

SI: Effect of Polymerization Statistics on the Electronic Properties of Copolymers for Organic Photovoltaics

Gabriele Boschetto,[†] Hong-Tao Xue,^{†,¶} Jacek Dziedzic,^{†,§} Michal Krompiec,[‡] and Chris-Kriton Skylaris^{*,†}

[†]*School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom*

[‡]*Merck Chemicals Ltd., Chilworth Technical Centre, University Parkway, Southampton SO16 7QD, United Kingdom*

[¶]*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*

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

E-mail: c.skylaris@soton.ac.uk

Band Gap Extrapolation

An alternative method that can be used to predict the band gap of conjugated polymers is the extrapolation of the linear (or quadratic) curve of the band gap against $1/n$, where n is the number of monomer units.¹ A comparative study between this method and the use of periodic boundary conditions (PBC) is provided for a subset of structures (4, 15, 22, 23); for these, the band gaps have been computed both using the PBE and the B3LYP functionals, and experimental data is also available (the reader is referred to Table 3 and Figure 7 in the main text). Moreover, for structures 4 and 15, the band gaps of the corresponding long chain oligomers (> 1000 atoms) were also computed. Results are shown in Table S1 and Figures S1-S5.

For all structures the band gaps obtained by linear extrapolation are smaller in magnitude (within 0.05-0.09 eV) with respect to the band gaps obtained under PBC. This is because the empirical linear fit is known to provide an underestimate of the “true” band gap, while a better estimate should be given by the use of a quadratic fit. As expected, the quadratic fit provides in general band gaps closer to, and in one case exactly as, the ones obtained with PBC; however, these results should be treated with caution, since in order to obtain an accurate prediction of band gaps by using a quadratic polynomial, structures consisting of a moderate/large number of monomer units should be considered. For structures 4 and 15 the number of monomer units appears to be enough to obtain reliable band gaps, while when considering structures 22 and 23 a higher number of units is most probably needed.

As shown in Table S1, in the case of structure 4 the value of the band gap of the corresponding long chain oligomer (> 1000 atoms) lies halfway between the ones obtained under PBC (or by the quadratic fit) and by linear fitting, while the band gap of structure 15 long chain oligomer (> 1000 atoms) is much closer to the one obtained with PBC (within 0.01 eV), yet not too far from the one obtained by the quadratic fit (within 0.04 eV). Figure S1, which is a slightly modified version of Figure 7 in the main text, shows a comparison between the experimental and theoretical band gaps of this set of polymers, the latter obtained by

Table S1: Comparison between numerical values (in eV) of computed E_g of polymers using different methods.

polymer	PBE-linear fit	PBE-quadratic fit	PBC-PBE	oligomer (> 1000 atoms)
4	0.90	0.95	0.95	0.92
15	0.78	0.90	0.87	0.86
22	0.71	0.71	0.77	-
23	0.75	0.77	0.83	-

using different methods and different functionals. It is clear how the linear fit doesn't seem to provide a trend as good as the one provided by the PBC-PBE method; the quadratic fit seems to significantly improve the trend, but as previously mentioned, structures composed of a higher number of monomer units should also be considered while performing the extrapolation from monomer to infinite. This suggests that, at least for the systems here considered, periodic boundary conditions, with a sufficiently large unit cell to ensure an adequate Brillouin zone sampling, is a more reliable method for computing band gaps than the extrapolation by linear fit; an extrapolation by quadratic fit may instead provide results comparable with the ones obtained with PBC.

