The University Of Sheffield.

Mini-project report

Modelling the Interactions Between Polymer Solar Cell Materials

Tim Balhatchet – dtp10tbb@shef.ac.uk

25/05/2011

Research Councils UK Energy For a Low Carbon Future

Modelling the interactions between polymer solar cell materials

25/05/2011

By: Tim Balhatchet

Project supervised by: Dr Alan Dunbar

Table of Contents

1. Project Outline

The main purpose of this project was to work with a piece of software called Avogadro *(1)* that is freely available on the web, with the aim of using it to model polymers that are either currently being used for or are being investigated for use in organic photo-voltaic solar cells (OPVs). Avogadro allows the user to draw molecules in an infinite 3-dimensional space and then perform various calculations on those molecules through the use of different extensions.

2. Organic Photo-Voltaic Cells

Traditional silicon solar cells have been in use and development for a while but suffer from some significant problems, chief among them being the high cost involved in their manufacture, both in terms of energy and materials. Organic solar cells offer a cheaper alternative but are still a relatively new technology, having some problems with a shorter working lifespan and lower power conversion efficiencies (PCE). This aside, they are still an avenue of renewable energy technology that shows a lot of promise and there is ongoing research into how to address issues such as these.

The most common organic solar cells currently in use are made up of two polymer materials that perform different chemical functions: usually playing the role of electron donor and electron acceptor respectively. These are called bulk heterojunction cells, and there are a number of properties about them that are important to consider when evaluating their electricity generation capacity. These cells convert solar energy to electricity by a four step process:

1) Incident photons are absorbed by the electron donor material.
2) This absorption causes electrons to be excited to a higher energy level in the molecule, thus becoming excitons. Each exciton is paired with a hole, that is, the space within the lower electron orbital that it has vacated.
3) The exciton is separated from its paired hole by passing into the electron acceptor material.
4) The exciton and hole are conducted in opposite directions to the anode and cathode materials in the solar cell respectively, generating an electrical current.

For each step there are chemical and physical characteristics of the polymer constituents that affect the overall cell performance in that area. In simple terms, these are:

1) The macro-molecular surface properties of the cell and the phase separation of the polymeric materials, i.e.: the interface between the two.
2) The molecular orbital structure of the electron donor.
3) The vibrational and absorption spectra for the polymers.

Of bulk-heterojunction cells, the most common combination used currently is a blend of P3HT *(poly-3-hexylthiophene)* and PCBM *([6,6] phenyl-C_{61}-butyric acid methyl ester)*. P3HT is the electron donor in this mix, and was decided as the starting point for this investigation, to attempt accurately modelling the characteristics listed above, and comparing results to experimentally measured values.

3. Use of Avogadro

As mentioned before, Avogadro allows the user to draw the molecules they wish to investigate. It is a well presented and intuitive package in this respect and it is a simple matter to draw fairly complex

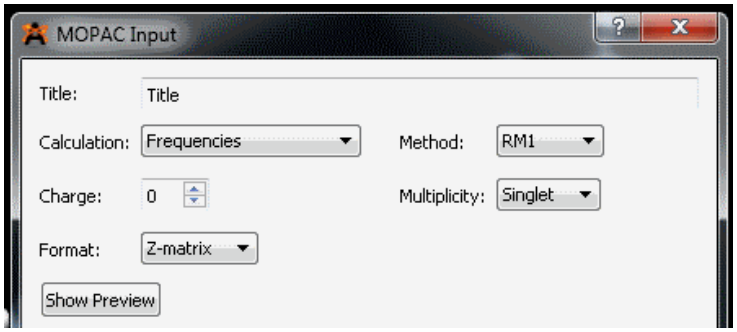
chemical structures. It also has an 'Optimize Geometry' button that will provisionally alter the bond lengths and angles to reflect reality, thus tidying up the molecule for further modelling.

