1) PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title: Theoretical Spectroscopy for Organic Photovoltaics: Finding the Fingerprints of Photodegradation

1.1. Project goals

The project aims to use **theoretical spectroscopy** to address the **stability of organic photovoltaics** (OPVs). OPVs are solar cells where the active layer is composed of a blend between a photoactive organic material responsible for light absorption (typically an organic polymer) and an organic electron acceptor responsible for charge separation (historically a fullerene derivative). In the last decade, through the development of new small molecule electron acceptors, OPVs have reached power conversion efficiencies (PCEs) of the same level as commercially available solar technologies. One of the best performing materials combinations is currently the PM6:Y6 blend which was used to build devices with up to 17.5% PCE [1], an *unprecedented performance* for organic solar cells. Thus, the biggest drawback of OPVs remains device stability, typically due to photochemical reactions with oxygen or water molecules which get trapped during fabrication, or diffuse through imperfect plastic encapsulation. In this project, we aim to determine the **spectroscopic fingerprints** of **photon-induced oxygen degradation** for a series of **electron donor co-polymers**. We will consider monomers built by combining molecular building blocks (see figure) with donor – D and acceptor – A character into a D-A monomer unit. **X-ray absorption** (XAS), **X-ray photoelectron** (XPS), and **resonance Raman (RR) spectroscopy** will be calculated for pristine oligomers, as well as possible photodegradation products with oxygen chemically attached at different molecular sites. As XAS, XPS, and RR can be used to determine precise chemical modifications, they will allow us to find the fingerprints of different degradation products for further experimental identification. An example of this approach is our work on the photodegradation of the fullerene derivative $PC_{60}BM$ [2].

1.2. Outline

Starting from D, A building blocks (see figure), we will construct possible D-A monomers. We will use density functional theory (**DFT**) and time-dependent DFT (**TDDFT**) to calculate the XAS, XPS and RR spectra of oligomers with selected D-A units. Here, RR scattering cross-sections will be implemented in **VeloxChem** [3] and will require the implementation of **complex polarizability gradients** [4, 5]. To determine RR spectra, we will also need to compute ultraviolet-visible (UV/vis) absorption spectra. RR is of particular interest for D-A copolymers because it can detect the (de)localization of excitons [5] – crucial for OPV functioning. In a second step, we will build possible photooxidation products and calculate the same spectra. By comparison to pristine oligomers, we will be able to determine the spectral features by which each photooxidation product can be identified.

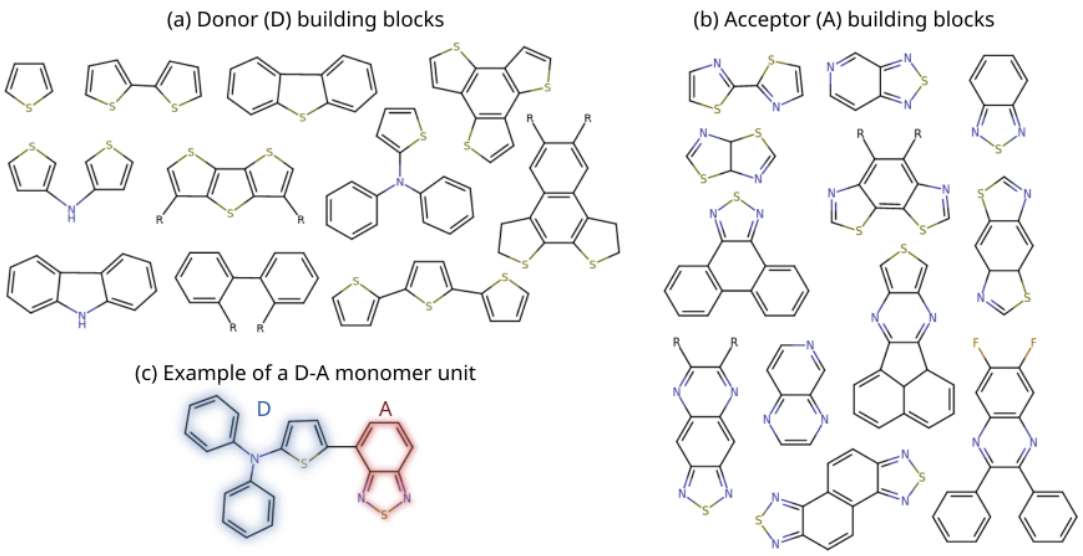

Fig 1. a) Donors, b) acceptors and c) a D-A monomer.

1.3. Work plan

The project is divided into four work packages, each planned for one year. The tasks and expected manuscripts (M) are listed below.

Year 1.

- construct possible D-A monomers and oligomers using PySoftK [6].
- Determine the oligomer size for which the HOMO-LUMO gap stabilizes.
- Calculate UV/vis absorption spectra and analyze the nature of the excited states [7].

Year 2.

- Calculate XAS and XPS spectra and compare them to experimental spectra of pristine films →**M1**, **M2**.
- Implement complex polarizability gradients in VeloxChem.
- Use the complex polarizability gradient to obtain the RR response.

Year 3.

