

Supplementary Material: Band Gap tunability in One-dimensional system

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1. Explanation for different bandgaps in isomers of polydialkylterthiophenes

In order to verify the proposed theory, we consider another synthetic polymer, poly-dialkylterthiophenes ($C_{36}H_{54}S_3$)_n having isomeric monomers 3',4'-didodecyl 2,2':5',2''terthiophene (3',4'-DDTT) and 3,3''-didodecyl 2,2':5',2''terthiophene (3,3''-DDTT)[1], which have different periodic lengths of 11.663 Å and 11.863 Å [Figure 1(a)], even though their ground state energies calculated per atom are - 5.795 eV, which are exactly the same. From band structures calculations for poly(3',4'-DDTT) and poly(3,3''-DDTT), bandgaps are found to be 1.131 eV, and 1.004 eV, respectively. Their potential profiles are plotted in the periodic direction of the unit cells [Figure 1(b)]. The width and depth of the potential well at global minimum for poly(3',4'-DDTT) are 2.734 Å (a_1) and 1.148 eV (V_1), respectively, while for poly(3,3''-DDTT) are 3.057 Å (a_2) and 0.635 eV (V_2), respectively. Since $a_2 > a_1$ and $V_1 > V_2$, therefore from the proposed theory, poly(3',4'-DDTT) should have higher band gap than that of poly(3,3''-DDTT) (**Case IV**), which is consistent with our theoretical band structure calculations using DFT.

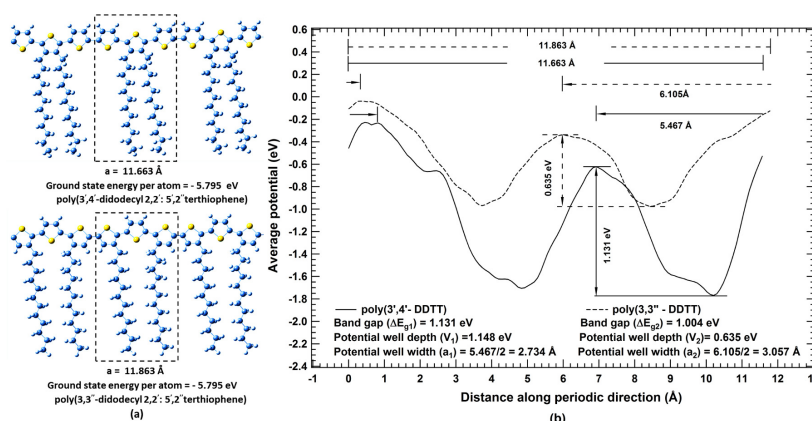


Figure 1. (color online)(a) Unit cells are represented in dotted line for poly(3',4'-DDTT) and poly(3,3''-DDTT), and (b) their corresponding potential profiles. Blue, yellow, and white spheres represent carbon, sulfur, and hydrogen atoms, respectively.

2. Explanation for different bandgaps in Cellulose and Starch

To verify the proposed theory for natural polymers, Cellulose and Starch ($C_{12}H_{20}O_{10}$)_n, isomeric polymers of glucose are considered. The length of periodic monomer for Cellulose and Starch are 10.012 Å and 10.796 Å, respectively [Figure 2(a)], even though their ground state energies calculated per atom are - 6.357 eV and - 6.338 eV, respectively, which are practically the same. For band structure calculations, cut-off energy is optimized to 800 eV for both Cellulose and Starch. Direct bandgaps are observed for both Cellulose and Starch with bandgaps of 4.844 eV and 5.039 eV, respectively. Band structures for these isomeric systems are significantly different, even though they have the same chemical formula, and practically the same ground state energy. Their potentials profiles are plotted in