The extensions themselves are in fact different pieces of software: modelling packages that use theoretical quantum mechanics to run simulations. Avogadro doesn't do the calculations internally; instead it writes output files in the appropriate language that they can be interpreted by the extensions. This requires the acquisition of at least one of the extensions, which for the most part are not free; in fact they are almost all very dear, ranging in cost from £2000 to £32000. However, academic licenses could be obtained for two of them free of charge: GAMESS (The General Atomic and Molecular Electronic Structure System) *(2,3,4)* and MOPAC (Molecular Orbital PACkage) *(5)*, developed by Iowa State University and the National Institute of General Medical Sciences respectively. Of these however, GAMESS encountered syntax errors when opening the files generated by Avogadro, a solution to which could not be found (it seemed Avogadro had some version incompatibility with the most recent GAMESS build).

3.1 MOPAC

According to MOPACs online description, it calculates molecular orbitals and vibrational spectra of molecules it simulates. The manual is a complex document and exact details on how to do this were not worked out within the project time. Basic functionality involves dragging and dropping the output file from Avogadro (a .mop file) and letting it run. At the end of the run, a few files will be generated (.arc, .aux and .out to name the most common).

A large number of simulations were run, starting with polymer chains of P3HT and of varying lengths, while changing the parameters in the Avogadro extension output interface. MOPAC would not run a lot of these, generating an error message to do with the input file in some cases. In some it would run without issue, generating a .out file that could be opened with notepad to see the results.



Field	Options
Calculation	Frequencies, Single point energy, Geometry optimisation.
Method	AM1, MNDO, MNDO-d, PM3, PM6, RM1
Multiplicity	Singlet, doublet, triplet, quartet, quintet
Charge	-99 to 99
Format	Z-matrix, Cartesian

The output files were also difficult to interpret. They could be opened with Avogadro but it was not clear what difference had been made. For 'Geometry Optimization' output files, values for HOMO and LUMO energies were given in eV about halfway down the results. This was taken to be a result of the simulation and compared to experimental results to determine their accuracy.

3.2 Simulation Results

In general, the results would differ from the expected values by between 7 and 4 eV. To determine the consistency of these results, further simulations were run on different polymer molecules. Some results are tabulated below, with other useful results found in Appendix 1.

Test (multiples refer to chain length)	HOMO (eV)	LUMO (eV)	Difference (Band gap) (eV)	Actual band gap for comparison (eV)	Error in modelled value (eV)
P3HT – PM6	-8.766	-0.340	8.426	1.9	6.526
P3HT x4 – PM6	-8.280	-1.291	6.989	1.9	5.089
F8 (triplet) – PM6	-8.141	-0.653	7.488	2.0	5.488
F8 x4 (singlet) – PM6	-8.066	-0.843	7.223	2.0	5.223
F8BT x2 – PM6	-8.587	-0.712	7.875	2.0	5.875
PCDTBT x2 – PM6	-8.242	-1.789	-6.453	1.88	4.573

Note: PM6 was the preferred calculation method based on the level of research behind it (6).

4. Results Discussion

The modelling of the HOMO-LUMO gap in this way is a positive result: though the error is large, the numbers are in a similar order of magnitude and show a relatively tight trend. If the reason/s for the error could be discerned and corrected or accounted for, then it shows that Avogadro could be used to begin predicting the behaviour of many polymer molecules, even new ones.

From the results, the error seems to decrease with molecule size, which predictably increases the computing time. The computing time was in fact a significant constraint, with MOPAC having a calculation time limit of 2 days, one that was easily used up with some of the larger atoms (e.g.: a P3HT chain of 16 units). Another factor that decreased the error was to increase the multiplicity, though it was only possible to do this for a triplet after adding C.I.=2 to the start-up line, a factor that again increased computing time significantly, to the point where only the shortest chain of F8 could be successfully modelled.

