Designing universal coarse-grained tight-binding models for simulating light-harvesting processes in π-conjugated macromolecules
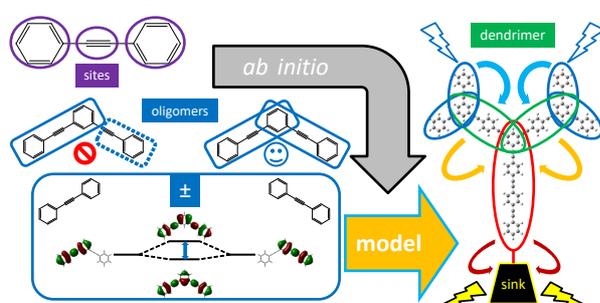
UMR – Équipe : ICGM (UMR 5253) — Département de Chimie Physique Théorique et Modélisation
Directeur de la thèse : Benjamin LASORNE
Début de la thèse : 1er octobre 2026
Financement : Contrat doctoral établissement
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Poly(phenylene ethynylene) dendrimers are outstandingly efficient macromolecular light-harvesting antennae for ultrafast excitation-energy conversion and transport. However, a comprehensive strategy for modelling their optoelectronic properties is still lacking to go beyond fundamental research and harness their full promises within real-life technological applications.

Constructing relevant *ab initio* vibronic Hamiltonian models for subsequent quantum-dynamics simulations within a brute-force approach typically takes years and must be redone for each new system of interest. The objective of the project is to design an alternative approach, based upon implementing a divide-and-conquer, multiscale-multimethod strategy that will take evident benefit from the clear hierarchy of interactions governing structure-property relations on their various scales and magnitudes. Highly-dimensional vibronic Hamiltonians will be generated through a global energy/coupling decomposition scheme inspired by fragment-orbital theory and coarse-grained tight-binding models. They will be expressed in terms of local site energies and pairwise interactions tuned by local vibrations and parametrised from high-level *ab initio* quantum chemistry. Repeated electronic and vibrational subunits will be coupled according to a connectivity graph reflecting the hierarchy of short- and long-range interactions.

We shall also investigate to some extent the modulation of light-induced properties by aromatic-carbon-to-nitrogen-or-boron substitutions and with functionalisation by electron withdrawing or donating chemical groups at various places of the covalent organic macromolecule.

Quantitative *ab initio* quantum-chemistry calculations will be run first with TD-DFT and then be systematically re-mapped to qualitative effective Hamiltonian approaches for designing a relevant coarse-grained tight-binding semiempirical-inspired description able to reconstruct effective multiconfigurational wavefunctions and Hamiltonian matrix elements for the manifold of coupled electronic states. Once such transferable Hamiltonian models are designed, high-dimensional ML-MCTDH wavepacket quantum-dynamics simulations will finally be run and post-processed to generate observables that will be directly compared with measurements from relevant types of time-resolved electronic and vibrational spectroscopies for safeguarding validation of the whole strategy and making our dialog easier with experimentalists.

About the candidate: some background and interest in theoretical physical chemistry will be appreciated, especially regarding molecular spectroscopy and quantum mechanics for chemistry. Previous experience in scripting and/or coding (Bash, Fortran, Python…) will be an asset.

E. K.-L. Ho, T. Etienne, and **B. Lasorne**, J. Chem. Phys. 146 (2017) 164303 [10.1063/1.4981802]; E. K.-L. Ho and **B. Lasorne**, Comput. Theor. Chem. 1156 (2019) 25 [10.1016/j.comptc.2019.03.013]
J. Galiana and **B. Lasorne**,. Chem. Phys. 160 (2024) 104104 [10.1063/5.0193264]; J. Galiana, M. Desouter-Lecomte, and **B. Lasorne**, J. Chem. Phys. 162 (2025) 244102 [10.1063/5.0270440]