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PBC-DFT Applied to Donor−Acceptor Copolymers in Organic Solar Cells: Comparisons between Theoretical Methods and Experimental Data

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Supporting Information

INTRODUCTION

Solar energy production is a key component to a sustainable future.[1] Among the technologies available for solar power conversion, organic photovoltaics are particularly attractive due to their potential low-cost production via low-temperature processing.[2] Bulk heterojunction (BHJ) solar cells based on a conjugated conducting polymer donor and fullerene acceptor[3] have been the most successful organic solid-state devices to date.[4] With respect to the conjugated polymer in these BHJ devices, donor−acceptor (D−A) copolymers consisting of an electron-rich donor and electron-deficient acceptor have received much attention.[5] Recently, power conversion efficiencies above 7% have been reported in cells using these D−A copolymer materials.[6]

In attempting to design the ideal polymer for use in a BHJ device, knowing the magnitude of the polymer band gap and the energy positions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are crucial. These are the most important characteristics for determining the optical and electrical properties of the resulting polymer.[7] For example, the ideal polymer should have a low-lying HOMO energy (relative to the acceptor material) to provide a large open-circuit voltage (V_{OC}) and achieve maximum power conversion efficiency.[6−8] In addition, designing polymers with the appropriate band gap, E_g, are critical for capturing as much as the solar spectrum as possible.[2]

Quantum mechanical methods have been widely utilized to rationalize experimental data of organic molecules and to predict properties of yet unknown materials. For example, Blouin et al. have shown that density functional theory (DFT) calculations on the repeat unit of conjugated D−A polymers used in solar cells provide good estimations of HOMO, LUMO, and band gap energies.[9] A more traditional approach is to utilize Kuhn fits by plotting HOMO−LUMO gaps versus $1/n$ (where n is the number of monomer units).[10] The oligomer method has been utilized by a number of groups investigating D−A copolymers in BHJ solar cells.[11] This current investigation seeks to explore additional methods of calculating energetics of D−A copolymers.

Although the oligomer approach to obtain Kuhn fits has proven reliable for estimation/rationalization of HOMO, LUMO, and band gap energies, the computational cost can be high for polymeric systems. This is especially true for D−A copolymers containing many atoms in the repeat unit. Furthermore, the linear relationship based on the traditional oligomer approach of obtaining the polymer band gap does not hold up for higher values of n.[12−14] An alternative method, utilizing hybrid DFT methods, calculates infinitely long polymer chains using periodic boundary conditions (PBC) for those polymers with one-dimensional periodicity.[15] Led by the work of Bendikov and co-workers, PBC-DFT has been shown to be a very good method to reliably predict the band gaps of conjugated polymers.[16] The vast majority of these and other investigations using PBC-DFT, however, have focused on homopolymers.[17] To our knowledge, application of PBC-DFT to D−A copolymers used in BHJ solar cells has not yet been reported.[18] In addition, investigations that compare both the oligomer and PBC methods to experimental data are rare.[16a] Additional reports are needed to help clarify the methods available to chemists in the evolving field of organic materials and photovoltaics. In this study, we investigate the application of PBC-DFT to a number of D−A copolymers used in photovoltaic devices from the recent literature and provide comparisons to traditional Kuhn fits as well as comparisons to experimental data.

COMPUTATIONAL DETAILS

DFT calculations were performed with the Gaussian 03 program.[19] Geometries and orbital energies were calculated by means of the hybrid density functional B3LYP.[20,21] All polymers (via PBC) and oligomers were initially calculated with the 3-21G(d) basis set as it has proven reliable for large D−A copolymer systems.[22] PBC calculations were also performed using the 6-31G(d) basis set for comparison purposes as this basis set has proven reliable for a number of conjugated homopolymers.[12,16a] The input files were generated with GaussView. All alkyl groups in the polymers were replaced by n-propyl groups to save computational time. Alternating cisoid−transoid conformations were used for all oligomer and polymer calculations. This conformation was chosen based on the relative energies of unit cell conformers. As an example, data for **P1** unit cells are provided in Table S1. Additional data can be found in the Supporting Information including optimized geometries of oligomers and polymer unit cells.

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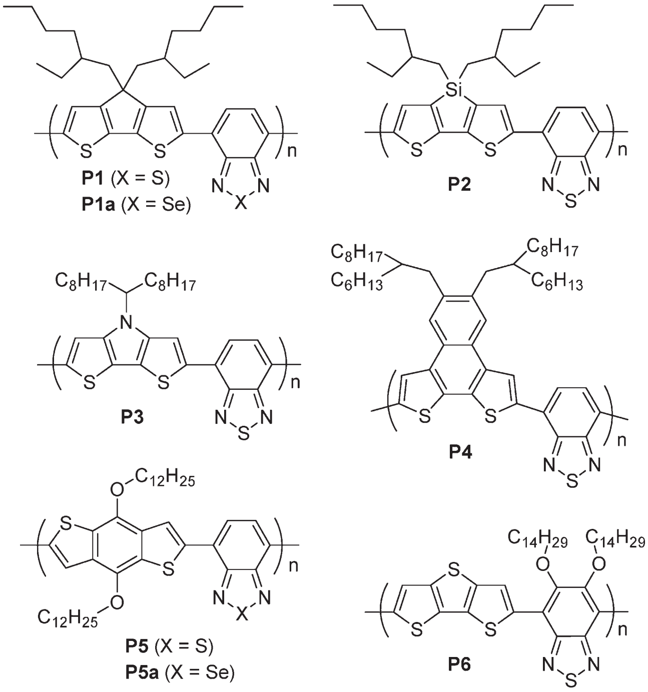

Figure 1. Chemical structures of copolymers in this study.

