

Comparative Computational Study of Fullerene Derivatives: Effects of Addends, Buckyball Size, and Crystallinity on Bandstructure, Charge Transport, and Optical Properties

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Fullerene derivatives are the most widely used acceptor material in organic solar cells and as ETL in planar perovskite cells. While C60-PCBM has been the most popular choice, other molecules, either C70-based or using different addends, have led to better performance depending on the donor used and type of cell. It is difficult to disambiguate effects due to molecular choice from other factors affecting experiments. For rational rather than ad hoc design, it is therefore important to have a theoretical/computational comparison of different fullerene derivatives which would identify the effects of various addends on key properties affecting solar cell performance such as the reduction potential, reorganization energy, etc.

While there exist computational studies picking up the “low hanging fruit” by standard DFT calculations on selected fullerenes as free molecules, the effects of the fullerene choice on the oxidation potential, electron and hole transport and optical properties remain largely unstudied. This has to do with significant effects due to aggregate state e.g. crystallinity on these properties, which are costlier to compute ab initio.

We present a systematic comparative Density Functional Theory (DFT) – Density Functional Tight Binding Study (DFTB) of multiple derivatives of C60 and C70 with different addends, in molecular as well as solid state. Specifically, effects due to fullerene size, type and number of addends, and of crystallinity on bandstructure, charge transport, and optical properties are investigated.

We find that by the choice of type and number of addends, one can modulate the LUMO within 0.4 eV. Changes in the HOMO can be reached 0.6 eV. Substituting C70 for C60 results in destabilization of the HOMO by about 0.1 eV for indene and quinodimethane addends and by a less significant amount for PCBM addends. The effect of C70 - C60 substitution on LUMO is of similar magnitude. A more significant change in HOMO-LUMO energy is seen for the aryl addends. On the other hand, all C70 based molecules have strong visible absorption. For most addends, the crystal structure leads to a stabilization of both LUMO and HOMO by about ~0.2 and ~0.1 eV, respectively, vs single molecules. When using bis-addends, it is also possible to enhance the visible absorption. Explicit consideration of crystal packing with the help of DFTB allowed us to compute electron and hole transport rates, which vary vastly depending on the addends chosen.