- Calculate RR spectra and benchmark the performance of the new implementation →**M3**.
- Generate possible photooxidation products for each D-A monomer.
- Calculate UV/vis spectra of photodegraded oligomers and analyze the nature of the excited states →**M4**.
- Calculate XAS and XPS spectra of photodegraded oligomers to identify their unique spectral features →**M5**.

Year 4.

- Calculate RR spectra of pristine and photodegraded oligomers →**M6.**
- For selected D-A oligomers, compare the calculated data to measurements of photodegraded films →**M7**.

1.4. **Literature** *(max. 10 listed, as a suggestion for a PhD candidate)*

[1] D. H. Kim, F. T. A. Wibowo, D. Lee, N. V. Krishna, S. Park, S. Cho, S.-Y. Jang, Non-Fullerene-Based Inverted Organic Photovoltaic Device with Long-Term Stability, *Energy Environ. Mater.* **0** (2022), 1–8.

[2] **I. E. Brumboiu**, L. K. E. Ericsson, V. Blaznic, R. Hansson, A. Opitz, B. Brena, E. Moons, Photooxidation of $PC_{60}BM$: New Insights from Spectroscopy, *Phys. Chem. Chem. Phys.* **24** (2022), 25753–25766.

[3] Z. Rinkevicius, X. Li, O. Vahtras, K. Ahmadzadeh, M. Brand, M. Ringholm, N. Holmgaard List, M. Scheurer, M. Scott, A. Dreuw, P. Norman, Veloxchem: a Python-Driven Density-Functional Theory Program for Spectroscopy Simulations in High-Performance Computing Environments, *WIREs Comput. Mol. Sci.* **10** (2020), e1457.

[4] W. A. Al-Saidi, S. A. Asher, P. Norman, Resonance Raman Spectra of TNT and RDX Using Vibronic Theory, Excited-State Gradient, and Complex Polarizability Approximations, *J. Phys. Chem. A* **116** (2012), 7862–7872.

[5] W. A. Saidi, P. Norman, Probing single-walled carbon nanotube defect chemistry using resonance Raman spectroscopy, *Carbon* **67** (2014), 17–26.

[6] A. Santana-Bonilla, R. Lopez-Rios De Castro, P. Sun, R. Ziolek, C. Lorenz, Modular Software for Generating and Modelling Diverse Polymer Databases. *ChemRxiv.* Cambridge: Cambridge Open Engage; 2023.

[7] T. B. Masood, S. Thygesen, M. Linares, A. I. Abrikosov, V. Natarajan, I. Hotz, Visual Analysis of Electronic Densities and Transitions in Molecules, *Comput. Graph. Forum* **40** (2021), 287–298.

[8] T. Fransson, **I. E. Brumboiu**, M. L. Vidal, P. Norman, S. Coriani, A. Dreuw, XABOOM: An X-Ray Absorption Benchmark of Organic Molecules Based on Carbon, Nitrogen, and Oxygen 1s⟶ π* Transitions, *J. Chem. Theory Comput.* **17** (2021), 1618–1637.

[9] T. Fransson, M. Delcey, **I. E. Brumboiu**, M. Hodecker, X. Li, Z. Rinkevicius, A. Dreuw, Y. Min Rhee, P. Norman, eChem: A notebook exploration of quantum chemistry, *J. Chem. Eudc.* **100** (2023), 1664–1671.

1.5. Required initial knowledge and skills of the PhD candidate

The PhD candidate should have a **Master degree** (or equivalent) in **Physics**, **Chemistry**, or a related field. Proficiency in **English** and **programming** knowledge in Python, C++, or related programming languages are also required.

1.6. Expected development of the PhD candidate's knowledge and skills

The PhD candidate will specialize in electronic structure calculation of free-standing organic molecules. Additionally, he/she will focus on the computation of UV/vis absorption, XAS, XPS and resonance Raman spectroscopy using DFT and TDDFT. The PhD candidate will also be involved in method development using Python to enable the computation of resonance Raman in VeloxChem. Besides these practical aspects of performing calculations and method development, the PhD candidate will be involved in the analysis and visualization of calculated results and their effective scientific

communication. These skills will be acquired and improved by collaborating on and preparing manuscripts for publication in scientific journals, as well as presenting oral and poster presentations at scientific conferences, internal meetings and seminars. Thus, at the end of the PhD studies, we expect the graduate to:

- be able to independently **perform** electronic structure and theoretical spectroscopy **calculations**, choosing the appropriate method for a given system and problem;
- **understand** the **equations** involved in the calculation of different spectroscopies;
- **understand** the **code** used to compute different spectroscopic properties;
- be able to independently **carry out scientific code implementation** – from deriving the necessary equations, to writing the code, testing, and debugging it;
- be able to **analyze** and effectively **visualize** different types of **data** (molecular structures, excited state properties, spectra);
- be able to **present scientific results** in various formats and context, from scientific manuscripts, posters, and oral presentations, to popular science presentation for a broader audience;
- be able to **design a small-scale independent research project** by asking new research questions starting from previous results, form hypotheses, find suitable approaches to test these hypothese, and organize the project into manageable research tasks.