5. Conclusions and Further Work

These results do suggest that Avogadro and MOPAC together are useful for photo-voltaic applications, but the main constraints to developing this knowledge further have been the previously mentioned time issue, and the fact that some of the functionality is very difficult to learn. Further work would involve gaining a deeper understanding of the quantum theory behind the inner workings of MOPAC, the programming language that is used to get it to do exactly what you want and how Avogadro can be used to better display the results from the output files, which apparently it can. An engineer of appropriate background would likely be better suited to this. The time constraint could be overcome by purchasing a more complete license of MOPAC or one of the other extensions.

References and Bibliography

1. Avogadro: an open-source molecular builder and visualization tool. Version 1.01. http://avogadro.openmolecules.net/ (2010). [accessed 20/05/2011]
2. GAMESS homepage, http://www.msg.ameslab.gov/gamess/gamess.html (2007) [accessed 20/05/2011]
3. "General Atomic and Molecular Electronic Structure System" M.W.Schmidt, K.K.Baldridge, J.A.Boatz, S.T.Elbert, M.S.Gordon, J.H.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.Su, T.L.Windus, M.Dupuis, J.A.Montgomery J. Comput. Chem., 14, 1347-1363(1993).
4. "Advances in electronic structure theory: GAMESS a decade later" M.S.Gordon, M.W.Schmidt pp. 1167-1189, in "Theory and Applications of Computational Chemistry: the first forty years" C.E.Dykstra, G.Frenking, K.S.Kim, G.E.Scuseria (editors), Elsevier, Amsterdam, 2005.
5. MOPAC2009, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, http://OpenMOPAC.net (2008). [accessed 20/05/2011]
6. J.J.P. Stewart, (2007). "Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements." Springer-Verlag
7. S. Dag, L.W. Wang, (2010). "Packing structure of Poly(3-hexylthiophene) Crystal: Ab Initio and Molecular Dynamics Studies." Journal of Physical Chemistry **114:** 3.
8. M. Shin, H. Kim, J. Park, S. Nam, K. Heo, M. Ree, C.S. Ha, Y. Kim, (2010). "Abrupt Morphology Change upon Thermal Annealing in Poly (3-Hexylthiophene)/Soluble Fullerene Blend Films for Polymer Solar Cells." Advanced Functional Materials **20:** 6.
9. F.C. Spano, J. Clark, C. Silva, R.H. Friend, (2009). "Determining exciton coherence from the photoluminescence spectral line shape in poly(3-hexylthiophene) thin films." The Journal of Chemical Physics **130:** 16.
10. Y. Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J.Nelson, J.R. Durrant, D.C. Bradley, M. Giles, I. McCulloch, C.S. Ha, M. Ree, (2006). "A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene:fullerene solar cells." Nature Materials **5:** 7.
11. L.M. Chen, Z. Hong, G. Li, Y. Yang, (2009). "Recent Progress in Polymer Solar Cells: Manipulation of Polymer:Fullerene Morphology and the Formation of Efficient Inverted Polymer Solar Cells.

Appendix 1 - Further results from various simulations.

Test (multiples refer to chain length)	HOMO (eV)	LUMO (eV)	Difference (Band gap) (eV)	Actual band gap for comparison (eV)	Error in modelled value (eV
Calculation comparison					
P3HT – AM1	-8.849	-0.203	8.646	1.9	6.746
P3HT – MNDO	-9.362	-0.214	9.148	1.9	7.248
P3HT – MNDO-d	-8.865	-0.141	8.724	1.9	6.824
P3HT – PM3	-8.971	-0.853	8.118	1.9	6.218
P3HT – PM6	-8.766	-0.340	8.426	1.9	6.526
P3HT – RM1	-8.814	-0.048	8.766	1.9	6.866
Chain length comparison					
P3HT – PM6	-8.766	-0.340	8.426	1.9	6.526
P3HT x2 – PM6	-8.635	-0.754	7.881	1.9	5.981
P3HT x4 – PM6	-8.280	-1.291	6.989	1.9	5.089
Other polymers					
F8 (triplet) – PM6	-8.141	-0.653	7.488	2.0	5.488
F8 (singlet) – PM6	-8.683	-0.241	8.442	2.0	6.442
F8 x4 (singlet) – PM6	-8.066	-0.843	7.223	2.0	5.223
F8BT – PM6	-8.661	-0.503	8.158	2.0	6.158
F8BT x2 – PM6	-8.587	-0.712	7.875	2.0	5.875
PCDTBT – PM6	-8.219	-1.770	6.449	1.88	4.569
PCDTBT x2 – PM6	-8.242	-1.789	6.453	1.88	4.573

