

Comparative Density Functional Theory - Density Functional Tight Binding study of fullerene derivatives: effects of addends, buckyball size, and crystallinity on properties affecting solar cell functionality

Amrita Pal ¹, Chia Yao Jun ¹, Lai Kai Wen ¹, Sergei Manzhos ¹

¹ Department of Mechanical Engineering, National University of Singapore, Block EA #07-08,
9 Engineering Drive 1, Singapore 117576

E-mail: mpemanzh@nus.edu.sg

Fullerene derivatives are the most widely used acceptor material in organic solar cells and as ETL in OPV-type perovskite cells.^[1] 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.^[2] 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^[3], 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^[4].

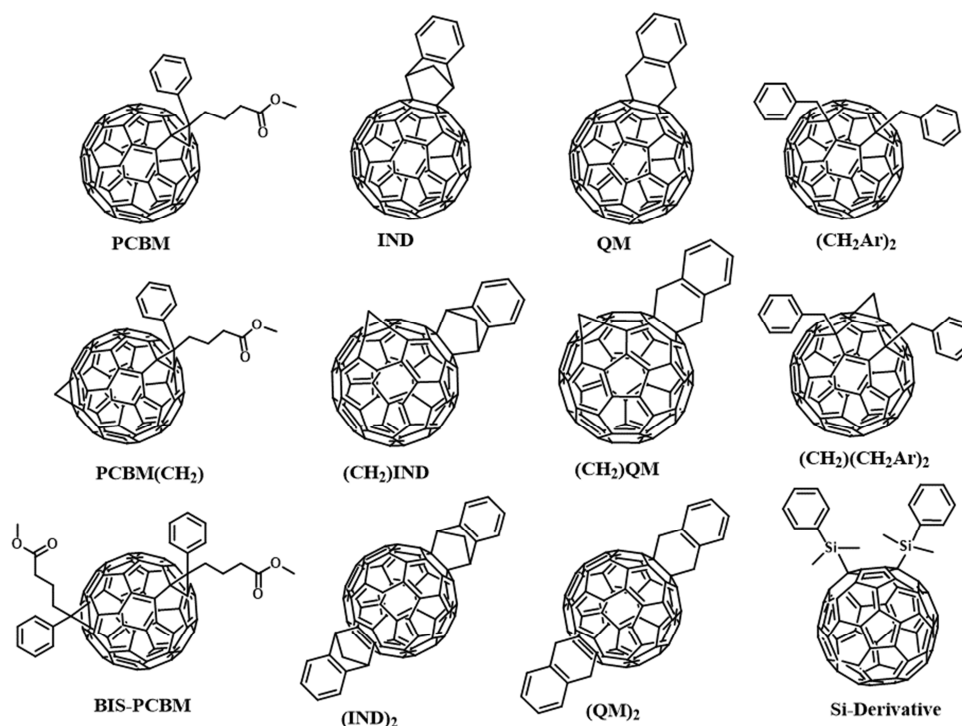


Figure 1. Fullerene derivatives studied in this work; only the C₆₀ derivatives are shown; their C₇₀ analogs are also studied.

We present a comparative density functional based computational study of a dozen popular fullerene derivatives differing by the type of fullerene (C60 or C70) as well as by type and number of addends. The studied molecules are shown in Fig. 1. We not only compare the electronic and optical properties of single molecules but also *account for the effects of crystallinity*, including effects on band structure (redox potentials) as well as calculations of electron and hole transfer rates between molecular units in a given crystal structure (Fig. 2). To optimize crystal structure, Density Functional Tight Binding is used. We find that it is possible to modulate the band edges by about 0.5 eV by the choice of fullerene derivative. The electron and hole transfer rate change by 2 orders of magnitude depending on the molecule and direction and are computed to be in the range 10^{9-12} s^{-1} .

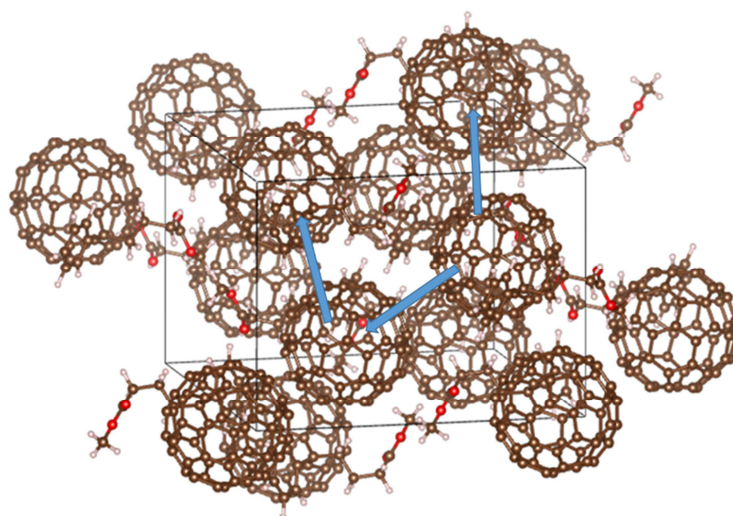


Figure 2. The crystal structure of PCBM showing non-equivalent directions of charge transfer between molecules.

Funding: Ministry of Education of Singapore (AcRF Tier 1 grant)

References:

- [1] L. Lu et al., *Chem. Rev.* **2015**, 115, 12666; H. Kim, K.-G. Lim, T.-W. Lee, *Energy Environ. Sci.*, **2016**, 9, 12
- [2] C.-H. Chiang et al., *J. Mater. Chem. A*, **2014**, 2, 15897; Y. He et al., *J. Am. Chem. Soc.* **2010**, 132, 1377; C.-Z. Li et al. **2011**, 47, 10082; R. Ganesamoorthy et al., *Solar Energy Mater. Solar Cells* **2017**, 161, 102
- [3] A. Mohajeri, A. Omidvar, *Phys. Chem. Chem. Phys.* **2015**, 17, 22367
- [4] H. Tamura, Y. Matsuo, *Chem. Phys. Lett.* **2014**, 598, 81