RESULTS AND DISCUSSION

The chemical structures of the polymers in this study are found in Figure 1. We chose to investigate copolymers with 2,1,3-benzothiadiazole (with or without selenium substitution) as the acceptor since benzothiadiazole-based D−A polymers have been one of the most widely investigated systems in BHJ solar cells.[5] Power conversion efficiencies of over 6% have been reported for devices utilizing these materials.[23] Experimental and calculated data for these eight polymers are found in Table 1. HOMO−LUMO values for the polymers were obtained from Kuhn fits using model oligomers (n = 1−6). Highest occupied crystal orbital (HOCO) and lowest unoccupied crystal orbital (LUCO) values were obtained from DFT calculations using periodic boundary conditions. The theoretical band gaps are the difference between the HOMO−LUMO and HOCO−LUCO values.

On average, the band gaps from the oligomer approach are 0.11 eV lower than those of the PBC method. This feature can be rationalized by the fact that the linear extrapolation method fails to consider asymptotic behavior for higher values of n.[12] We did not, however, confirm this feature in our study as our calculations did not exceed n = 6.

Additional insight between the two methods can be obtained by plotting the frontier orbital energies of each polymer for each method. HOMO/LUMO and HOCO/LUCO values are plotted in Figure 2. A strong correlation is seen between the two methods. HOMO/HOCO, LUMO/LUCO, and resulting band gap values generate correlation coefficients of 0.996, 0.994, and 0.995, respectively (Figures S5−S7). As can be seen from Figure 2, LUMO values are stabilized relative to LUCO values, whereas HOCO values are stabilized relative to HOMO values. These trends combined help account for the lower resulting band gaps for the oligomer approach relative to the PBC calculations.

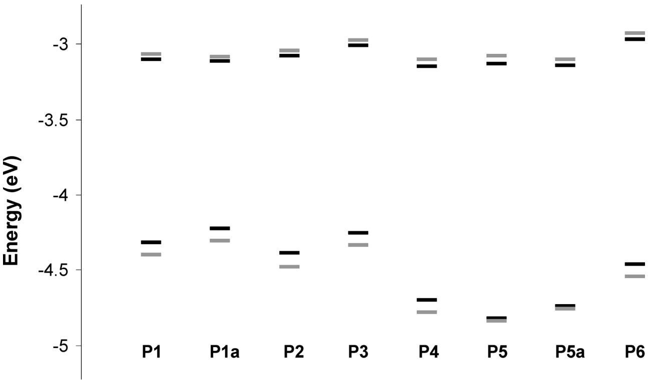

Figure 2. Frontier orbital energies of the polymers: HOMO/LUMO values represented in black; HOCO/LUCO values represented in gray.

Figure 2 also demonstrates the ability to tune the band gap of the polymer as a function of chemical structure. In comparison to the HOMO/HOCO values, the LUMO/LUCO values are relatively fixed as is expected for D−A copolymers with a constant (or relatively constant) acceptor. The largest deviation from the trend is seen in **P6** which is anticipated since the donor is substituted with electron donating alkoxy groups which should destabilize LUMO/LUCO levels. Larger changes are observed for HOMO/HOCO values since there is greater variation for the donor in the D−A copolymers **P1**−**P6**. These values can be useful in screening polymers for relatively low HOMO values which can help maximize the V_{OC} in BHJ solar cells.

The data in Table 1 also allow for comparisons to experimental band gaps. PBC band gaps calculated at B3LYP/3-21G-(d) are in excellent agreement with experimental values as all eight polymers are within 0.13 eV. Band gaps calculated using the oligomer method also agree well with experimental data as all are within 0.24 eV. Statistical correlations between the two methods and experimental data afford R = 0.984 and R = 0.986 for the PBC and oligomer methods, respectively (Figure S8). These data suggest both methods are suitable for providing reasonable energy gaps for the D−A copolymers in this study.

PBC band gaps calculated at B3LYP/6-31G(d) have also been performed for comparison purposes (Table S2) as the literature suggests this level of theory provides good estimations of band gaps for conjugated polymers.[16] The values in this study at the larger basis set are very similar to the 3-21G(d) basis set as all are identical or only slightly elevated (within 0.1 eV). Statistical correlation for the PBC calculations at the higher basis set with experimental data provide R = 0.995 as shown in Figure 3. These data suggest a slight advantage for using the higher basis set to correlate calculated and experimental data for this series of D−A copolymers.

