1) Motivation:

I propose a system as a model/benchmark for the study based on donor-acceptor molecular aggregates for organic solar cells. This system is composed of a carbazole derivative as donor interacting through its alkyl chains with a Perylene diimide (PDI) derivative acting as the acceptor of electrons (see figure 1a).

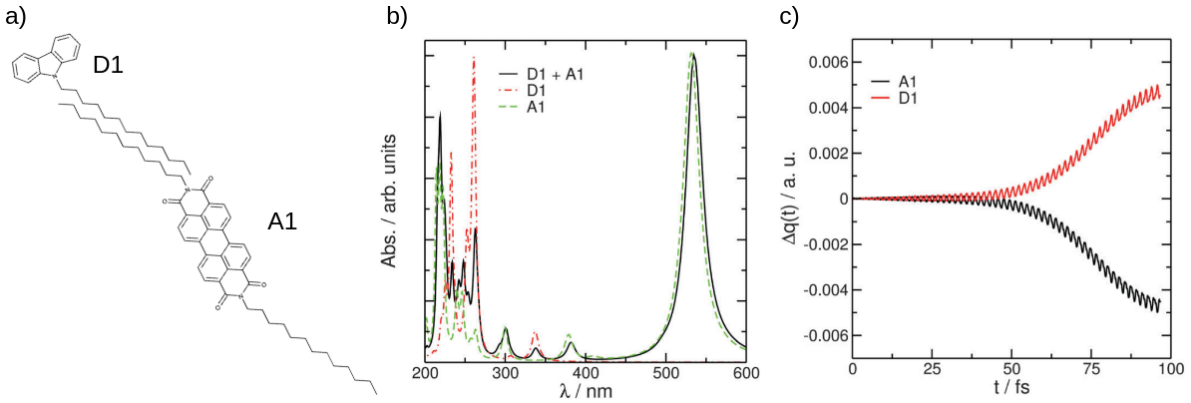


Figure 1. a) Schematic representation of the Donor-acceptor aggregate composed by carbazole derivative (D1) as donor and PDI derivative (A1) as acceptor. **b)** Simulated absorption spectra of the aggregate and its separate parts. **c)** Charge transfer dynamics after photoexcitation of the PDI molecule. All the simulations presented are within the real-time electron dynamic TD-DFTB method

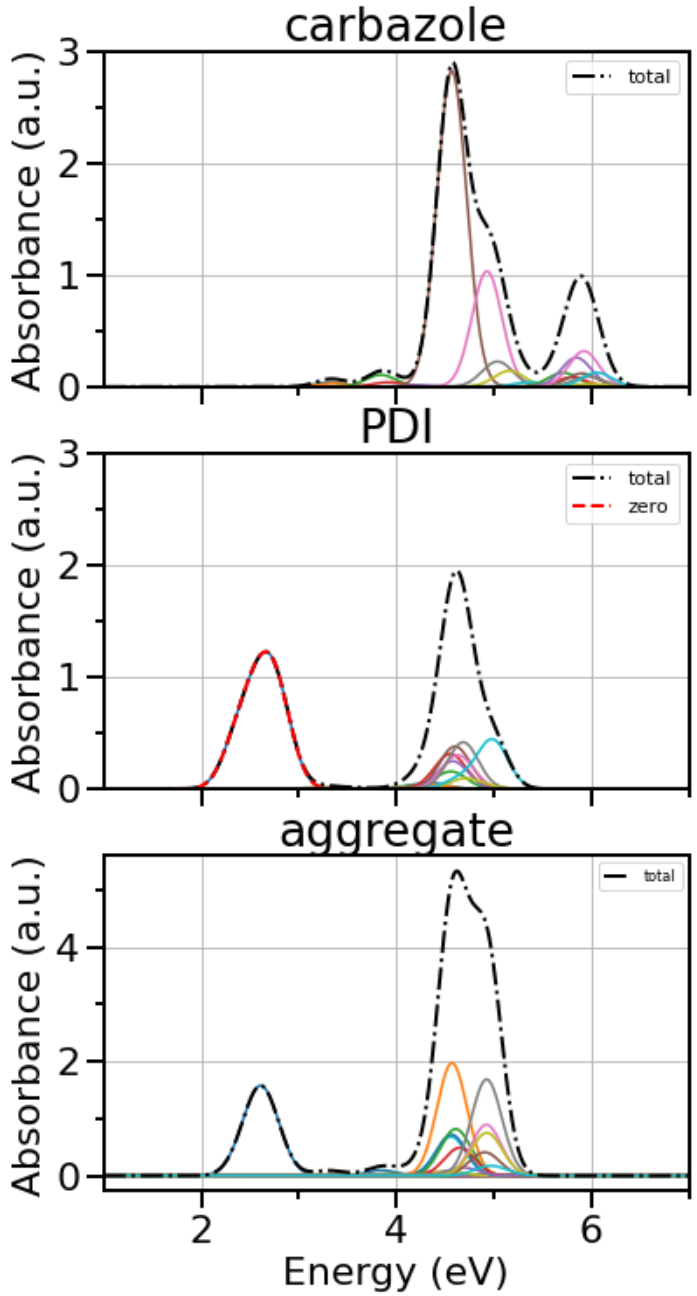
Taking into account these previous results from the adiabatic pure electron dynamic TD-DFTB, I propose to go further in the charge transfer analysis now, performing non-adiabatic molecular dynamics using the Newton-X or NEXMD packages. The starting point will be to compare the adiabatic and non-adiabatic charge transfer processes following the charges dynamics, and then analyse the electron-phonon couplings with the relevant vibrational modes.