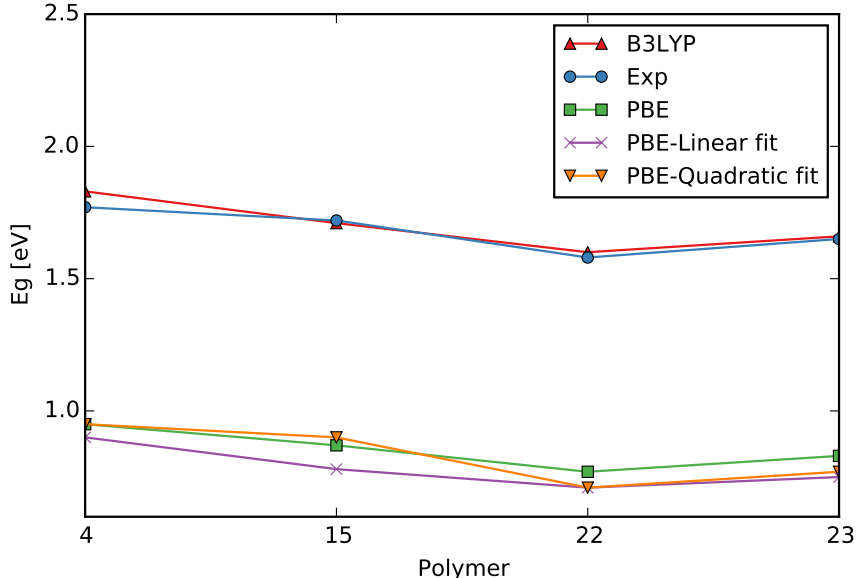


Figure S1: Comparison between theoretical and experimental band gaps of polymers.

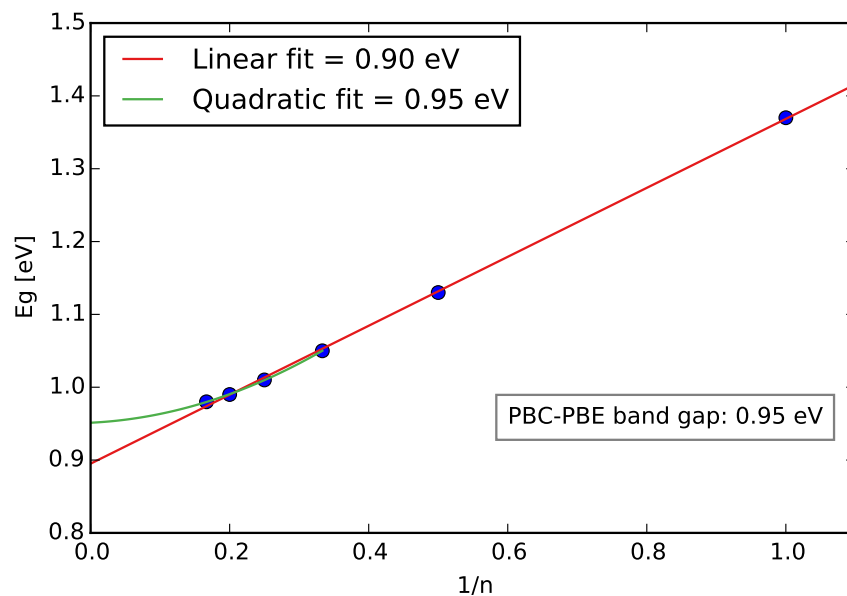


Figure S2: Linear extrapolation of the band gap of structure 4 at the PBE level.

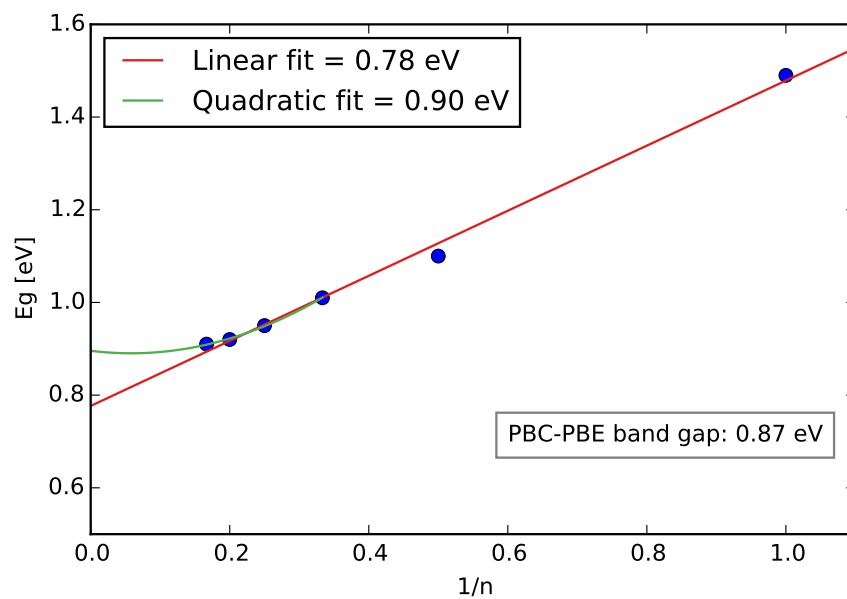


Figure S3: Linear extrapolation of the band gap of structure 15 at the PBE level.

