First principles elaboration of low band gap ladder-type polymers
(Supplementary Material)

Simon Pesant, Guillaume Dumont, Sébastien Langevin, and Michel Côté*
Département de physique et Regroupement Québécois sur les Matériaux de Pointe (RQMP),
Université de Montréal, Case Postale 6128,
Succursale Centre-ville, Montréal, Québec, H3C 3J7 Canada∗
POLYMERS AND OLIGOMERS OPTIMIZED GEOMETRIES

We report the optimized geometries of all the polymers for both exchange-correlation B3LYP and LDA functionals (see Fig. 1). It is worth noting that the atomic structure optimization procedure with the B3LYP functional led to two different ground state geometries for the LPPyB with the same total energies\[1\]. Each of them corresponding to indirect band gaps of 0.66 eV (A) and 0.29 eV (B), the latter being closer to the LDA structure than the former. Both structures are shown in Fig. 1, where structure B is indicated by distances between parentheses.

Since the optimized structures of the LPPyB-based oligomers were closer to structure A, we conclude that this is the correct one and that structure B is artificial and comes from the fact that the polymer is constrained to remain straight.

BADER CHARGE ANALYSIS

In order to have a better understanding of the electronic properties of the LPPyB polymer, the static charge of each atom in the unit cell has been calculated and the results are summarized in the Table I. These values were obtained using Bader charge density analysis [2]. The Bader charges show that the N-H group contains more electrons compared to the B-H group which is expected considering the electronegativity of the atoms involved. Despite this fact, the numbers indicate that the boron atom shares more of its charge with its surrounding carbon atoms than the nitrogen atom gains from its neighbor carbon atoms. This results in a net negative charge on the carbon backbone of the structure of approximately 0.6 electron, spread over the four carbon atoms in the unit cell.

The symmetry breaking in the charge density between the boron and nitrogen groups has a direct effect on the band structure. A closer look at the LDA band structure of the LPPyB reveals that at the frontier of the Brillouin zone, the degeneracy found between the LUMO and LUMO+1 for the LPB and HOMO and HOMO-1 for the LPPy has been lifted for the 13\textsuperscript{th} and the 14\textsuperscript{th} bands of the mixed polymer LPPyB. This splitting between these bands at the X-point can be explained in terms of the electronegativities of the unit cell’s atoms. The nitrogen atom has an electronegativity of 3.0 while it is 2.0 for the boron atom. That creates an asymmetry in the charge density of the polymer. To further minimize the
FIG. 1: Optimized unit cells of all polymers for the B3LYP and LDA functionals. For LPPyB, the bond lengths between parentheses correspond to structure B ($E_g = 0.29$ eV) and the others to structure A ($E_g = 0.66$ eV).
splitting, the variation of electronegativity between the two groups (N-H and B-H) could be reduced by functionalizing the nitrogen or the boron atoms. These added groups could also help with the solubility of this polymer.

<table>
<thead>
<tr>
<th>Atom Type</th>
<th>Bader Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3.40</td>
</tr>
<tr>
<td>N</td>
<td>7.60</td>
</tr>
<tr>
<td>C(linked to the B atom)</td>
<td>6.57</td>
</tr>
<tr>
<td>C(linked to the N atom)</td>
<td>5.73</td>
</tr>
<tr>
<td>H(linked to the B atom)</td>
<td>1.50</td>
</tr>
<tr>
<td>H(linked to the N atom)</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**WORK FUNCTIONS**

To further investigate the stability of these new polymers, their ionization energies (i.e. their work functions) were calculated with different basis sets and functional. These values, shown in the Table II, are estimated by considering the binding energy of the last occupied state. This method is known to underestimate the real value but the trend between different systems should be respected. The low value of LPPy explains that NFE states are observed for this system. This value can be further compared to computed values for known polymers. For poly(p-phenylene) (PPP) and poly(p-phenylenevinylene) (PPV), two polymers widely used in electronic devices, the calculated ionization potentials are 5.0 eV and 4.63 eV respectively, using the plane-wave basis set. With the gaussian basis, the value for PPP is calculated at 4.83 eV. Finally, these results indicate that the LPPy is most likely unstable and will react readily whereas the LPPyB and LPTB should be more reactive than PPP and PPV but it are still stable. The discrepancy between the value obtained with the different basis-sets can be explained by the fact that the gaussian is a localized basis set whereas plane-wave basis set completely fills the space. Also, the code used to calculate the band structure with the plane-wave basis set constructs a 3 dimensional matrix of polymeric chain instead of the 1 dimensional chain in the other program. Consequently, the description
TABLE II: Calculated Ionization Potentials with B3LYP and LDA calculated with gaussian basis set. Values within parentheses were calculated with a plane-wave basis set.

of the vacuum is different between the two approach and can account for the difference in the results of the ionization energy.

DETAILS OF THE GW CALCULATIONS

The GW results shown in the article were obtained using the following parameters. The LDA part of the calculation was done using an energy cut-off of 25 Ha for the plane-wave basis set. A cut-off energy of 8 Ha was then used for the plane wave set which represents the wave functions that generate the independent-particle susceptibility $\chi_{KS}^{(0)}$, the dielectric matrix $\epsilon$, and its inverse. In addition, a cut-off energy of 8 Ha was used for the plane-wave set that generates the exchange part of the self-energy operator and for the independent-particle susceptibility $\chi_{KS}^{(0)}$, and the self-energy $\Sigma$. Also, 120 LDA bands were used towards constructing a complete basis set from the LDA wave functions as well as a k-point grid of 10x4x4.

We also did calculations in which we applied a scissor operator to the LDA band structure, to force an insulating behavior in the calculation of the dielectric matrix. In this case too, the GW corrections were observed to increase the HOMO-LUMO overlap.
[1] The total energy difference was of 0.7 meV which is much lower than the convergence criterion of 27.2 meV per atom in the unit cell.

[2] R. F. W. Bader. Atoms in molecules - a quantum theory. *Oxford University Press*, 1990. In order to get satisfying results, the charge density was calculated with an energy cut-off of 50 Ha in order to obtain a density with high resolution in real space.