# Quantum dynamics around PPEs' conical intersections for both spectroscopic and real-time studies

**GALIANA Joachim**;[A] **LASORNE Benjamin**;[A]

*A)ICGM, Univ Montpellier, CNRS, ENSCM, France*

joachim.galiana@umontpellier.fr

In this presentation, we discuss the use of nonadiabatic quantum dynamics for the study of different poly(phenylene) ethynylenes (PPEs, fig. 1 left), building-blocks of light-harvesting dendrimers.

PPEs exhibit strongly nonadiabatically coupled electronic excited states. In this context, the Born-Oppenheimer approximation breaks down, which requires molecular dynamics to explicitely take into account the coupling between the electronic excited states. We propose linear and quadratic vibronic coupling diabatic model Hamiltonians for reproducing the PESs of the simplest PPEs. We use these diabatic potentials and inter-state couplings to run quantum dynamics calculations using the Multi-Configuration Time-Dependent Hartree (MCTDH) formalism for explicit wavepacket propagation.

The first building block of interest is the symmetrically *meta*-substituted phenylene (m22, fig. 1 left). The absorption spectra of m22 and its localized 2-ring fragment (p2, fig. 1 left) are similar.[1,2] However, their emission spectra are different, with m22 exhibiting an unusual Stokes shift of about 2000 cm$^{-1}$. In a recent work[3], we identified this red-shifted spectrum as a contribution resulting from the strong inter-state coupling between the first two electronic excited states (fig. 1 right), mostly due to acetylenic vibrations.

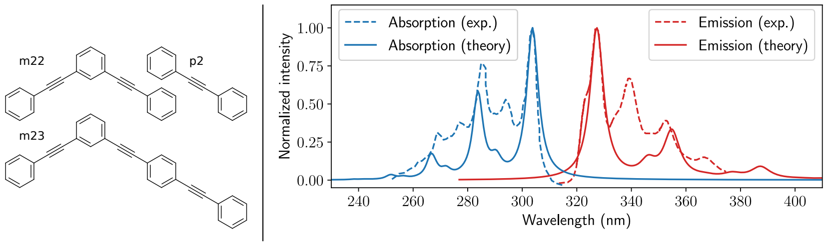

Figure 1. Left: poly(phenylene)ethynylenes studied in this work. Right: Absorption and emission spectra of m22 (normalized intensity), experimental measurement[1] and theoretical simulation[3]

The second building block of interest is an asymmetrically *meta*-substituted PPE (m23, fig. 1 left) for which excitation-energy transfer (EET) occurs thanks to different branch lengths hence a significant energy gradient. Using analogous Hamiltonian models and wavepacket propagation, we are able to reproduce the expected ultrafast (< 25 fs) EET from an excitation on the shortest branch toward the second branch.[4] We further characterize the EET phenomenon *via* electronic-vibrational relations, vibrational energy analysis and evaluation of the electronic coherence.

**Keywords**: quantum dynamics, nonadiabatic coupling, vibronic coupling, uv-visible spectroscopy, excitation-energy transfer

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[4] J. Galiana and B. Lasorne, "Excitation-Energy Transfer and Vibronic Relaxation through Light-Harvesting Dendrimer Building Blocks: a Nonadiabatic Perspective", *J. Chem. Phys.* 160, 104104 (2024)