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## COMMUNICATION

# Graphene-based acceptor molecules for organic photovoltaic cells: a predictive study identifying high modularity and morphological stability

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## Contents

# I        Theoretical investigation

## I.1       *ab-initio - Computational methods*

All DFT and *ab initio* calculations were performed using Gaussian 09.[S1] Due to the size of the systems envisaged, DFT methods were preferred in particular using the functional ωB97XD, which is based on the ωB97 functional but includes an empirical dispersion term to treat long-distance interactions.[S2] This functional, validated in previous studies,[S3] was found to be equally well adapted to the treatment of HBC molecules, as indicated by results given here. In this study, the geometrical properties of an isolated HBC molecule (in both circular and triangular configurations) were calculated at different levels of theory, namely DFT (B3LYP[S4] and ωB97XD[S2,S5] functionals), through to reference *ab initio* methods (MP2). For the DFT and *ab initio* methods, we tested three different basis sets of increasing quality: 6-31G, 6-31G* and 6-31+G*.[S6] The functional ωB97XD, chosen *in fine*, was found to be little dependent on the basis set employed. However, as the objective was to study the characteristics of the whole donor:acceptor system, not only a compromise between precision and calculation time but also consistency with previous calculations for an optimised donor had to be taken into account, so we decided to use ωB97XD/6-31G*. The results were compared with those available for the HBC component given by Goddard *et al* (Figure S1).[S7]
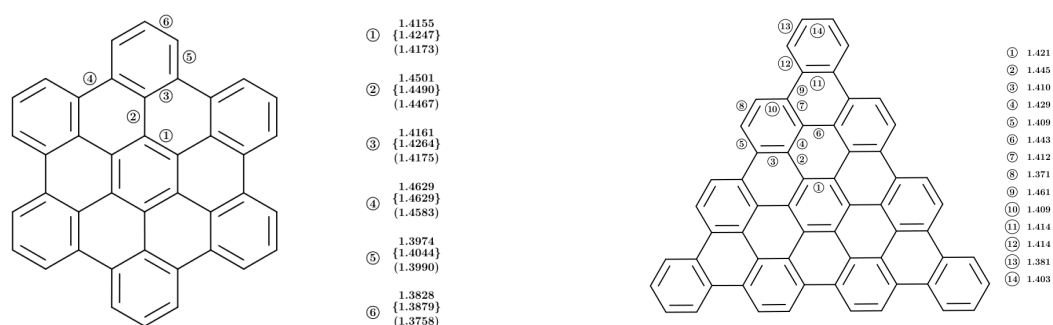


**Figure S1.** Comparison of the ωB97XD/6-31G* structural parameters of circular HBC and triangular forms of PAH. The values in braces refer to the use of B3LYP/6-311G calculations.[S8] The values in the parentheses refer to the Goddard's experimental work.[S7]

## I.2       *Molecular Dynamics*

**Parameters:** The topology and parameter file in CHARMM format for chlorobenzene and P3OPT—HBC(R=COOH)—P3OPT haven been generated by Antechamber; ESP charges from B3LYP/6-31+G* calculations were used. The full parameter and topology file can be obtained from sebastian.metz@stfc.ac.uk.

For MD simulations, we made use of the AMBER force field[S9] and Antechamber[S10] to generate the topology and parameter files for the acceptor molecule and the solvent (chlorobenzene) in CHARMM format.[S11] Starting from the crystal structure of chlorobenzene,[S12] we generated periodic cubic box with the side length of 28.010 Å containing 128 chlorobenzene molecules, equilibrated at room temperature 310 K and used it together with VMD[S13] to set up the complete MD system and ran it using NAMD.[S14] For the non-bonded parameter of the force field , we used a cut off value of 12 Å and a switch distance of 10 Å, the electrostatics interactions  are calculated with a PME (Particle Mesh Ewald) with a grid spacing of 1 Å. The simulations were performed using Langevin dynamics for the temperature control.

| stage | Simulation type | Number of time steps | Active part |
|-------|-----------------|----------------------|-------------|
| 1 | minimization | 10.000 | solvent |
| 2 | NVT | 200.000 | solvent |
| 3 | NPT | 100.000 | solvent |
| 4 | Minimization | 10.000 | whole system |
| 5 | NPT | 200.000 | solvent + side chains |
| 6 | Minimization | 10.000 | whole system |
| 7 | NPT | 500.000 | whole system |
| 8 | Minimization | 10.000 | whole system |
| 9 (production run) | NPT | 2.500.000 | whole system |

**Table S1:** Details on equilibration of the MD system (stage 1-8) and production run. The side chains include all R attached to the HBC core, the time step was 1 fs.
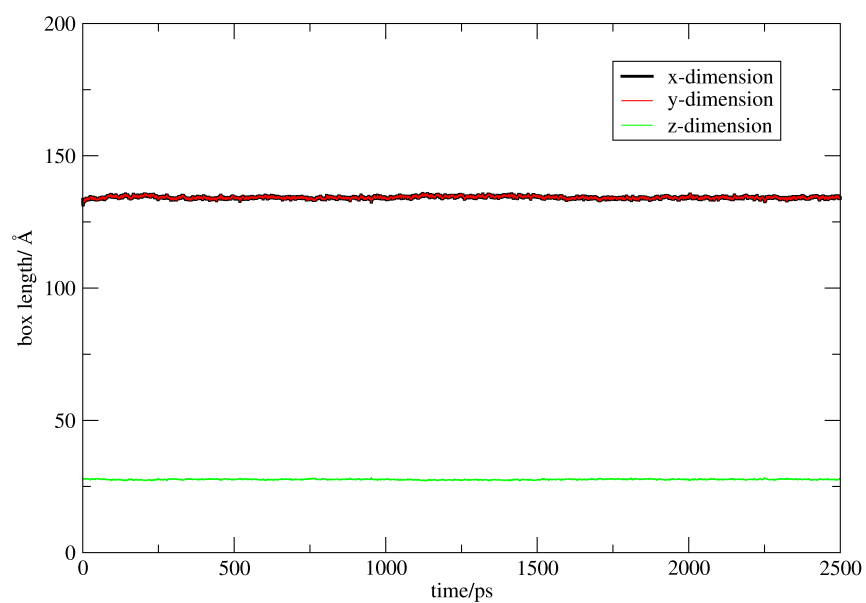