Appendix 2 - Screenshots of the molecules drawn in Avogadro

(Background changed to white to reduce printing costs).

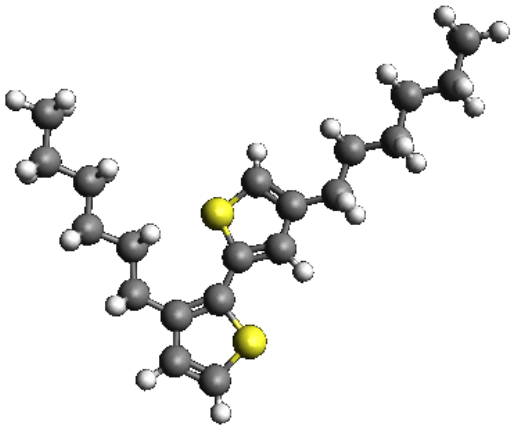


Fig 1. P3HT

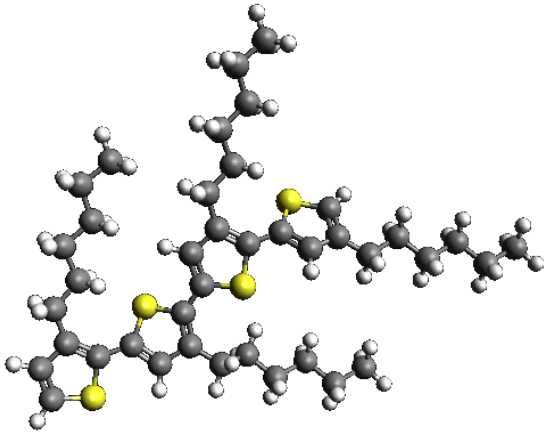


Fig 2. P3HT x2

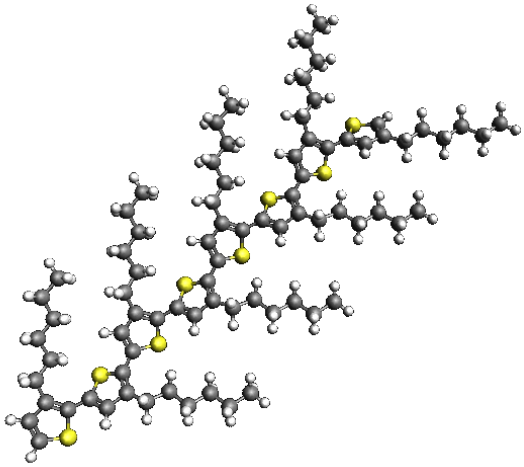


Fig 3. P3HT x4

