

Push-Pull dyes for Grätzel cells: a time resolved fluorescence study using upconversion in non-transparent systems

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Ultrafast charge dynamics occurring at the dye/mesoporous metal oxide interface in Dye-Sensitized Solar Cells (DSSCs) are still investigated, particularly in p-type cells. Understanding how the molecular structure impacts the dynamics will lead to the improvement of the overall efficiency by using kinetics-tailored dyes. Time-resolved optical spectroscopy techniques have been intensively used to investigate charge transfer, injection and recombination in these systems. Transient absorption spectroscopy, the major technique used to study DSSCs, is not well adapted to quasi opaque system.¹ As a consequence, very thin and, therefore, transparent samples are often used as model systems. In addition, in a complete cell, the sheer number of excited species and the multiplicity of relaxation paths lead to complex dynamics.

With this in mind, we have undertaken the study of these dynamics using time resolved fluorescence in order to: 1) limit the complexity of the signal obtained and 2) work in a reflection mode allowing complete cell studies. This approach also enables potentiostatic control of the system which has recently resulted in new insights in the charge dynamics of DSSCs.² In parallel, we have investigated photodynamics of push-pull dyes in solution from the fs to the ns timescale using two different detection techniques: fluorescence upconversion (FU) and time-correlated single photon counting (TCSPC). Depending on the dye and the solvent used, we found that the evolution from the excitation of the first $\pi\pi^*$ state towards an intramolecular charge transfer state (ICT) is not a straight-forward process and may involve several excited states.

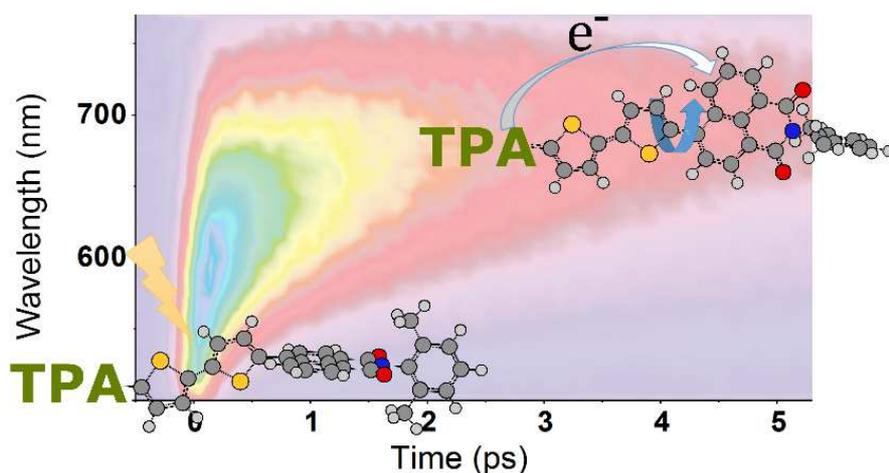


Figure 1. Time Resolved Fluorescence Spectra (TRFS) of dye TPA-2T-NI and associated relaxation of the excited state.

[1] Ghadiri, E.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M.; Moser, J.-E., *Sci. Rep.* **2016**, 6, 24465.

[2] Dillon, R. J.; Alibabaei, L.; Meyer, T. J.; Papanikolas, J. M., *ACS Appl. Mater. Interfaces*, **2017**, 9, 26786.