Theoretical data are also consistent with some band gap trends within the D−A copolymers. For example, experimental data suggest substitution of 2,1,3-benzothiadiazole with 2,1,3-benzoselenadiazole (e.g., polymers **P1a** and **P5a**) in a copolymers with constant donor groups affords a reduced band gap.[25,29] All theoretical methods in this study agree with this trend. In addition, within the **P1**, **P1a**, and **P2** series where the polymers differ slightly by atom substitutions in the donor or acceptor, all methods accurately calculate the increasing band gap values in the order of **P1a** < **P1** < **P2**.

Theoretical HOCO/LUCO values calculated at B3LYP/6-31G(d) have also been compared with experimental HOMO and LUMO data obtained from electrochemical measurements (Table S3). Within the **P1**, **P2**, and **P3** series where the polymers differ by the bithiophene bridging atom, HOCO trends are

Table 1. Experimental and Calculated Data of the Polymers Investigated

polymer	ref	expt optical E_g (eV)	theor LUMO (HOMO) (eV)[a]	theor E_g (eV)[b]	theor LUCO (HOCO) (eV)[c]	theor E_g (eV)[d]
P1	24	1.40	−3.104 (−4.318)	1.21	−3.069 (−4.400)	1.33
P1a	25	1.35	−3.113 (−4.227)	1.11	−3.086 (−4.305)	1.22
P2	26	1.45	−3.082 (−4.390)	1.31	−3.042 (−4.479)	1.44
P3	27	1.40	−3.011 (−4.255)	1.24	−2.977 (−4.337)	1.36
P4	28	1.59	−3.146 (−4.703)	1.56	−3.102 (−4.781)	1.68
P5	29	1.70	−3.130 (−4.824)	1.69	−3.080 (−4.841)	1.76
P5a	29	1.60[e]	−3.140 (−4.739)	1.60	−3.102 (−4.759)	1.66
P6	30	1.60	−2.971 (−4.462)	1.49	−2.931 (−4.542)	1.61

[a] B3LYP/3-21G(d) gas-phase HOMO and LUMO values extrapolated from Kuhn fits of oligomer ($n = 1-6$) calculations. [b] HOMO−LUMO values from Kuhn fits. [c] PBC/B3LYP/3-21G(d) HOCO and LUCO values. [d] HOCO−LUCO values from PBC calculations. [e] Band gap determined directly from absorption spectrum provided in reference.

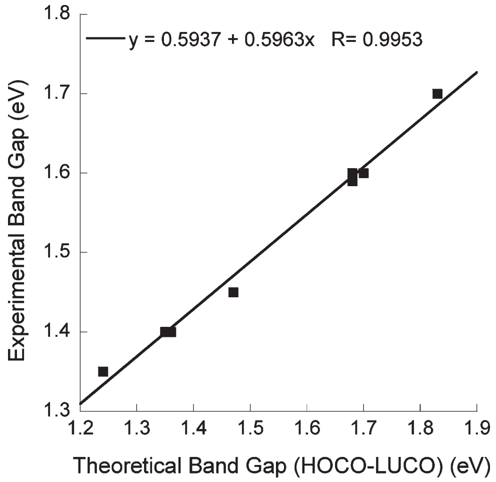

Figure 3. Theoretical (PBC/B3LYP/6-31G(d)) and experimental band gap correlation.

consistent with increasing HOMO values in the order of **P2** < **P1** < **P3**. The value of **P3** can be rationalized by the electron-rich nature of the dithieno[3,2-*b*:2′,3′-*d*]pyrrole donor unit,[31] whereas the introduction of silicon in **P2** has been shown to provide polymers with deeper HOMO levels relative to carbon substitution as in **P1**.[32] Within the **P1**/**P1a** and **P5**/**P5a** subsets, the observed reduced optical bandgap upon selenium substitution in the donor unit can be related to the destabilized HOMO levels in these polymers.[29] Calculated HOCO levels are consistent with the experimental HOMO trends for these subsets and are most clearly seen in Figure 2 (i.e., HOCO/HOMO levels become destabilized upon selenium substitution).

CONCLUSIONS

In summary, we have performed DFT calculations on a series of D−A copolymers using the oligomer approach and periodic boundary conditions. The two methods provide data that agree well with one another and correlate with experimental data in a nearly identical manner. This study shows that theoretical investigations on D−A copolymers can be used to rationalize the properties of known polymers and predict those of yet unknown materials. Application of the PBC method to other D−A copolymers should proceed with some caution; however, as others have suggested, calculated values of D−A polymers using PBC/B3LYP/6-31G(d) can overestimate experimental band gaps.[33] The data from this investigation, however, suggest additional studies are warranted to determine the true value of these methods.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional computational details including linear fits of oligomer data, correlation plots, and optimized geometries of select structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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