Comparison of P3HT Energy Levels from ORCA to DFT

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1 Systems Studied

We have randomly selected several pairs of chromophores from the ordered P3HT morphology (T1.5) to explore using both ORCA's ZINDO/S calculations, and Chris' more rigorous DFT methods. The systems studied contained 50 atoms (2 monomers) from the following pairs of chromophores:

- 0469-3714
- 0841-1237
- 2032-2900

2 Energy Levels

Level	DFT eV	ZINDO/S eV
0469-3714		
HOMO - 1	-6.508	-8.271
HOMO	-6.312	-8.176
LUMO	-0.695	0.085
LUMO + 1	-0.457	0.230
Bandgap	5.617	8.091
HOMO Split	0.196	0.095
0841-1237		
HOMO - 1	-6.600	-8.266
HOMO	-6.401	-8.208
LUMO	-0.714	0.147
LUMO + 1	-0.502	0.222
Bandgap	5.687	8.061
HOMO Split	0.199	0.058
2032-2900		
HOMO - 1	-6.578	-8.343
HOMO	-6.492	-8.335
LUMO	-0.727	0.004
LUMO + 1	-0.523	0.169
Bandgap	5.765	8.331
HOMO Split	0.086	0.008

Table 1: A comparison of the frontier molecular orbital energy levels, predicted bandgap, and dimer HOMO splitting from ZINDO/S and DFT for each examined chromophore pair.

- The results don't look super promising.
- ZINDO consistently reports deeper HOMOs (by an average of 28% corresponding to around 2 eV) and shallower LUMOs (by 11%, around 0.7 eV) for each chromophore dimer pair.
- Since we scale the HOMO levels anyway and don't even touch the unoccupied orbitals for donor chromophores, this might not be a big problem - a more important comparison is the HOMO splitting value.
- **The ZINDO/S calculations consistently underpredict the HOMO splitting**, suggesting less significant orbital overlap and therefore slower charge transport. This is a bit of an issue, as we're already on the high-side of the experimental mobilities in our mobility calculations, so we can't really afford for it to be significantly faster.
- In the best case, ZINDO/S predicts the HOMO splitting correct to a factor of about 2, but in the worst case, it's an order of magnitude too low.
- The absolute deviation between the two calculations also varies by a factor of about 2, from 78 meV to 141 meV. These numbers correspond to the approximate binding energy of an exciton so, although we don't consider it, in a real device this could make the difference between an exciton being allowed to form and not.