensional lattice: The case of anatase TiO<sub>2</sub>*

E. Baldini, L. Chiodo, S. Moser, J. Levallois, E. Pomarico, G. Auböck, A. Magrez, L. Forro, M. Grioni, A. Rubio and M. Chergui, arXiv:1601.01244 and *Nature Materials* (under review)