2D Electronic Spectroscopy Study of Coherent and Structural Dynamical Effects in Porphyrin Chromophores

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In order to successfully create efficient novel porphyrin based artificial light harvesting materials the excited state dynamics associated with conformational heterogeneity have to be determined and understood. Multi-timescale processes are present in conjugated molecular structures as well as coherent phenomena. Here we address early time dynamics with 2D electronic spectroscopy.

The search for artificial biomimetic light harvesting structures has been gathering pace over the last couple of years. Among new structures being proposed, synthetic nanorings based on covalently linked porphyrin chromophores are showing promising physical properties, making them strong candidates for biomimetic light harvesting applications.[1] In order to develop a complete understanding of the dynamical processes present in such complex structures we recently performed a full electronic 2D and pump-probe study of the porphyrin dimer shown in Figure 1a.[2] This dimer is the main structural motif present in biomimetic nanorings. Our studies revealed that the porphyrin dimer is driven to planarization in the excited state on a tens of picoseconds timescale. However many unresolved features, mainly at early times, were not clearly explained. For example, a spectral broadening (Figure 1b) on a picosecond time scale could not be clearly assigned either to further excited state structural dynamical motion or to some other inter- or intramolecular re-equilibration mechanism. Further, coherent oscillations are observed in the dimer that are not present in the corresponding monomer, possibly indicative of excitonic coupling.

In this work we explore carefully the early time 2D electronic spectra as a function different polarization configurations of the excitation beams (in order to assess the origin of the coherent oscillation), temperature (to freeze out structural motions) and for different molecular structures (for example, with ligand added or with lighter substituents).

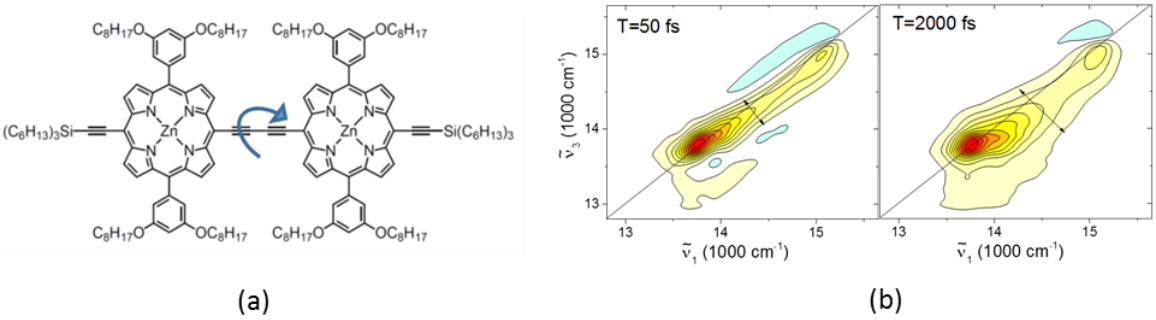

Figure 1. (a) Porphyrin dimer molecular structure. (b) 2D spectra at two population times.

[1] C.K. Yong *et al.*, Chem. Sci. **6,** 181 (2015).
[2] F.V.A. Camargo *et al.*, J. Phys. Chem. B **119,** 14660 (2015).
[3] F.V.A. Camargo *et al.*, Struc. Dyn. **3**, 023608 (2016)