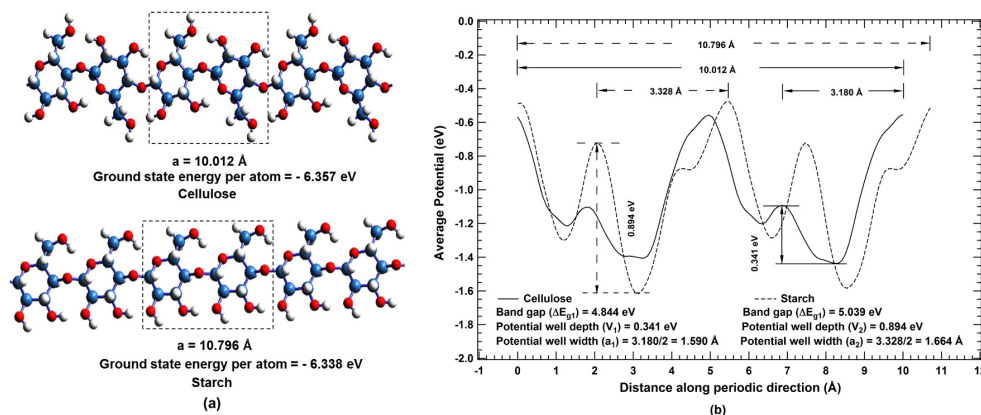


Figure 2. (color online)(a) Unit cells are represented in dotted line for Cellulose and Starch, and (b) their corresponding potential profiles. Blue, red, and white spheres represent carbon, oxygen, and hydrogen atoms, respectively.

the periodic direction of the unit cells [Figure 2(b)]. It is observed that width and depth of the potential well at global minimum for Cellulose are 1.590 Å (a_1) and 0.341 eV (V_1), respectively, while for Starch are 1.664 Å (a_2) and 0.894 eV (V_2), respectively. Since $a_2 > a_1$ and $V_2 > V_1$, therefore when equation (1) is solved, bandgap for Starch is found to be higher than Cellulose (**Case V**), consistent with our band structure calculations using DFT.

3. Explanation of different bandgaps in Kevlar and Nomex

For further generalization, we consider organic polymer polyaramid, which exists in two isomeric forms known as Kevlar and Nomex with the same molecular formula ($C_{14}H_{10}O_2N_2$)_n. The polymeric chains (without folding/coupling with other chains) for these isomers are considered as one-dimensional periodic systems, whose unit cells are shown in [Figure 3(a)]. It is observed that length of the monomer for Kevlar and Nomex are 12.867 Å and 12.102 Å, respectively, which are different in the periodic direction, however, ground state energies per atom for Kevlar and Nomex are - 6.908 eV and - 6.882 eV, respectively, which are practically the same. Bandgaps calculated for Kevlar and Nomex using DFT are 3.516 eV and 2.919 eV, respectively. The periodic potential profiles for Kevlar and Nomex is shown in Figure 3(b). The width and depth of the potential well at global minimum for Kevlar are 1.027 Å (a_1) and 0.517 eV (V_1), respectively, while for Nomex are 0.605 Å (a_2) and 0.427 eV (V_2), respectively. Since $a_1 > a_2$ and $V_1 > V_2$, therefore when equation (1) is solved, bandgap for Kevlar is found to be higher than that of Nomex (**Case V**), consistent with our band structure calculations using DFT.

4. Explanation for different bandgaps in isomeric even zigzag graphene nanoribbons ($N_z = 6$)

For further clarification of the concept of bandgap tunability in one-dimensional systems, we consider even width zigzag graphene nanoribbons with $N_z = 6$ having the same functional groups in the periodic unit cell but of different arrangements. Zigzag nanoribbons ($N_z = 6$) passivated with oxygen

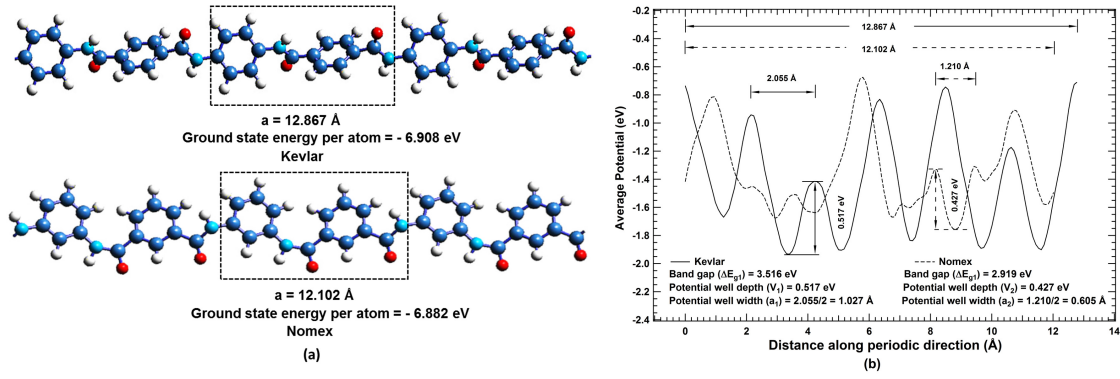


Figure 3. (color online) (a) Unit cell for Kevlar and Nomex are represented by dotted lines and (b) their corresponding potential profiles. Blue, red, sky blue, and white spheres represent carbon, oxygen, nitrogen, and hydrogen atoms, respectively.