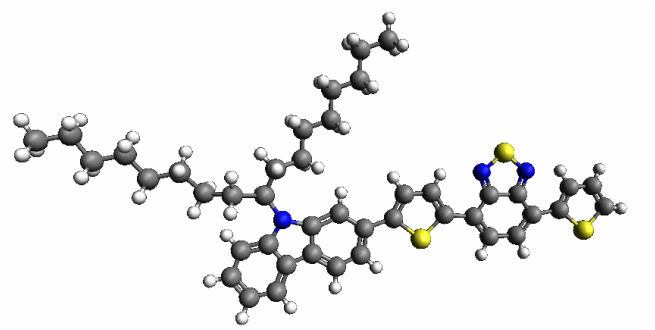


Fig 4. PCDTBT

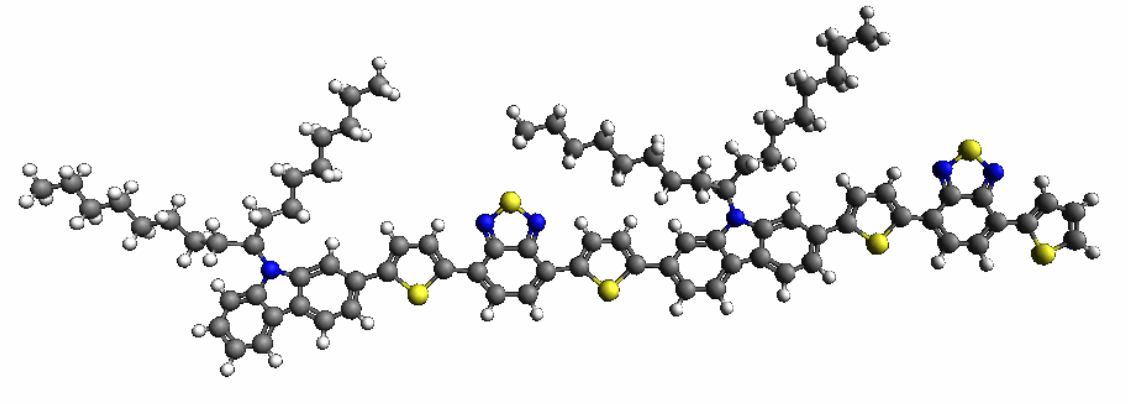


Fig 5. PCDTBT x2

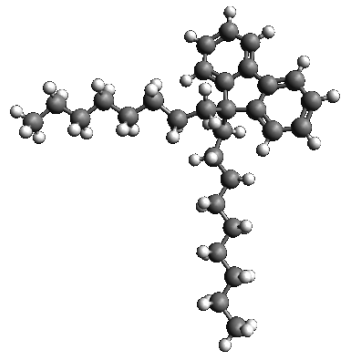


Fig 6. F8

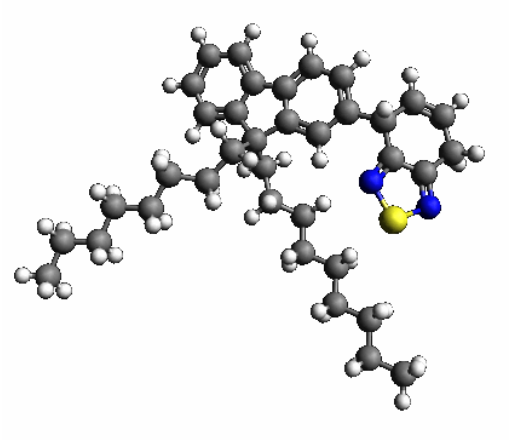


Fig 7. F8BT

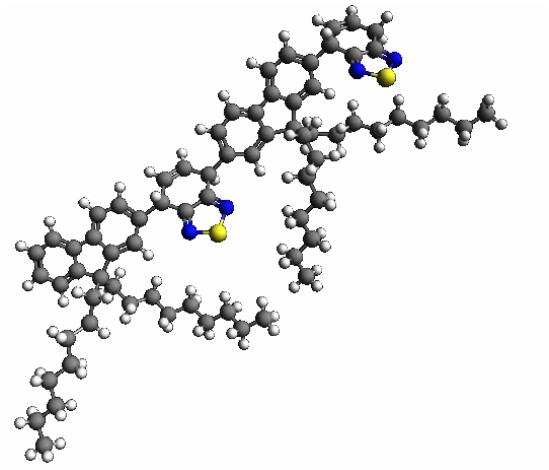


Fig 8. F8BT x2