

# Influence of H-aggregate formation on the photophysics of a push-pull phtalocyanine

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The relaxation dynamics of a push-pull Zn-phtalocyanine has been investigated by means of two-dimensional electronic spectroscopy and narrow-band transient absorption. The photophysics of monomer solution and H-aggregates have been compared on a time scale spanning from a few tens of femtoseconds up to 1.5 nanoseconds.

The molecule 9(19),16(17),23(24)-tri-*tert*-butyl-2-[ethynyl-(4-carboxymethyl)phenyl] zinc(II)-phtalocyanin (ZnPc) is a push-pull phtalocyanine able to inject electrons into the conduction band of TiO<sub>2</sub>, and function as photosensitizer for DSSC applications.<sup>1</sup> We have characterized its photophysics in solution, by analyzing the time evolution of its excited states in a time interval spanning from tens of femtoseconds up to 1.5 nanoseconds. The ultrafast relaxation processes have been analyzed by applying two-dimensional electronic spectroscopy (2DES), exciting the sample with a <20 fs time pulse, while the longer time interval has been probed by recording narrow-band transient absorption spectra. At increasing concentrations, the absorption spectrum of this Zn-Pc shows the progressive increasing intensity of a band at 625 nm and the concomitant decreasing intensity at 670 nm, which indicates the formation of H-aggregates. The comparison of time resolved data recorded for the monomer and aggregate solutions allows us to identify different relaxation pathways. By comparing the kinetics recorded upon S1 and S2 excitation it has been possible to estimate a very fast internal conversion dynamics in the monomer solution, occurring on a sub-picosecond time scale. The formation of H-aggregates complicates the relaxation dynamics, by introducing a further non radiative decay channel, and inducing an overall faster relaxation. The analysis of 2DES spectra allows to disentangle the mechanism of energy equilibration in the aggregate, evidencing the formation of exciton states.

[1] A. Iagatti *et al.*, J. Phys. Chem. C, **119**, 20256 (2015).