atoms in two possible ways at the edges are considered for the studies. The unit cells corresponding to Config. I and Config. II are shown in Figure 4(a) for $N_z = 6$. The lattice parameters in periodic direction for both the isomeric nanoribbons are equal to 7.378 Å, a special case of systems having lattice parameters different. The ground state energy per atom for Config. I and Config. II are -8.692 eV and -8.690 eV, respectively, which are practically the same. Average potential profiles in the periodic direction of unit cell corresponding to Config. I and Config. II are plotted in Figure 4(b). The width and depth of potential well at global minimum for Config. I are 0.702 Å (a_1) and 1.210 eV (V_1), respectively, while for Config. II are 0.614 Å (a_2) and 0.718 eV (V_2), respectively. Since $a_1 > a_2$ and $V_1 > V_2$, therefore from the proposed theory, when equation (1) is solved, bandgap for Config. I should be higher than Config. II (**Case V**).

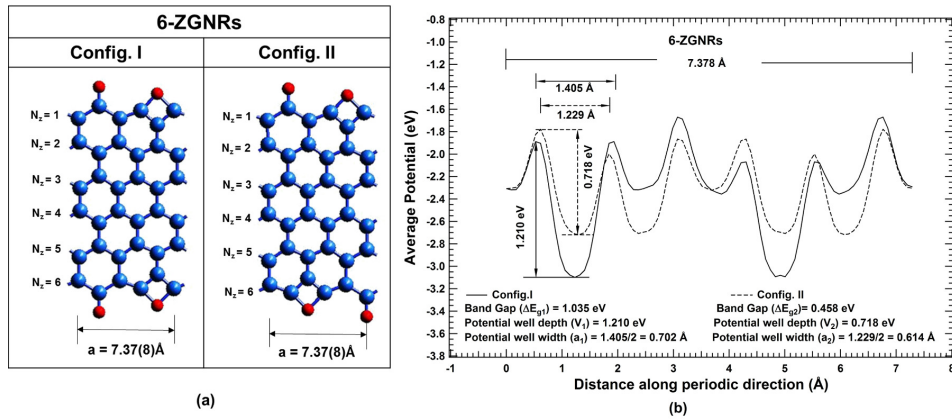


Figure 4. (color online) (a) Unit cells corresponding to two different configurations Config. I and Config. II of even width ZGNRs corresponding to $N_z = 6$, where blue and red spheres represent carbon and oxygen atoms, respectively. (b) their corresponding potential profiles.

To check the validity of derived correlations, band structure calculations are performed for 6-ZGNRs with a cut-off energy of 450 eV and plotted from Γ to X point [Figure 5]. Direct bandgaps of 1.035 eV and 0.458 eV are observed at Γ point for Config. I and Config. II, respectively [Figure 5]. Thus, bandgap for Config. I is higher than that for Config. II, which is in agreement with the derived correlation using potential profiles [Figure 4(b)]. On the basis of proposed theory, the different bandgaps in even width N_z -ZGNRs for $N_z < 8$ are explainable on the basis of **Case V**.

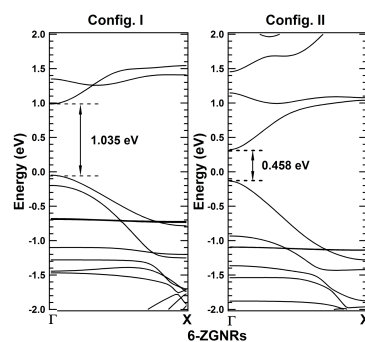


Figure 5. Band structure plots corresponding to Config. I and Config. II. for $N_z = 6$

References

1. Dini, D.; Decker, F.; Andreani, F.; Salatelli, E.; Hapiot, P. A comparative study of isomeric polydialkylterthiophenes with regular regiochemistry of substitution. Electrochemical synthesis. *Polymer* **2000**, *41*, 6473.

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