**Figure S2**: Plot of the box length for the x=y and z dimension of the production run. Despite a very short increase in the very first steps of the simulation, the individual dimensions (and therefore the volume) stayed constant throughout the simulation (2.5 ns).
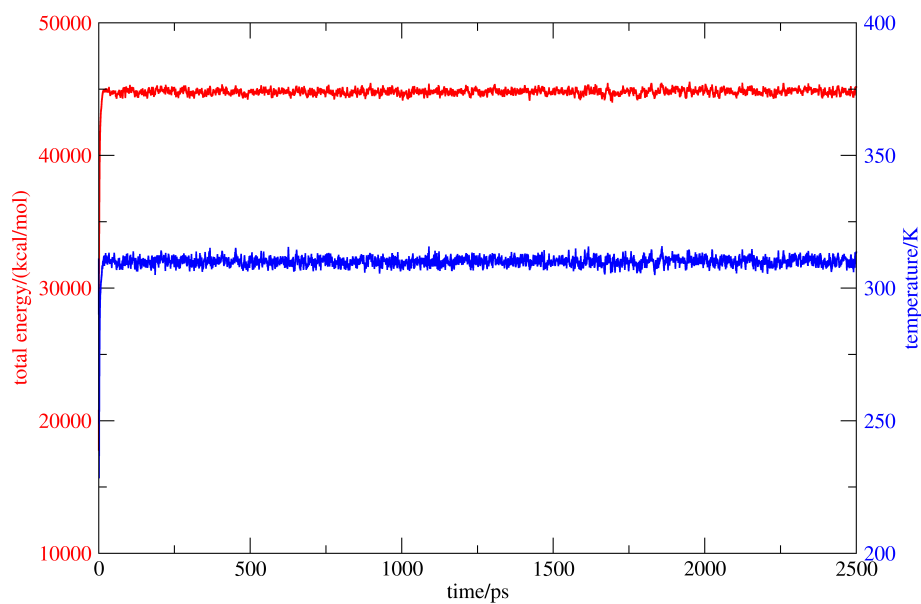
**Figure S3**: Plot of the total energy of the simulation box (red) and the temperature (blue) throughout the production run. Despite a very short increase in the very first steps of the simulation (due to starting from velocities of zero), both properties stayed constant throughout the simulation (2.5 ns).
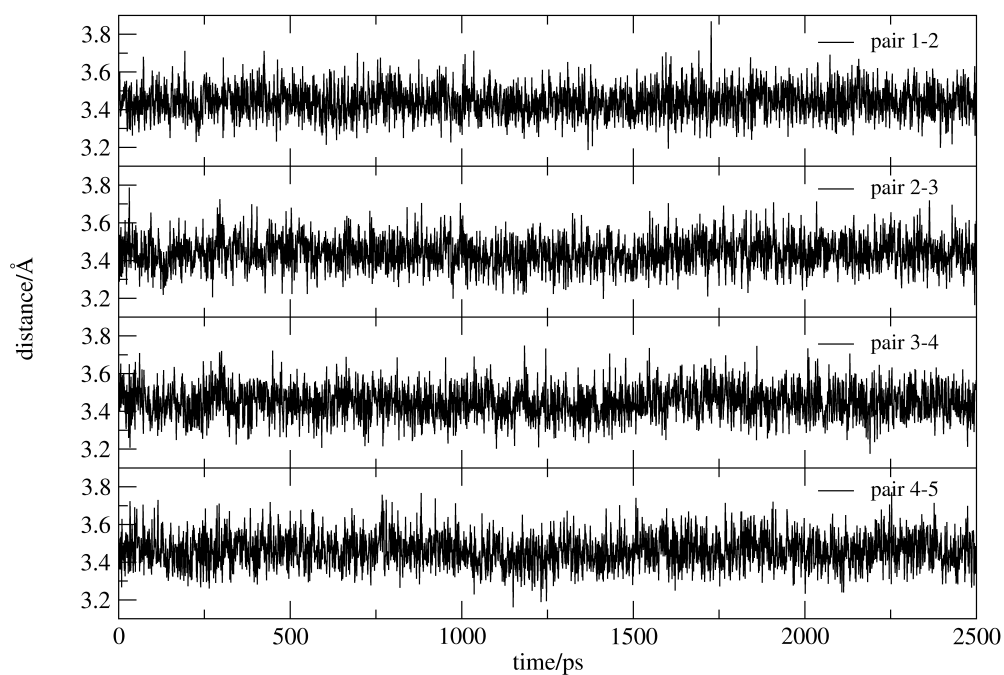


**Figure S4**. Distance plot for four pairs of neighbouring central HBC cores (averaged over the six atoms). Throughout the simulation time of the production run (2.5 ns), the distance stays about constant and no structural change occur.

## II    References

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