LARGE-SCALE FIRST PRINCIPLES QUANTUM MECHANICAL CALCULATIONS ON MATERIALS FOR ORGANIC PHOTOVOLTAICS

Gabriele Boschetto[a], Hong-Tao Xue[ab], Jacek Dziedzic[ac], Michal Krompiec[d], Graham E. Morse[c], Fu-Ling Tang[b] and Chris-Kriton Skylaris[a]

[a]University of Southampton, Highfield, Southampton SO17 1BJ, UK

[b]State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Department of Materials Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, People's Republic of China

[c]Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Gdańsk, Poland

[d]Merck Chemicals Ltd., Chilworth Technical Centre, University Parkway, Southampton SO16 7QD, UK

Organic photovoltaic (OPV) devices composed of polymer/fullerene blends show promise as low-cost but efficient renewable energy sources. A great deal of research effort has been devoted to studying OPV physics, but the connection between molecular structure of materials and device performance is still far from clear. With the aim to try to shed some light into these highly complex problems, we used first principles quantum mechanical calculations to help provide an atomic-level understanding of OPV materials on a far larger scale than possible before by using the ONETEP(1) program for linear-scaling density functional theory calculations. We first focused on the electron donor material, a "push-pull" statistical block copolymer, and our studies suggested that its electronic structure can be significantly affected by the ratio of the blocks that compose the polymer chain(2), making this an alternative strategy to functionalization for the synthesis of polymers with suitable energy levels. We then focused on the acceptor materials, fullerenes, by studying the effect of crystallographic structure on the electronic and optical properties of co-crystallized solvent/fullerene solvates. While the solvent molecules are essential to stabilize the crystals, the effect of the solvent on the UV-Vis spectra is much more intense for C_{60} rather than for PCBM.(3) A greater challenge concerns the interaction between polymer and fullerene, in particular the charge-transfer excitation energies of this complex. Towards this goal, we are examining the use of linear-scaling TD-DFT calculations to obtain insights into more realistic models of bulk heterojunctions.

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