Coherent Vibrational Coupling in Singly Fused Diporphyrins

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Electronic and vibrational dynamics of singly-fused diporphyrins with different metal centers are studied by 2D visible spectroscopy and ultrafast transient absorption spectroscopy. By investigating the timescales between 10 fs and 7 ps, we witness the rise of the coupling between the Q bands.

Highly π-conjugate systems such as fused diporphyrins are receiving considerable attention due to their numerous applications as efficient molecular photonic and electronic wires, reverse saturable absorbers, and photochemical up-conversion in the near IR [1,2]. These systems also exhibit interesting spectroscopic properties, such as splitting of the Soret band, due to the strong excitonic coupling between the adjacent rings, along with a significant increase in the Q bands oscillator strength.

In this work we investigate the excited state dynamics of an Mg- and free-base porphyrin fused together by a single bond at the meso-position. Ultrafast 2D visible spectroscopy with <10 fs pulses spanning from 560 nm to 730 nm is used to study the electronic and vibrational dynamics. We could trace the rise of the cross peaks between the Q bands in <80 fs. The 2D results are combined with the transient absorption experiments exciting the Soret bands as well as the Q bands. Multiple vibrational modes are apparent in the transients, of which the most prominent is at 128 cm^{-1}, corresponding to a porphyrin in-plane mode. The relevance of such modes in the relaxation process will be discussed.

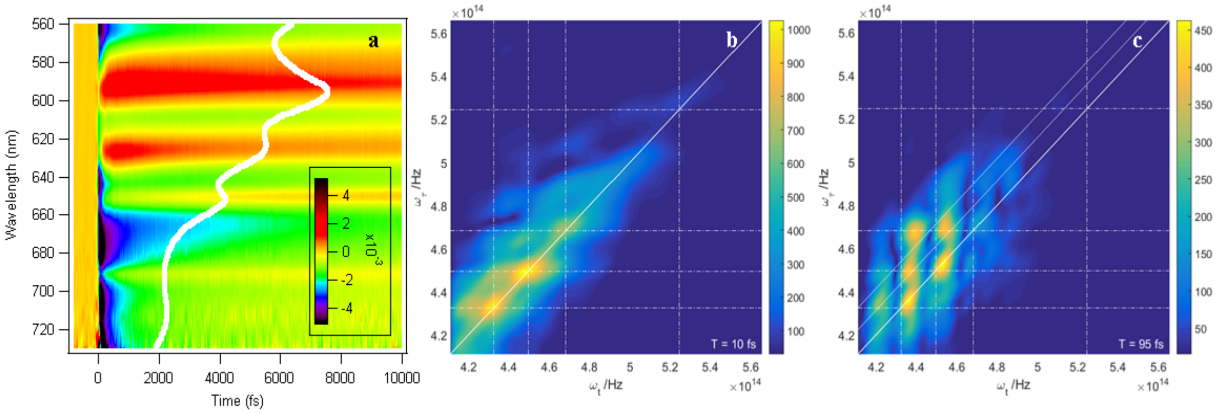

Fig.1 (a) Transient absorption measurements showing the first 10 ps of relaxation upon the 490 nm excitation. The white trace shows the static absorption spectrum. (b) 2D spectrum at 10 fs population time showing the diagonal peaks with. (b) The 2D spectrum at 95 fs shows the appearance of cross diagonal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

[1] D. T. Schmidt et al, J. Phys. Chem. A, 2012, 116, 7898-7905.
[2] D. Kim, A. Osuka, J. Phys. Chem. A, 2003, 107, 42, 8791-8816.