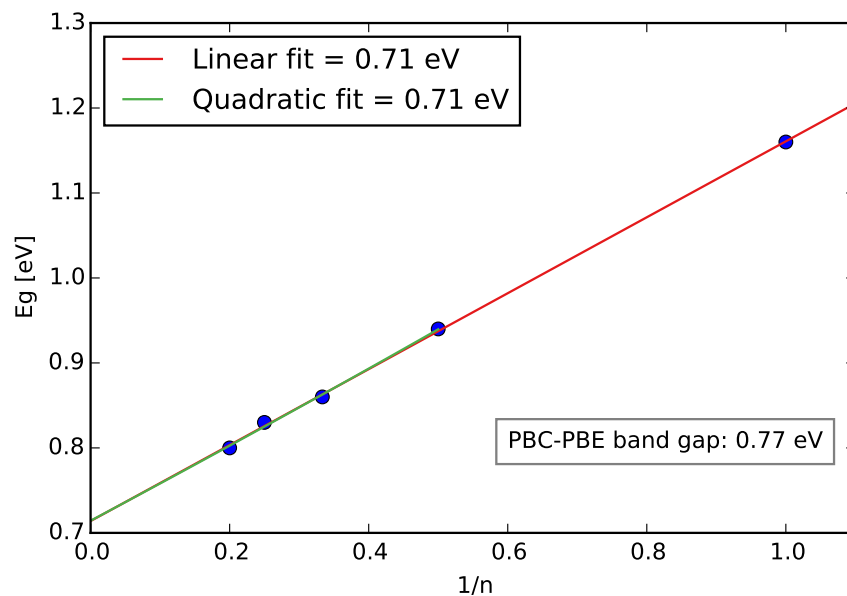


Figure S4: Linear extrapolation of the band gap of structure 22 at the PBE level.

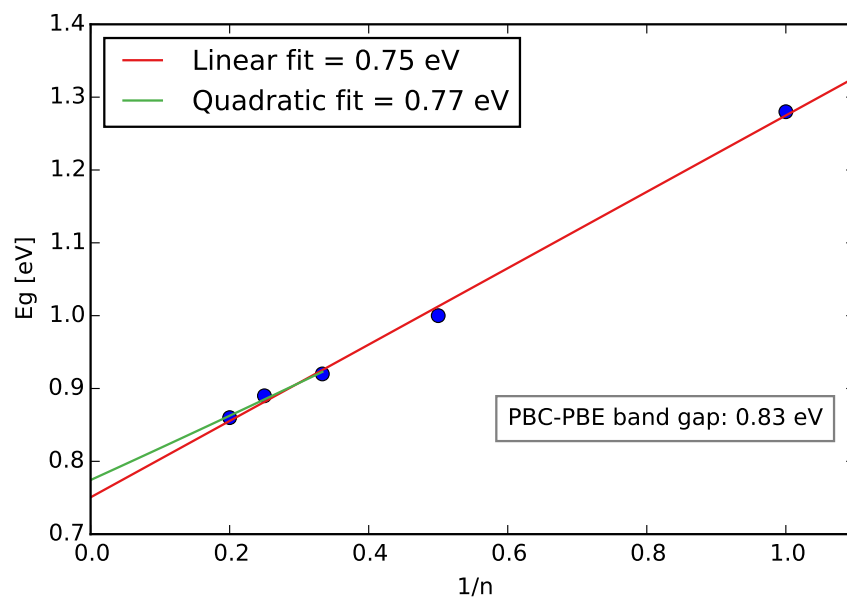


Figure S5: Linear extrapolation of the band gap of structure 23 at the PBE level.

References

- (1) Zade, S. S.; Bendikov, M. From Oligomers to Polymer: Convergence in the HOMO-LUMO Gaps of Conjugated Oligomers. *Org. Lett.* **2006**, *8*, 5243–5246.