2) Geometry optimization with NEXMD using AM1

I performed geometry optimizations for the system D1 (carbazole), A1 (PDI) and the A1+D1 (aggregate) using the AM1 level of theory within the NEXMD package. In all cases I started from previous geometries obtained by dftb+. In the NEXMD otimizations a maxcycle number of 200 and a tolerance of 1.0d-2 was used.

3) Absorption spectra of the systems:

After each geometry optimization I performed ground state trajectories for the 3 systems. I simulated 1 ps at 300 K for the carbazole and PDI derivatives. In the case of the aggregate I simulated 8 ps at 300 K.
Then, I selected 10 trajectories from the ground state trajectories in order to perform singlepoints calculations. I prepared the inputs using the get_excited.py tool.
From this single points calculations, I was able to obtain the absorption spectrum of each system of interest that is shown in the next figure :



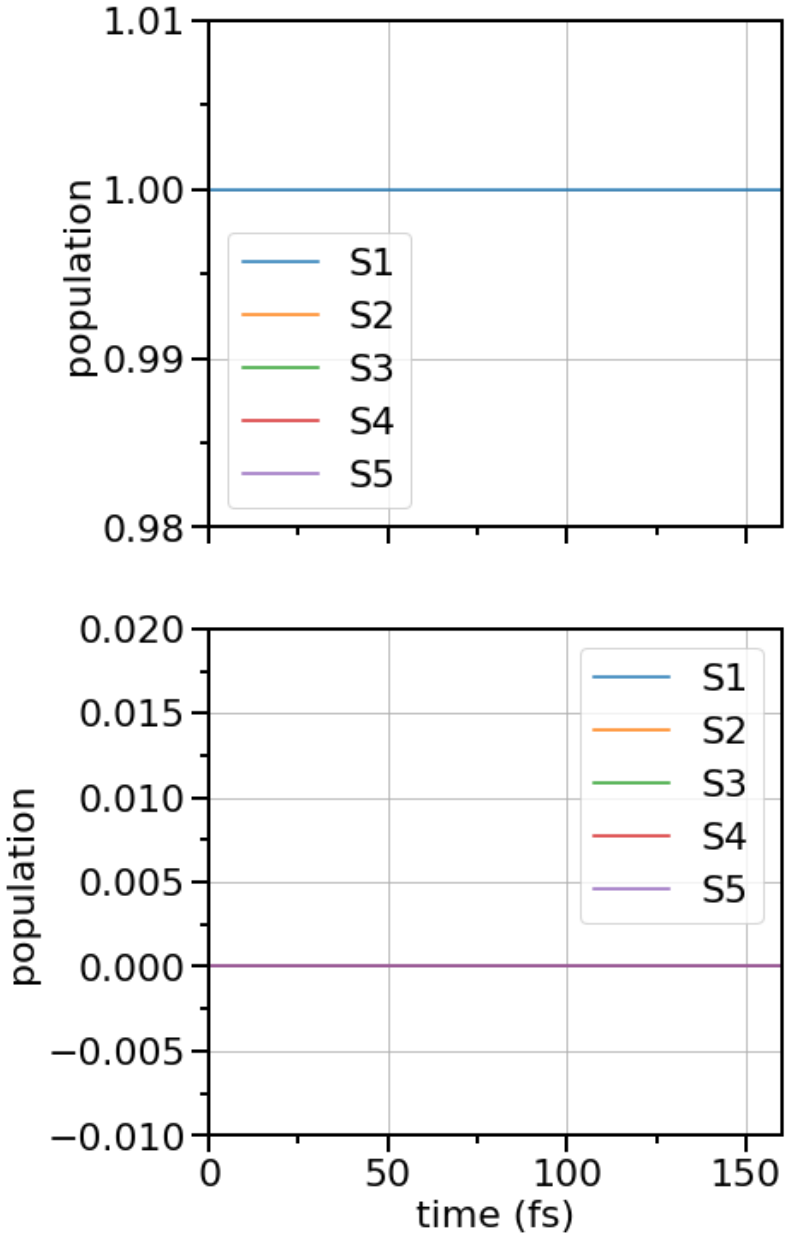
The results look quite similar to the experimental ones and also to the simulated ones obtained from td-dftb+ in my previous works. Also, It seems like the spectrum of the aggregate is the sum of the separate parts.

4) NEXMD dynamics

In order to study the charge transfer process between the two molecules I performed a nexmd for 10 trajectories using 5 excited states and exciting at the lowest energy excitation of the spectrum. The idea was to follow throughout the time the charge transfer process running a population analysis after the trajectories are finished. However, I realised that the system was too big to performed the entire trajectories requested.

5) Populations analysis

Using the get_excited tool, I performed a populations analysis within the simulated nexmd trajectories. The results are shown in the next figure:



The population of the S1 is always 1 within the time window simulated and there is no charge transfer process observed. This could be due to the lack of a big number of trajectories simulated and also probably because the time window is short.